DEVELOPMENT OF LOW COST ADSORBENTS FOR WASTE WATER TREATMENT

A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY

by

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APRIL, 2012

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DEVELOPMENT OF LOW COST ADSORBENTS FOR WASTE WATER TREATMENT** in partial fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy** and submitted in the **Department of Chemistry** of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from **July 2009 to April 2012** under the supervision of **Dr. V.K.Gupta**, Professor, and **Dr. Bina Gupta**, Associate Professor, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee..

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(ARUNIMA NAYAK)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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Dated: April 23 , 2012

The Ph.D. Viva-Voce Examination of **Ms. ARUNIMA NAYAK**, Research Scholar, has been held on......28/6/12.................

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ACKNOWLEDGEMENTS

At the outset, I wish to express my deepest sense of gratitude and reverence to my mentors and guides **Prof. V.K.Gupta and Dr. Bina Gupta** for introducing me to this present field of study, which was new to me. Their invaluable and meticulous guidance with lots of constructive criticisms have served as a vital source of inspiration for bringing the present work in the final shape. I thank Prof. V.K.Gupta for giving me fundamental knowledge, pertinent suggestions and constructive criticisms, which not only helped in strengthening my skills in research methodology but also helped me to develop a more confident personality.

I would like to thank the Ministry of Human Resource Department (MHRD), for the Fellowship grant. I offer my sincere thanks to Prof. V.K Gupta, Head, Department of Chemistry, IIT Roorkee for providing the basic infrastructural facilities.

I acknowledge with a deep sense of gratitude to the Head, Institute Instrumentation Centre, for providing XRD, FE-SEM, TEM and other instrumental facilities during the course of this work. I wish to record my appreciation to Mr. Sharma and Shiv Kumar for the technical assistance rendered by them. I am thankful to Mr. V. P. Saxena and Mr. Abdul Haque for the technical assistance in the department. I express my sincere thanks to the official staff in the Department; sincere thanks to Shri Amar Singh, Shri Madanpal, and Shri Netrapal for their timely help.

I offer my tender sentiments to Mr. Brij Bhushan, my all time support, friend and colleague for his crucial help and moral support all through this work. Besides, other laboratory colleague and friends Arvind Kumar Bharti, Satya Prakash Singh and Jay Singh Meena are thanked for their friendly cooperation.

As I look back, I find some people have left deep impact on my life. Sentiments bring the memories of my association with my teacher Dr. Arshi Rastogi, Assistant Professor, K.L.D.A.V (PG) College, Roorkee for her valuable help and support in giving me fundame knowledge on the research topic.

This thesis could not have been completed without the endless love, support blessings from my mother who has been a constant support and inspiration to me. A spe mention of my brother- Anshuman, sister-in-law- Smita, sister- Susmita, niece-Trisha brother-in-law-Thyagarajan, for their love, respect and needless to say high demands keeping me on my toes and going even in most demanding situations.

My tender sentiments and respect are for Ammaji, Prerna Aunty, Rajat, Shilpi, Vartika and course Shriya and Shirinya for their homely affection all through my stay at IIT, Roorkee

Last but not the least I will like to dedicate this thesis to my late father, Dhanes Nayak, who, apart from providing me the best available education, had also encouraged me all my endeavors and in making me the person that I am today.

IIT Roorkee

April, 2012

(ARUNIMA NAYA

ABSTRACT

Fresh water is an important and essential component of this universe and plays a vital role in the proper functioning of the Earth's ecosystem. In spite of this, safe drinking water is not available in many parts of the world. Rapid industrialization, modern methods of agricultural, domestic activities and other geological, environmental and global changes has put undue pressure on the demand and quality of fresh water, and this has resulted in the generation of large amount of waste water containing diverse types of pollutants. According to United Nations World Water Development Report, some two million tonnes of waste are discharged to the water bodies per day including industrial wastes, dyes and chemicals, human waste and agricultural wastes (fertilizers, pesticides).

The main sources of water contaminations are industrial, domestic and agricultural activities. More than one thousand pollutants are present in water and these include organic, inorganic and biological contaminants. Such pollutants in various forms are highly toxic, lethal and carcinogenic in nature due to their long environmental persistence and capability to control/affect the vital activities. Widespread concern over the toxicity and the environmental impact of the toxic pollutants has led to extensive research into developing effective technologies for the removal of these potentially damaging substances from effluents and industrial wastewater. The last decade has seen adsorption technology evolving as an efficient and universal method of water treatment as per the guidelines of WHO and EPA. Its wider applicability and greater momentum is due to its cost effectiveness and environmental-friendliness. The cost effectiveness of this technology is due to the use of effective adsorbents from solid industrial and agricultural wastes. Conversion of such negative–valued solid waste to value-added products finding use in environmental applications has further boosted its

demand. Research is ongoing in the search of more efficient adsorbent development from solid waste products.

In this context, we have utilized two different waste products viz waste rubber tires and orange peel inorder to develop novel adsorbents for removal of various types of pollutants from waste water.

It is worth mentioning that discarded tires comprise the biggest share amongst waste polymers in the world. Waste rubber tire does not decompose easily owing to its crosslinked structure and the presence of stabilizers and other additives and hence, traditionally they are being disposed by incineration or landfilling. However, this poses two problems: wasting of valuable rubber and environmental pollution. Literature study reveals that carbon black obtained by untreated rubber tire pyrolysis may be treated physically and/or chemically to develop its physico-chemical properties and hence to improve its adsorption behavior. As a means of reuse, we have developed various forms of novel activated carbon from waste tires for potential use in waste water treatment for adsorption of various types of toxic pollutants. This not only will provide a way for waste disposal and solid waste management but also their reuse will lower the cost of adsorbent production. My research activity will thereby demonstrate a double benefit by utilizing waste tire as a feedstock for inexpensive, quality activated carbon production, enabling both material recovery and reuse and water pollution abatement.

Novel adsorbents combining nanotechnology and magnetic separation technique have not only demonstrated high adsorption efficiency due to their large surface to volume ratio, but have shown additional benefits like ease of synthesis, easy usage, easy recovery and manipulation via subsequent coating and functionalization, absence of secondary pollutants, cost-effectiveness and environmental-friendliness. In this study, a novel magnetic nano-adsorbent (MNP-OPP) was developed by the surface modification of Fe_3O_4 nanoparticles (MNP) with orange peel powder (OPP) with the aim of exploring its feasibility as adsorbent for the removal of cadmium taken as a model toxic metal ion.

The main objectives of this research work were: to develop novel adsorbents

(i) RTAC, CTRTAC and $RTAC_{ox}$ from waste rubber tire granules by various physical and chemical activation methods for the removal of dyes, pesticides, metal ions and aromatic amines and

(ii) magnetic nano-adsorbent (MNP-OPP) for metal ion removal from aqueous solutions.

The physical and chemical properties of the adsorbents were evaluated with a view to incorporate a mechanistic approach to the adsorption phenomenon. The originality of this work was mainly based on the systematic investigations of adsorption over a wide range of pH, initial adsorbate concentration, contact time, adsorbent dosage, temperature and ionic strength. The experimental results were modeled by isotherm, kinetic and thermodynamic equations. Column adsorption and desorption studies were also evaluated.

The entire work is presented in seven chapters. **Chapter 1** describes the background of the research work, the problem statement and objectives of the present study. A detailed description of the various pollutants present in the contaminated water bodies and the various waste water treatment technologies used is discussed. The chapter gives a short literature review emphasizing on the adsorption technology and various adsorbents widely used for the adsorption of various types of pollutants.

Chapter 2 comprises the details of the experimental procedures adopted for the preparation of the adsorbents and the methods adopted for the adsorption and desorption studies. It also describes the various analytical and instrumental techniques used for the characterization of the adsorbents and adsorbates. Various isotherm, kinetic and thermodynamic models are discussed which enable for the theoretical aspect of the adsorption particularly at solid-liquid interface.

In **Chapter 3**, a mesoporous carbon (RTAC) developed from physical activation (carbonization-activation) of the waste tire rubber, characterized by chemical analysis, FTIR, and SEM studies, was used as an adsorbent for the removal and recovery of a hazardous azo dye, Acid Blue 113. Surface area, porosity, and density were determined. The adsorption of the dye over the prepared adsorbent and a commercial activated carbon was achieved under different pH, adsorbate concentration, sieve size, adsorbent dosage, contact time and temperature conditions. Langmuir and Freundlich adsorption isotherm models were applied and thermodynamic parameters were calculated. Kinetic studies indicated that the adsorption process follow first order kinetics and particle diffusion mechanisms are operative. By percolating the dye solution through fixed-bed columns the bulk removal of the Acid Blue 113 was carried out and necessary parameters were determined to find out the percentage saturation of both the columns. Recovery of the dye was made by eluting 0.1M NaOH through the column.

In **Chapter 4,** an inexpensive, mesoporous, carbonaceous adsorbent (CTRTAC) is prepared from a combined physical-chemical treatment (carbonization-chemical treatment-activation) of waste rubber tire and is used for the removal of toxic pesticides from waste water. SEM, porosity, FTIR studies reveal not only a well developed surface textural properties but also favorable surface chemistry. The developed characteristics were tantamount to admirable adsorption efficiency observed for the studied pesticides: methoxychlor, methyl parathion and atrazine. Batch adsorption studies revealed maximum adsorption of 112.0mgg^{-1}, 104.9mgg^{-1} and 88.9mgg^{-1} for methoxychlor, atrazine and methyl parathion respectively occurring at a contact time of 60mins at pH 2 from an initial pesticide concentration of 12mg/L. These promising results were confirmed by column experiments; thereby establishing the practicality of the developed system. The adsorption process has a physisorption nature, follows Langmuir isotherm, first order kinetics and is pore diffusion controlled. Spontaneous, exothermic and random characteristics of the process are confirmed by thermodynamic studies. The developed sorbent has a far better efficiency for pesticide removal than most other adsorbents reported in literature.

Chapter 5 has focused on utilizing the mesoporous adsorbent- RTAC to assess its adsorption efficiency for the removal of toxic lead and nickel ion from synthetic and real waste water. Effect of various operating parameters along with equilibrium, kinetic and thermodynamic studies reveal the efficacy of the RTAC for lead and nickel removal. The adsorption equilibrium data obeyed the Langmuir model and the kinetic data were well described by the pseudo-second-order model. A physical electrostatic adsorbate-adsorbent interaction is revealed from pH_{PZC} studies and from D-R model constants. The adsorption process is believed to proceed by an initial surface adsorption followed by intraparticle diffusion. Thermodynamic studies revealed the feasibility and endothermic nature of the system. Such promising results were confirmed by column experiments. Adequate desorption as well as reusability without significant loss of efficiency established the practicality of the developed system and demonstrated an important criterion of advanced adsorbent in RTAC for waste water treatment.

In **Chapter 6,** a novel adsorbent $RTAC_{ox}$ developed by HNO_3 treatment of thermally activated tire carbon (RTAC) (carbonization-activation-HNO_3 treatment) revealed superior physico-chemical properties. The higher mesoporosity and excess oxygen enriched surface chemistry has played a significant role in enhancing the adsorption capacity and kinetics of $RTAC_{ox}$ for liquid phase adsorption. Batch adsorption studies revealed the optimum levels of various environmental parameters for maximizing efficiency. Langmuir and D-R model helped in indicating the underlying mechanism of the adsorption process. Kinetic modelling revealed the applicability of the pseudo-second-order model and intra particle diffusion to be more suitable to describe the adsorbate-adsorbent system for both RTAC and $RTAC_{ox}$. Thermodynamic studies revealed the feasibility and exothermicity of the developed system. The regeneration and reuse without significant loss in efficiency showed an important criterion of advanced adsorbent in $RTAC_{ox}$ for waste water treatment. The work demonstrates a cost-effective utilization of modified waste rubber tires for enhanced pollutant removal.

Chapter 7 focused on assessing the adsorption efficiency of a novel MNP-OPP adsorbent developed from a local agricultural waste-orange peel powder for a toxic cadmium metal ion. Characterization studies revealed the various physico chemical properties on MNP-OPP which are favorable for metal binding. Comparative preliminary batch studies demonstrated not only the optimal process parameters for maximizing metal sorption but also the principle underlying mechanism. Langmuir adsorption plot showed maximum Cd^{2+} removal by MNP-OPP at 76.92 mg/g at optimal conditions and thermodynamic studies revealed the feasibility of the process. Pseudo-second-order model was determined as the best fit model. Column studies with a breakthrough capacity of 55.38 mg/g as well as 82% Cd^{2+} removals from an electroplating effluent simulated wastewater revealed the practical utility of the developed adsorbent. Finally, desorption and reusability studies indicate a fulfilling of important criteria for advanced adsorbents. The developed MNP-OPP has demonstrated not only high adsorption efficiency, faster kinetics but also have shown additional benefits like ease of synthesis, easy recovery, absence of secondary pollutants, and environmental-friendliness.

LIST OF PAPERS

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Chapter 1

INTRODUCTION

1.1. BACKGROUND

Water is a valuable environmental resource which requires special attention. Although, water covers 70% of the earth, but only limited quantities (approx. 1%) are available as fresh water. The search for clean, fresh, and potable water has always been one of mankind's priorities. However, with rapid industrialization and modern methods of agricultural and domestic activities, the demand for water [1] has increased tremendously, and this has resulted in the generation of large amounts of wastewater [2-4] containing a number of pollutants that are harmful to both human and animal life. Table 1.1 lists some important sources of water pollution. According to the United Nations World Water Development Report, [5] some 2 million tonnes of waste per day are disposed of within receiving waters, including industrial wastes and chemicals, human waste, and agricultural wastes (fertilizers, pesticides, and pesticide residues). In addition, according to the World Water Council and the World Health Organization [6] there is already more wastewater generated and dispersed today than at any other time in the history of our planet, and more than one out of six people lack access to safe drinking water. Also, according to a WHO report [7] there are an estimated 2.6 billion people in the world without proper sanitation facilities, representing close to 42% of the world's population, and approximately 1.1 billion people do not have access to any type of improved drinking water facility. It is also estimated that by the middle of this century, at worst 7 billion people in sixty countries and at best 2 billion people in forty-eight countries will be water-scarce [5].

1.2. POLLUTANTS

The term pollutant, in a broad sense, refers to a substance/material that changes the natural quality of the environment by physical, chemical, or biological means. The three main activities that mankind indulges in are domestic, agricultural, and industrial. Table 1.2 gives a comprehensive list of different industries discharging various pollutants. In all of these activities, a large amount of fresh water is used, which is discharged as wastewater containing different pollutants depending on the type of activity. These may be various inorganic and organic chemicals [8-10] and biological agents as well as heat and radiations. A pictorial classification of major water pollutants (on the basis of chemical nature) is shown in Figure 1.1. Some of the important pollutants are discussed below.

1.2.1. Biological Agents

A number of biologically active agents, [10] such as *Vibrio comma, Salmonella typhosa, Yersinia enterocolitica, Escherichia coli, and Shigella dysenteriae,* may be present in domestic effluent and sewage water and need to be removed. Some of the important waterborne diseases caused by biological agents are cholera, typhoid, dysentery, gastroenteritis, and jaundice.

1.2.2. Heat

Ideally, the temperature of water should be constant or undergo minimum variation. Because of its high heat capacity, water is used as a cooling medium. Thus, many industrial plants discharge water carrying away waste heat [11]. The high temperature of this wastewater not only affects aquatic life but is known to cause many chemical and bacteriological reactions, such as formation of trihalomethane (THM) and higher corrosion activity.

1.2.3. Dissolved and Non-Dissolved Chemicals

During the course of domestic, industrial, and agricultural operations, a number of chemicals are used or produced and often get mixed up with fresh water, which is then discharged as wastewater. The chemicals present in wastewater may be in a dissolved or non-dissolved state.

Non-dissolved substances are generally present as suspended solids in a dispersed form. The suspended solids make the water turbid and sometimes they may also slowly settle down with the formation of silt. The presence of suspended solids clogs waterways, fills up dams, and is harmful to aquatic life in many ways [12]. The most common chemicals [10] found in wastewater in a dissolved state and considered as potential pollutants are heavy metals, dyes, phenols, detergents, pesticides, polychlorinated biphenyls (PCBs), and a host of other inorganic and organic substances.

1.2.3.1. Heavy Metals

The wastewater generated from many industries may contain a number of heavy metals which have significant toxic effects [13, 14] and they are therefore considered as pollutants [15, 16] requiring removal. The various industries that generate such water include the tanning, battery, glassware, ceramics, electroplating, mining, paints, and photographic industries. These wastewaters contain heavy metals such as chromium, lead, cadmium, arsenic, copper, iron, manganese, vanadium, nickel, mercury, cobalt, molybdenum, and bismuth, among others. The amount and the number of metals present in any wastewater are related directly to the operations carried out in an industry. For example, tanneries discharge chromium in wastewater; copper, chromium, zinc, and cadmium are widely generated from metal plating; the production of electrical equipment and mining, smelting, and fossil fuel combustion contribute to mercury pollution; and lead is generated from a number of industrial and mining sources. In most wastewaters, the concentration of heavy metals present is much larger than the safe permissible limits and, therefore, they need to be removed.

1.2.3.2. Dyes

Dyes are important materials that are currently in use both for domestic and industrial purposes. Since the invention of synthetic dyes [17] in 1856, several forms of dyes are now available, and more than 8000 dyes are being manufactured and consequently used for specific purposes. The dyes in use are both water soluble and insoluble. The big consumers of dyes are textile, dyeing, paper and pulp, tannery, and paint industries. Hence, the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities for them to be considered an objectionable type of pollutant for two reasons: they impart colour to water, which is not acceptable on aesthetic grounds, and they are toxic and adversely affect life [18-21].

1.2.3.3. Pesticides

Whereas many other pollutants are only important in the urban setting, pesticides are pre-eminently a problem arising from rural activities. Depending on their function, pesticides [22] are sub classified as insecticides, molluscides, nematicides, rodenticides, avicides, piscides, fungicides, bactericides, slimcides, algicides, and herbicides. Among these, insecticides and fungicides are important pesticides with respect to human exposure in food because they are applied shortly before or even after harvesting. Herbicide production has increased significantly, as chemicals are being increasingly used during the cultivation of land for controlling weeds and now accounts for the majority of agricultural pesticides. Although DDT has been banned, various substitutes such as toxaphene, lindane, parathion, malathion, heptachlor, and endrin can also cause environmental pollution. The problem of pesticide pollution arises not only due to agricultural operations but also from pesticide manufacturing plants.

1.2.3.4. Phenols

Like dyes and metals, phenols are also considered priority pollutants [23,24] as they impart bad taste and odour to water and are also toxic, [25-27] even at low concentrations. The determination and removal of phenols from water is therefore important. These are present in wastewaters generated from pulp and paper, chemical, paint, resin, pesticides, gas and coke manufacturing, tanning, textile, plastics, rubber, pharmaceutical and petroleum industries.

1.2.3.5.Detergents

Most detergents are phosphate based, which are major water pollutants, responsible, for 42 per cent of human and animal diseases. According to literature “the main problem is that of phosphate-based detergents promoting eutrophication of aquatic environments". Eutrophication or nutrient pollution is a process by which water bodies gradually age and become more productive. Sewage perhaps is a particular source of phosphorus when detergents containing large amounts of phosphates are drained during washing. Nowadays sewage contains appreciable quantities of synthetic detergents too [13]. The persistent surfactants like alkyl benzene sulphonate (ABS) interfere with the waste treatment process by stabilizing the small particles as colloidal suspensions and thereby decreasing the activity of biological filter beds and activated sludge.

1.2.3.6. PCBs and PBDEs

The term polychlorinated biphenyls (PCBs) refer to a group of 209 different chemical compounds. PCBs were used primarily for lubrication and insulation in electrical equipment and are generated in a variety of manufacturing processes which include manufacture of brake linings, glass ceramics, grinding wheels, various types of coatings, flame proof paints, varnishes, sealants, electrical equipments, plastic coatings etc. They show high chemical, thermal and biological stability: low vapour pressure and high dielectric constants. They do not cause biochemical oxygen demand problem in aquatic ecosystems but are extremely toxic [21]. PCBs are considered among the most dangerous of life threatening substances created by humans. They pollute the food chain and are present as contaminants in wildlife and humans at levels thousands of times higher than the surrounding air, water, and soil. Many studies have shown that PCBs are capable of disrupting the endocrine system and are associated with reproductive failure, immune system disorders, behaviour and learning disorders, and cancers.

Polybrominated diphenyl ether (PBDE) is a flame-retardant sub-family of the brominated flame-retardant group. They have been used in a wide array of household products, including fabrics, furniture, and electronics. These pollutants are of three main types, according to the bromine atoms in the molecule i.e. penta, octa and deca. The family of PBDEs consists of 209 different substances, which are called congeners. There are two sub-groups viz. lower brominated and higher brominated. Lower brominated PBDEs have 1-5 bromine atoms and are regarded as the most dangerous ones, because of the smaller size which can be absorbed by living organisms easily. These PBDEs have been known to affect hormone levels in the thyroid gland [22]. Whereas, higher brominated PBDEs have more than 5 bromine atoms and were formerly regarded as environmentally harmless chemical compounds.

1.2.3.7. PAHs

Polycyclic aromatic nuclear hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings and do not contain heteroatom or other substituent. Some of them are known as suspected carcinogens. They are formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, or tobacco [23]. PAHs toxicity is very structurally dependent, with isomers (PAHs with the same formula and number of rings) varying from being nontoxic to being extremely toxic. Thus, highly carcinogenic PAHs may be small or large. One PAH compound, benzoic[a]pyrene, is regarded as first chemical carcinogen to be discovered. Other common PHAs, which are known for their carcinogenic effects are benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, coronene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, ovalene and phenanthrene.

1.2.3.8. Dioxins

Dioxins are possibly the most cancer causing chemicals known because their chemical structure mimics that of hormones. They are toxic mainly because they are persistent organic pollutants [24]. Dioxins can exist in our body for up to seven years before they kill. The only known way to destroy dioxins is by burning the contaminated material, by heating it to almost 1000°C. The reason why dioxins are some of the most toxic chemicals in existence is because they do not dissipate naturally.

1.2.3.9. Radioactive Substances

Radioactive substances [13] are handled with all precautions in view of harmful nature of radiations emitted by them. In spite of this, radioactive materials are often found in effluents coming from research laboratories, hospitals, nuclear power plants, and ore processing industries, military and natural sources. Nowadays, many nuclear weapons are tested underground which is contaminating ground water radioactively.

1.2.3.10. Other organic chemicals

A host of other organic chemicals may also be present in effluents generated from different industries. These include: trihalomethanes, such as chloroform and bromoform; trichloroethylene; tetrachloroethylene; aromatic hydrocarbons, such as benzene, toluene, xylene, and biphenyls; halogenated aromatics, such as cholorobenzene, dicholorobenzene, chlorotoluene, and chloroxylene; halogenated aliphatic compounds, including bromocholoromethane, dibromomethane, and tetrachloromethane; halogenated ethers; polycyclic aromatic hydrocarbons, such as naphthalene, acenaphthene, fluorene, and phenanthrene; aldehydes; esters; alicyclic hydrocarbons and ketones

The majority of the chemicals present in wastewater are toxic above certain concentration level and are, therefore, considered as pollutants. The lethal effects of the pollutants are well documented in literature [7, 14, 15, 19]. In view of general awareness created by modern methods of communication and information, it has become imperative on the part of government, industries and municipal authorities to work out methods for pollution control. A number of methods are of course available but sometimes cost factors override the importance of pollution control. The search for cost effective technology for safe and effective treatment of wastewater is always on.

1.3. WASTEWATER TREATMENT TECHNOLOGIES

Wastewater treatment and reuse is an important issue and scientists are looking for inexpensive and suitable technologies. Water treatment technologies are used for three purposes i.e. water source reduction, wastewater treatment and recycling. At present, unit operations and processes are combined together to provide what is called as primary, secondary and tertiary treatment. The primary treatment includes preliminary purification processes of physical and chemical nature while the secondary treatment deals with the biological treatment of wastewater. In tertiary treatment process, wastewater (treated by primary and secondary processes) is converted into good quality water that can be used for different types of purposes i.e. drinking, industrial, medicinal etc. supplies. In the tertiary process, the pollutants are removed up to 99% and water is converted into the safe quality for a specific use. In a complete water treatment plant, all these three processes are combined together for producing good and safe quality of water. The complete scheme of wastewater treatment is shown in Figure 1.2.

Despite the development of various technologies for water treatment and reclamation, economic, effective and rapid water treatment and reclamation at commercial level is still a challenging problem. The management of the removed pollutants (sludge) should be kept in mind. The systematic approach of water treatment and recycling technologies involves the understanding of the technology that includes construction and operational cost, maintenance and management of removed pollutants. Water treatment and recycling technologies have been classified on the following headings.

1.3.1. Primary Water Treatment Technologies

1.3.2. Secondary Water Treatment Technologies

1.3.3. Tertiary Water Treatment Technologies

1.3.1. Primary Water Treatment Technologies

In this category, water is treated at the primary level using screening, filtration, centrifugation [25, 26], sedimentation [27, 28], coagulation [29] and flotation [30, 31] methods. Normally, these methods are used when water is highly polluted.

1.3.2. Secondary Water Treatment Technologies

Secondary water treatment includes biological routes for the removal of soluble and insoluble pollutants by microbes [32, 33]. Water is circulated in a reactor that maintains a high concentration of microbes. The microbe usually bacterial and fungal strains convert the organic matters into water, carbon dioxide and ammonia gases [34-38]. The biological treatment includes aerobic [39, 40] and anaerobic digestion [41-46] of wastewater. Depending on the materials use, the cost of biological treatment varies between 20 and 200 US$ / million litre. The disadvantage of the method is the production of a large quantity of biosolids, which require further costly management. The aerobic process is carried out by trickling filters or activated sludge processes or oxidation ponds.

1.3.3. Tertiary Water Treatment Technologies

Tertiary water treatment technologies are very important in wastewater treatment strategy as these are used to get the safe water for human consumption. The techniques used for this purpose are distillation [47], crystallization [48], evaporation [49], solvent extraction [50, 51], chemical oxidation carried out by potassium permanganate, chlorine, ozone, H_2O_2, Fenton's reagent (H_2O_2 and Fe catalyst) and chlorine dioxides [52-60], advanced oxidation method using ozone [61-64], combined ozone and peroxide [65], ultra violet enhanced oxidation such as UV/Fenton or photo-Fenton [66, 67], UV/hydrogen peroxide, UV/ozone [68], UV/air wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant), photocatalysis using oxides such as TiO_2, ZnO, ZrO_2, CeO_2, etc. or sulfides such as CdS, ZnS, etc. [69-77], sonolysis [78], precipitation [79], ion exchange [80-84], micro and ultra filtration [85-87] reverse osmosis [88-94] and adsorption [95], electrolysis [96-101] and electrodialysis [102-105].

A particular treatment process may not be effective sometimes in removing all pollutants and in such cases a number of processes may be used in conjunction so that all types of pollutants can be tackled. Under such situation adsorption process is considered better as compared to other methods because of convenience, ease of operation, simplicity of design and universal in use. Further, this process can remove/minimize different type of pollutants and thus has a wider applicability in pollution control. As this thesis deals with the removal of various types of pollutants it is desirable to survey literature on adsorption methodology. This is being discussed in the following sections

1.4. ADSORPTION TECHNOLOGY

The resourcefulness and wider applicability of adsorption in pollution control have been recognized [106-111]. The importance of adsorption [112-114] in chemical, food, petroleum and pharmaceutical industries is also well established.

The term adsorption refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings. It is now customary to differentiate between two types of adsorption. If the attraction between the solid surface and the adsorbed molecules is physical in nature, the adsorption is referred to as physical adsorption. Generally, in physical adsorption, the attractive forces are van der Waals forces, and as they are weak, the resulting adsorption is reversible in nature. On the other hand, if the attraction forces between adsorbed molecules and the solid surface arise due to chemical bonding, the adsorption process is called chemisorption. In view of the higher strength of the bonding in chemisorption, it is difficult to remove chemisorbed species from the solid surface. The strength of bonding in physical adsorption and chemisorption is manifested in the values of enthalpy of adsorption which are much lower (≤ 25 kJmol-1) for the former as compared to later (of order 200 $kJmol^{-1}$). The solids adsorbing the material are called adsorbents whereas the substances that are adsorbed are called adsorbates.

Although certain phenomenon associated with adsorption were known in ancient times, the first quantitative studies were reported by C.W. Scheele [114] in 1773 on the uptake of gases by charcoal and clays. This was followed by the observations of Lowitz who used charcoal for the decolorization of tartaric acid solutions. Larvitz in 1792 and Kehl in 1793 observed similar phenomenon with vegetable and animal charcoals, respectively. However, the term 'adsorption' was proposed by Bois-Reymond but introduced into the literature by Kayser [115]. Ever since then, the adsorption process has been widely used for the removal of solutes from solutions and gases from air atmosphere. The extent of adsorption is found to depend on the nature of adsorbent especially its porosity and surface area. As such, various adsorbents showing higher and sometimes selective adsorption have been developed by different workers and some of these are discussed here.

1.5. ADSORBENTS

The important characteristics of good adsorbents [116, 117] are their high porosity and consequently larger surface area with specific adsorption sites. Most adsorbents which have been used in pollution control tend to have porous structure. The porous structure not only increases surface area and consequently adsorption but also affects the kinetics of the adsorption. A better adsorbent is considered one which has high surface area with less time for adsorption equilibrium. Thus, for the removal of pollutants, one generally looks to adsorbents with high surface area and faster kinetics. There are numerous types of adsorbents, which have been used for wastewater treatment. In context of their relative cost, these adsorbents can be categorized as traditional expensive adsorbents and low cost alternative to inexpensive adsorbents. A pictorial classification of adsorbents is given in Figure 1.3.

1.5.1. TRADITIONAL ADSORBENTS

This class of adsorbent consists of costly adsorbents, which are in use for many years. High cost of these adsorbents is due to their manufacture by private companies and sale as per their high profit. As already discussed, their use is often restricted due to their high cost and necessity of regeneration. Few of them are given below:

1.5.1.1. Silica Gel

Silica gel is an amorphous adsorptive substance with stable chemical properties and has a highly complicated porous structure. It is used in various fields of our daily life as high adsorbent of high safety. Both siloxane, -Si-O-Si-, and silanol -Si-O-H-, bonds are present in the gel structure. The silica gels are classified into three types: regular, intermediate and low density gels. Regular density silica gel is prepared in an acid medium and show high surface area ($750m^2/g$). Intermediate and low density silica gels have low surface areas (300-350 m^2/g and 100-200 m^2/g, respectively). The gel is considered good adsorbent and is used in many industries for drying of gases and liquids, purification of hydrocarbons etc. [118, 119]. Its cost varies with its particle size and purity, an ideal sample of silica gel with 99% purity, costs about US $ 180 per kg.

1.5.1.2. Activated Alumina

The activated alumina comprises a series of nonequilibrium forms of partially hydroxylated alumina, Al_2O_3. They are porous solids made by thermal treatment of aluminum hydroxide precursors and find applications mainly as adsorbents, catalyst and catalyst support. In general, as a hydrous alumina precursor is heated, hydroxyl groups are driven off leaving a porous solid structure of activated alumina. One of the earliest uses for activated alumina was removal of water vapors from gases and this remains an important application. Activated alumina having the surface area ranging from 200-300 m^2/g [120], is also used to remove water from organic liquids including gasoline, kerosene, oils, aromatic hydrocarbons and many chlorinated hydrocarbons. Activated alumina is receiving renewed attention as an adsorbent and a wealth of information has been published [121-123] on its adsorption characteristics. The cost of alumina used for water purification is about US $ 58 per kg.

1.5.1.3. Zeolites and Ion Exchange Resins

Zeolites are basically hydrated alumino-silicate minerals with an "open" structure that can accommodate a wide variety of positive ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. There are 40 natural and over 100 synthetic zeolites, among them the more common mineral zeolites are: analcime, chabazite, heulandite, natrolite, phillipsite, and stilbite. The zeolitic channels (or pores) are microscopically small, and in fact, have molecular size dimensions such that they are often termed "molecular sieves". The size and shape of the channels have extraordinary effects on the properties of these materials for adsorption processes, and this property leads to their use in separation processes. Molecules can be separated via shape and size effects related to their possible orientation in the pore, or by differences in strength of adsorption. They are also considered as selective adsorbents. Zeolites generally show a surface area in the range 1-20 m^2/g [120]. Zeolites-based materials are extremely versatile. Various zeolites have been employed for the removal of pollutants [124, 125]. A number of ion-exchange resins have also been used widely in household and industrial water purifications to produce soft water. This is accomplished by exchanging calcium Ca^{2+} and magnesium Mg^{2+} cations against sodium Na^+ or hydrogen H^+ cations for the removal of specific compounds e.g. the removal of ammonia-nitrogen in ammonium chloride wastewater from rare earth smeltery by Wang et al. [126], the removal of geosmin and methylisoborneol from drinking water by Ellis and Korth [124] and the removal of phenols and chlorophenols by Okolo et al. [125]. These adsorbents also have widespread applications in petroleum industry. The cost of zeolites, which are usually used for water treatment purpose, is about US $ 210 per kg.

1.5.1.4. Activated carbon

Activated carbon is the most popular and widely used adsorbent in wastewater treatment throughout the world. It has a random imperfect structure which is highly porous over a broad range of pore sizes from visible cracks and crevices to molecular dimensions.

The graphite structure gives carbon it's very large surface area which allows the carbon to adsorb a wide range of compounds. It has the strongest physical adsorption forces or the highest volume of adsorbing porosity of any material known to mankind. Activated carbon can have a surface area greater than 1000 m^2/g. The use of carbon extends so far back into history that its origin is impossible to document. Charcoal was used for drinking water filtration by ancient Hindus in India since 2000 B.C. [114, 116], and carbonized wood was used as a medical adsorbent and purifying agent by the Egyptians as early as 1500 B.C. Modern development and use has been documented more precisely.

The activated carbon generally exists in two forms (i) powdered activated carbon (PAC) and (ii) granular activated carbon (GAC). Since granular form is more adaptable to continuous contacting and there is no need to separate the carbon from the bulk fluid, most of the work on the removal of pollutants from water has been on GAC. On the other hand, the use of PAC offers some practical problems like requirement of separation of the adsorbent from the fluid. However, in spite of these problems, PAC is also used for wastewater treatment due to low capital cost and lesser contact time requirements [127]. Two more specific forms viz. activated carbon fibrous (ACF) and activated carbon clothe (ACC) are also in use [128, 129]. The cost of activated carbon varies from US $ 2.5 – 55 per kg depending upon the purity and particle size.

Activated carbon was first generated industrially in the first part of the twentieth century, when carbon activated from vegetable material was produced for use in sugar refining [130]. The first documented use of activated carbon in a large scale water treatment application was in 19th-century in England, where it was used to remove undesirable odours and tastes from drinking water [131]. This carbon was found effective in decolorizing liquids. Activated carbon has since been used extensively for this purpose in many industries. In particular, it has been commonly used for the removal of organic dyes from textile wastewaters. In recent years, the use of activated carbon for the removal of priority organic pollutants has become very common. Today, hundreds of brands of activated carbon are manufactured for a large variety of purposes [132]. The credit of developing commercial activated carbon goes to Raphael von Ostrejko [133] whose inventions were patented in 1900 and 1901. Early applications of carbon in water treatment plant to remove chlorophenolics tastes were reported by Baylis in U.S. and Sierp in Germany in 1929. Hassler [134] has summarized in his book the successful application of activated carbon in providing potable water. In USA, for the first time in 1928, activated carbon was used for the water supplies and within ten years the figure of water treatment plants with activated carbon increased to a thousand marks. The applicability of activated carbon for water treatment has been demonstrated by Weber et al. [135] and Green et al. [136] who talked about the potentiality of activated carbon for water and air purification. Stenzel [137] in his article describes the adsorption with granular activated carbon to be a proven technology for water purification.

It is thus seen that a wide variety of raw materials have been used to prepare activated carbon. However, the activated carbon used in wastewater treatment is generally prepared from coconut shells, peat, sawdust, wood char, lignin, petroleum coke, bone char, anthracite coal etc. [138].

Activated carbon has become the standard adsorbent for the reclamation of municipal and industrial wastewaters to a water potable quality. It has been successfully utilized for the removal of metal ions [139-141], dyes [142-146], phenols [147-151], detergents [152, 153], pesticides [154, 155], humic substances [156, 157], chlorinated hydrocarbons [158, 159] and many other chemicals and organisms [160-166].

1.5.1.5. Modified activated carbon

The adsorption efficiency of activated carbons is strongly dependent on their surface chemical features. Therefore, the surface chemical modification of carbon is of great interest in order to produce materials for specific applications. It has been observed by various workers that chemical treatment at the time of activation during the manufacture of activated carbons often enhances the adsorption properties [167-170]. This modification has been mainly carried out by oxidative methods, producing a more hydrophilic structure with a large number of oxygen-containing groups. Various reagents have been used as oxidants: concentrated nitric or sulphuric acid, sodium hypochlorite, permanganate, bichromate, hydrogen peroxide, transition metals and ozone-based gas mixtures. It was found that the type of surface structures and the extent of their formation depend on the oxidizing agent, the concentration and the pH of the oxidizing solution.

1.5.2. ALTERNATIVE LOW COST ADSORBENTS

As already stated, the activated carbon is the most popular adsorbent for the removal of pollutants from wastewater, but it has certain limitations. Activated carbon presents several disadvantages [171] as it is costly and cannot be afforded at an economical level. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [172]. This has led research interest towards various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. According to Bailey et al. [173], a sorbent can be considered as low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative adsorbents. Many of them have been tested and proposed for pollutants removal.

1.5.2.1. Agricultural wastes as low-cost adsorbents

Agricultural materials particularly those containing cellulose show potential sorption capacity for various pollutants. The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing variety of functional groups. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable option for water and wastewater remediation. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness [174], therefore, conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and also to reduce the preparation costs. In the last several decades, various agricultural wastes have been explored as low-cost adsorbent. Some of them include the shells and/or stones of fruits like nuts [175-177], peels of fruits and vegetables [178-198], peanuts and ground nuts [199-209], tea and coffee wastes [210-223] coconut wastes [224-237] olive wastes [238], almonds [239], apricots stones [240] and cherries [241]; and wastes resulting from the production of cereals such as rice [242-256], wheat [257-261],maize [262] and corn [263] as well as sugar cane bagasse [264] and coir pith [265]. These agricultural waste materials have been used in their natural form or after some physical or chemical modification.

1.5.2.2. Industrial and municipal wastes as low-cost adsorbents

Widespread industrial activities generate huge amount of solid waste materials as by-products. Some of this material is being put to use while others find no proper utilization and are dumped elsewhere. The industrial waste material is available almost free of cost and causes major disposal problem. If the solid wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent if developed can reduce the pollution of wastewaters at a reasonable cost. In view of the low cost of such adsorbents, it would not be necessary to regenerate the spent materials. Thus, a number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewaters. Some of them are fly ash or thermal power plant waste [266-280], steel industry wastes [281-297], red mud or aluminum industry wastes [298-308], carbon slurry or fertilizer industry wastes [309-317], leather industry wastes [318-321], paper industry wastes [322-326], industrial sludge [327-337], distillery industry wastes [338], battery industry wastes [339], boron industry waste [340-340] discussed here.

1.5.2.3. Natural Materials as low-cost adsorbents

The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is termed biosorption. In this instance, biological materials, such as chitin and chitosan [341-346], peat [347, 348], yeasts, fungi or bacterial biomass [349-353] are used as chelating and complexing sorbents in order to concentrate and to remove pollutants from solutions. These biosorbents and their derivatives contain a variety of functional groups which can complex dyes. The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye concentration to ppb levels. Biosorption is a novel approach, competitive, effective and cheap.

1.6. PROBLEM STATEMENT

Water pollution is a serious threat to mankind in the present scenario and, hence, many techniques are in use for water treatment. Out of them adsorption is a commonly used method as it is simple, fast and universal in nature. Normally, activated carbon is used as an ideal adsorbent for wastewater treatment but it is costly and requires regeneration. The regenerated carbon exhibits lower adsorption capacity with further management problem of the effluent obtained from its regeneration. These facts have grown interest in many workers towards the search for low cost alternatives of activated carbon. Literature indicates some papers on adsorption using naturally occurring materials and industrial wastes as substitute adsorbents for the removal of water pollutants.

After the critical evaluation of the reported papers/reports, it was observed that most adsorbents show poor adsorption capacities, longer equilibration times, and maximum adsorptions at extreme pH values. Moreover, the management of the exhausted adsorbent is of serious concern which has not been considered in the previously reported papers. Besides, the developed adsorbents have not been tested for different pollutants especially under column studies. In addition to this, many waste by-products have not been used for the preparation of adsorbents. Briefly, a lot of work is required in this direction of the low cost alternatives to carbon. In view of the above discussed facts, it has been realized that development of low cost adsorbents exhibiting good adsorption potential is still required.

1.6.1. Waste tire and disposal problem

It is worth mentioning that discarded tires comprise the biggest share amongst waste polymers in world. Waste rubber tire does not decompose easily owing to its crosslinked structure and presence of stabilizers and other additives and hence, traditionally they are being disposed by incineration or landfilling. Literature study reveals that carbon black obtained by untreated rubber tire pyrolysis may be treated physically and/or chemically to develop its physico-chemical properties and hence to improve its adsorption behaviour. In this research, as a means of reuse, we have developed various forms of novel activated carbon from waste tires for potential use in waste water treatment for adsorption of various types of toxic pollutants.

1.6.2. Agricultural waste-Orange Peel

Novel adsorbents combining nanotechnology and magnetic separation technique have not only demonstrated high adsorption efficiency due to their large surface to volume ratio, but have shown additional benefits like ease of synthesis, easy usage, easy recovery and manipulation via subsequent coating and functionalization, absence of secondary pollutants, cost-effectiveness and environmental-friendliness. In this work, a novel magnetic nano-adsorbent (MNP-OPP) was developed by the surface modification of Fe_3O_4 nanoparticles (MNP) with orange peel powder (OPP) with the aim of exploring its feasibility as adsorbent for the removal of cadmium taken as a model toxic metal ion.

1.7. OBJECTIVE OF STUDY

a. To develop novel adsorbents
    (i) RTAC, CTRTAC and $RTAC_{ox}$ from waste rubber tire granules by various physical and chemical activation methods for the removal of dyes, pesticides, metal ions and aromatic amines and
    (ii) magnetic nano-adsorbent (MNP-OPP) by co-precipitation with orange peel powder (OPP) and Fe_3O_4 nanoparticles (MNP) for metal ion removal from aqueous solutions.

b. Characterization of activated carbon produced with respect to surface texture, morphology, porosity, surface area, surface functional groups and elemental composition.

c. To carry out batch adsorption experiments in order to determine the optimum parameters of the adsorption process,

d. Modeling of sorption data using various models inorder to determine the best fit model applicable to the process and to determine the mechanism with respect to thermodynamics and equilibrium.

e. To carry out kinetic studies using various kinetic models in order to determine the kinetics of the adsorption process and the rate process.

f. To carry out column adsorption study to determine the various parameters necessary for the development of fixed-bed contractors on to pilot scale and for practical application of the technique to real waste water treatment situations.

g. To carry out desorption studies on the adsorbent-adsorbate system for recycling and regeneration of adsorbent as well as the pollutants which is essential for the adsorption technology to have economic significance.

1.8. SCOPE OF STUDY

The research work has focussed on the development of activated carbon from waste materials which are available in abundance and have no economic value for the removal of various types of pollutants. The wastes studied are waste rubber tires and orange peel-an agricultural waste product. These wastes have been processed, converted into surface adsorbents and used for the removal of a number of dyes, pesticides, metal ions and aniline derivatives, by using batch processes. These adsorbents were also tried for the removal of the said pollutants by using column operations at laboratory scale. The results of these investigations are presented in this thesis, which indicate efficiency, effectiveness and universal nature of the developed adsorbents. Therefore, the developed adsorbents can be considered and used as low cost alternatives to activated carbon for the removal of a wide range of water pollutants from real water samples.

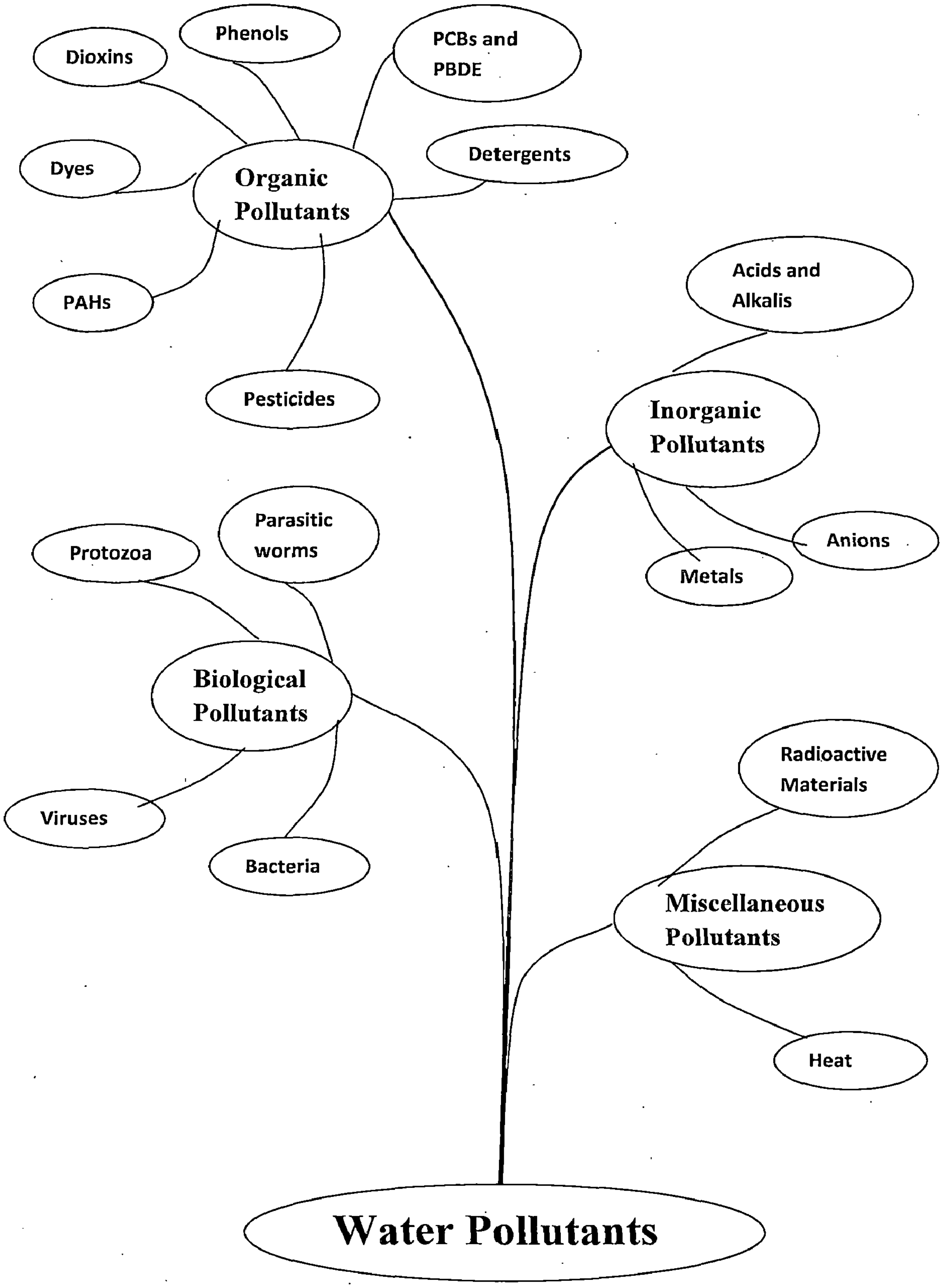

FIGURE 1.1:

Broad classification of water pollutants on the basis of their chemical nature

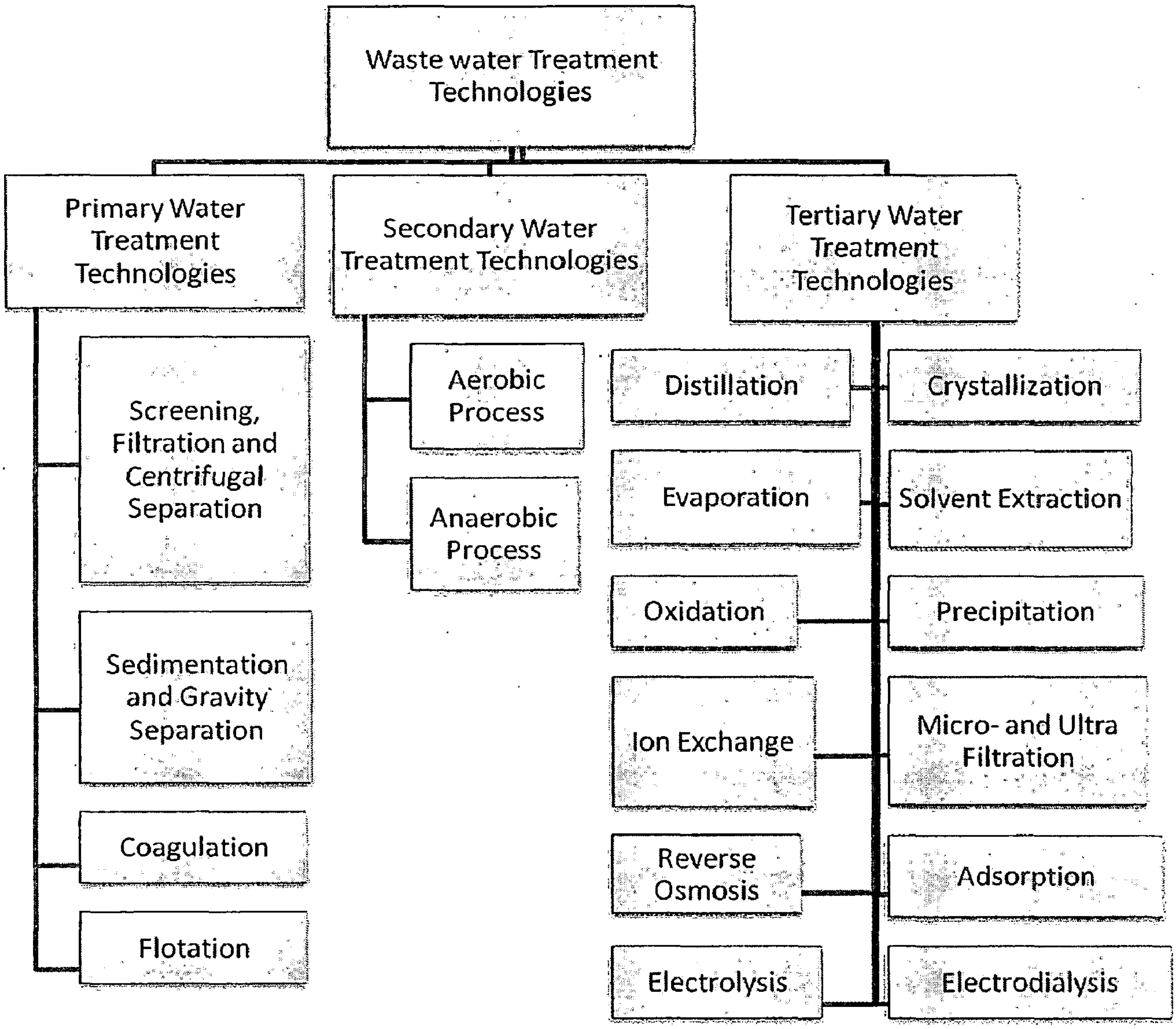

Figure 1.2:

Illustration of the classification of Waste Water treatment technologies

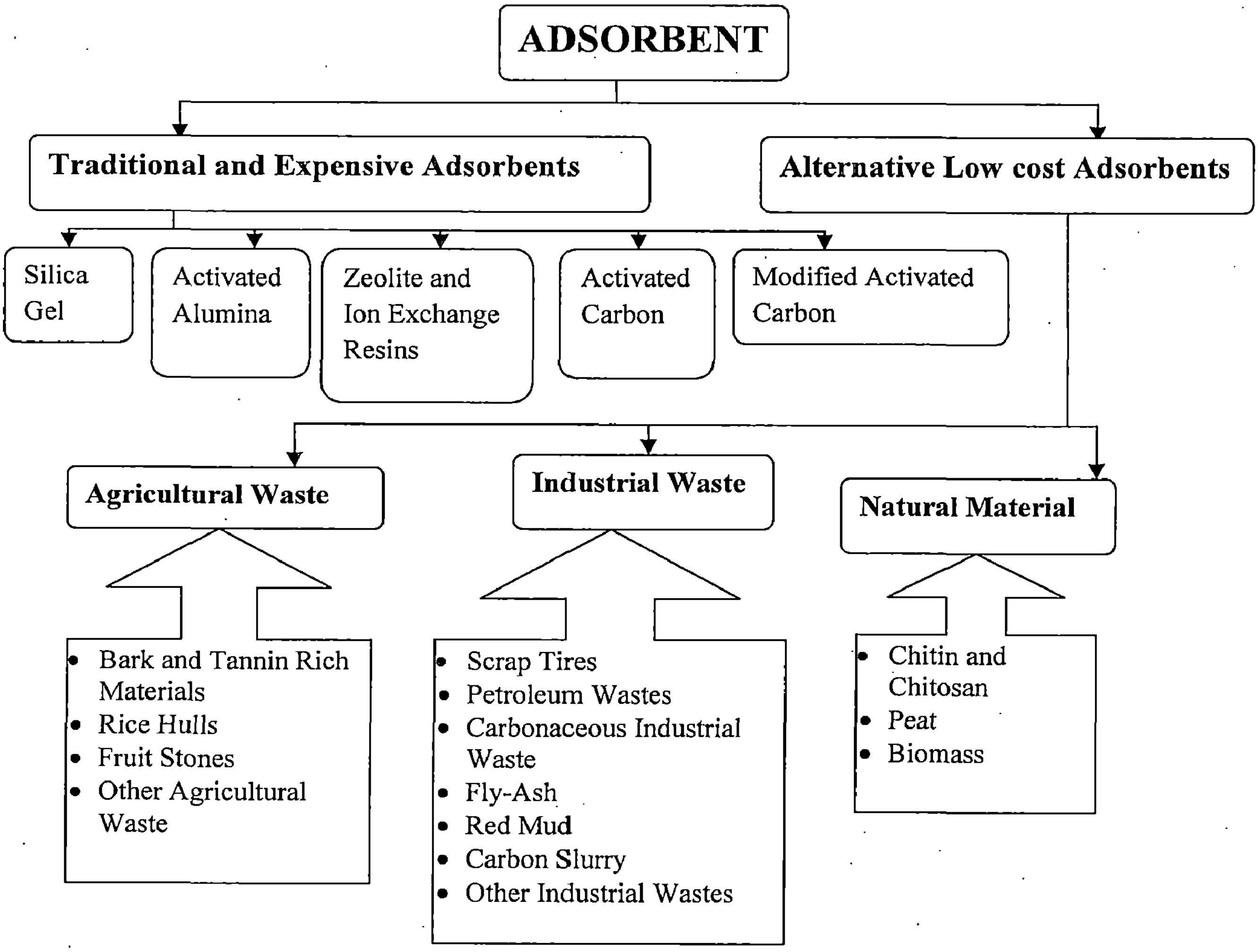

Figure 1.3:

Complete classification of adsorbent material used for the removal of toxic substances from wastewater.

TABLE 1.1:

Some sources of water pollution

Surface Water	Groundwater
• Urban runoff (oil, chemicals, organic matter, etc.) (U, I, M) • Agricultural runoff (oil, metals fertilizers, pesticides, etc.) (A) • Accidental spills of chemicals including oil (U, R, I, A, M) • Radioactive materials (often involving trucks or train accidents) (I, M) • Runoff (solvents, chemicals, etc.) from industrial sites (factories, refineries, mines etc.) (I, M) • Leak from surface storage tanks and pipelines (gasoline, oil etc.) (I, A, M) • Sediments from a variety of sources, including agricultural lands and construction sites (U, R, I, A, M) • Air fallout (particles, pesticides, metals etc.) intro river, lake, ocean (U, R, I, A, M)	• Leaks from waste disposal sites (chemical, radioactive materials etc.) (I, M) • Leaks from buried tanks and pipes (gasoline, oil, etc.) (I, A, M) • Seepage from agricultural activates (nitrates, heavy metals, pesticides, herbicides etc.) (A) • Saltwater intrusion into coastal aquifers (U, R, I, M) • Seepage from cesspools and septic systems (R) • Seepage from acid rich water from mines (I) • Seepage from mine waste pipes (I) • Seepage of pesticides, herbicides nutrients, and so on from urban areas (U) • Seepage from accidental spills (train or truck accidents, for example) (I, M) • Inadvertent Seepage of solvent and other chemicals including radioactive materials from industrial sites or small business (I, M)

Key: U = urban; R = rural; I = industrial; A = agricultural; M = military.

TABLE 1.2: List of different industries discharging various contaminants

Industry	**Inorganic Pollutant**	**Organic Pollutant**
Refineries	sulphides, Hg, Cr, Sb	Oil-30, phenol-30, Dioxin, Furan, PAH, PCBs
Production and processing of metals	As, Cd, Pb, Se, Fe, Zn, Al, Ni	PCB, PAH, dioxins, oil, cyanides
Glass manufacture	scrap silicates and other mineral oxides	Emulsified oil, soda ash
Ceramics industry	fluorides	not available
Coke-Chemical industries	Ammonia, cyanides	Phenols, hydrogen sulphide, tars, hydrocarbons, thiocyanates
Incineration and landfills	Cadmium, lead, mercury	Chlorobenzene, chlorophenols, furans and dioxins
Pulp & Paper, Board Mills	Sulphites, free Chlorine,	Methyl mercaptans, pentachlorophenol aldehydes, ketones, lignite sulphonate and organic suspension
Organic Chemicals	not available	Phenols, organic acids, nitro compounds
Fertilizers	Sulphuric acid, phosphoric and fluosilicic acids, fluorine compounds	Monoethanol amines
Petroleum Refining	sulphides, chlorides, sulphates,	Naphthalene acid, petroleum products, phenols, surfactants.
Steel Mills	NH_3/N-1000	Oil, grease, phenols 1300

Metal industry	Copper, lead, cadmium, chromium, zinc	not available
Textile industry	Cr	Dyes, detergents
Iron and steel industry	cyanogen	Coke, limestone, phenol, oils
Leather tanning and finishing	Chromium in the form of chromate, ammonical nitrogen, sodium chloride	Precipitated lime
Polymer and plastic industry	sulphates	Styrene, acetonitrile, acrylates, phenols, aromatic hydrocarbons, aldehydes
Synthetic rubber industry	not available	Butylenes, butadiene, organic acids, acetonitrile, aldehydes, alcohols
Chlorine industry	Mercury, chlorine and chlorides	not available
Distillery waste industry	Sodium, potassium, calcium, iron	not available
Soap and detergent industry	not available	Propylene derived alkyl benzene sulphonate
Photographic industry	Hypo, silver bromide spent solution	not available
Food processing industry	Alkali metals, phosphates	Amino acids
Pesticide industry		Dichlorophenol
Tannery industry	Chromium, sulphides	Phenols, tartaric acid
Explosive industry	Data not available	Nitro compounds
Laundry industry	Alkalies, free chlorine	Oils, grease

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Chapter 2

Experimental Methods and Materials

EXPERIMENTAL METHODS AND MATERIALS

This chapter involves details of various reagents, adsorbents and experimental methods used/followed during experimental work of this thesis. Besides, mathematical background of experimental calculations is also equally important to mention, which have been presented. A section-wise description of individual component of experimental work is documented.

2.1 REAGENTS AND MATERIALS

Technical grade Acid Blue 113 dye of 98% purity (IUPAC name: Disodium 8-anilino-5-[[4-(3-sulfonatophenyl) azo-1-naphthyl] azo] naphthalene-1-sulfonate; Molecular formula: $C_{32}H_{21}N_5O_6S_2Na_2$ and molecular weight 681.65) was obtained from M/s Merck, India. Physico chemical properties of the dye are given in Table-2.1. High purity, technical grade methoxychlor, atrazine and methyl parathion, were obtained from M/s Merck, India. Physico-chemical and toxicological properties of the pesticides are reported in Table 2.2. Analytical-grade salt of cadmium [$Cd(NO_3)_2 \cdot 4H_2O$] and humic acid was obtained from M/s Merck, India. All reagents (Ferric chloride 6-hydrate, ferrous chloride tetrahydrate, ammonium hydroxide (29.6%), NaOH, H_2SO_4, $NaNO_3$, HNO_3) nickel chloride, zinc nitrate used in the study were of analytical grade and purchased from Wiswani Chemicals. Oranges were purchased from local market. Lead nitrate for Pb^{+2} and anhydrous nickel chloride for Ni^{+2} were purchased from M/s Merck, India. Technical grade amino acid derivatives of 98% purity viz aniline, p-toluidine, p-chloroaniline, p-anisidine were obtained from M/s Merck, India. Besides the above mentioned chemicals, other reagents, like HCl, HNO_3, H_2O_2, and NaOH were also procured from Wiswani Chemicals and were of analytical grade. The ground tire granules and a commercial activated carbon Chemviron GW used in the study were provided by Wiswani Chemicals.

2.2 INSTRUMENTATION

The concentration of dyes, humic acid and aromatic amines was determined spectrophotometrically on a Specord 200 UV–visible spectrophotometer (Model UV–vis 200, Germany). The concentration of pesticides was determined by a gas chromatograph (Clarus 500 GC, India) with electron capture detector (ECD). The metal ion concentration was determined on an atomic absorption spectrophotometer (model Z-7000, Hitachi, Japan). pH measurements were made using a pH meter (Model Cyberscan 510, Singapore). A high-precision electronic balance (Sartorius GMBH) with an accuracy of 0.00001g was used for taking the weight of the adsorbates and adsorbents. LEO 435 VP (Leo Elektronenmikroskopie GmbH, Germany) scanning electron microscopy was used for scanning the adsorbent surface. Carbon, hydrogen, nitrogen analysis of the adsorbent was carried out on an Elementar Vario ELHI CHNS analyzer. The infrared spectra of adsorbents were recorded in KBr discs on a Perkin Elmer Fourier transform infrared spectrophotometer (Model Perkin Elmer-1600 Series). The BET surface area of the adsorbents was measured by nitrogen adsorption isotherms on micromeritics ASAP 2010 (UK). Porosity and density of the adsorbents was determined by mercury porosimeter (Pascal 440; M/s Spektron Instrument Inc., India) and by specific gravity bottles respectively. X-ray measurements were performed by using a Philips X-ray diffractometer employing Ni-filtered Cu K_R radiation and Ni filters. TEM images of the adsorbents were recorded by Transmission Electron Microscope (FEI TECNAI G2 microscope operating at 200 kV). The magnetic properties of the magnetic nano particles (MNP) and the composite (MNP-OPP) were evaluated using a Vibrating Sample Magnetometer (Model 155, Princeton Applied Research). Deionized water was prepared using a Millipore Milli-Q (Bedford, MA) water purification system.

2.3 METHODOLOGY

As already stated, the experimental work involves the adsorption studies of a dye Acid Blue 113, three pesticides: methoxychlor, atrazine and methyl parathion, metal ions: lead, nickel and four aromatic amines: aniline, p-toluidine, p-chloroaniline, p-anisidine onto waste rubber tire activated carbon and a commercial activated carbon. Adsorption studies of cadmium ion was also carried out onto orange peel powder (OPP), magnetic nano particles (MNP) and composite adsorbent viz. orange peel powder-magnetic nano particles (MNP-OPP). During each study, a set methodology was followed, which involves a particular sequence of experimental steps which enabled us to understand the adsorption behavior of adsorbent, kinetics and thermodynamics of adsorption. Stepwise details of these certain experiments and methods used in this are given in succeeding sub-headings.

2.3.1 Preparation of Adsorbents

In the present investigation, two different wastes materials viz waste rubber tires and an agricultural waste- orange peel powder have been converted into inexpensive adsorbents. These wastes have been processed in the following manner so that they can be used as adsorbents. During the past 10 to 15 years, many fundamental studies were reported on the production of activated carbon from pyrolysis of waste tires using conventional method; physical and chemical activation process. The potential of these products as possible adsorbents for various pollutants has been assessed and found very successful, thus stimulating a serious research interest. The latest approach in activated carbon production technology is physiochemical activation. This method is derived from a variety of combination of both physical and chemical activation method. From the literatures, it was found that this method could present a very high quality activated carbon in terms of surface area, pore volume, porosity and favorable chemistry [1].

Since no research has till date been carried out using this physiochemical activation method in production of activated carbon from tires, this study was carried out to investigate the performances of the prepared activated carbon using this method. The main purpose of the present work is to prepare highly mesoporous activated carbon from waste tires which are suitable for adsorbing relatively large molecules.

2.3.1.1 Preparation of Rubber Tire Activated Carbon (RTAC)

The ground tire granules was cleaned, thoroughly washed with deionized water, and then dried in an oven at 100°C for 2hrs. This dried material was then heated to 500°C for 5hrs for carbonization. This was followed by treatment with hydrogen peroxide solution for 24 hrs at 60°C to oxidize adhering organic impurities. The material was washed with deionized water three times to remove hydrogen peroxide and dried at 110° C for 2 hr in vacuum oven. The dried material was activated to 900°C for 2hrs in a covered silica crucible by heating in a muffle furnace. The crucibles were removed from furnace and cooled in a dessicator. The material were then treated with 1M HCl solution to remove the ash content and then washed with deionized water. This was followed by drying of the material at 100°C for 24 hrs. The dried product is referred to as RTAC throughout the study.

2.3.1.2 Preparation of Chemically treated Rubber Tire Activated Carbon (CTRTAC)

The ground tire granules was cleaned, thoroughly washed with deionized water, and then dried in an oven at 100°C for 2hrs. This dried material was then heated to 500°C for 5hrs for carbonization. This was followed by treatment with hydrogen peroxide solution for 24 h at 60°C to oxidize adhering organic impurities. The material was washed with deionized water three times to remove hydrogen peroxide and dried at 110° C for 2 hr in vacuum oven.

The dried material (approx 2g) was mixed with 8g of KOH; mixing was allowed for 10 mins, the product was further activated to 900°C for 2hrs. The material was then treated with 1M HCl solution to remove the ash content, washed with deionized water and then dried at 100°C. The dried product is referred to as chemically treated Rubber Tire Activated Carbon (CTRTAC) henceforth.

2.3.1.3 Preparation of Oxygen enriched Rubber Tire Activated Carbon ($RTAC_{ox}$)

To introduce oxygen surface groups the dried form of RTAC were treated with HNO_3 (10 wt % concentration). The mixture (carbon and acid solution) was stirred and heated at 60° C until dry. The ratio of carbon/HNO_3 was 1 g/10mL. The procedure was repeated three times. The resulting samples were washed with deionized water until there were no NO_3^- ions in solution. The resulting samples after drying were named $RTAC_{ox}$.

All the powdered adsorbents were sieved by passing through different British Standard Sieves (BSS) and fractions corresponding to 100-150, 150-200 and 200-250 mesh were collected and stored in different desiccators.

2.3.1.4 Preparation of Commercial Activated Carbon (CAC)

The commercial activated carbon was cleaned, thoroughly washed with deionized water, and then dried in an oven at 100°C for 2hrs. This is referred to as CAC throughout the study.

2.3.1.5 Preparation of OPP, MNP and MNP-OPP

The orange peel was washed with water and dried in a convection oven at 40^0C for 72 h. These were then crushed into smaller particles of approximate size between 0.1 and 0.2 mm (hereafter, abbreviated as OPP). MNP and MNP-OPP were synthesized by co-precipitation method modified from ref [2, 3]. Briefly, 6.1 g of $FeCl_3.6H_2O$and 4.2 g of $FeSO_4.7H_2O$ were dissolved in 100 mL water and heated to 90°C. Solution of 10 mL of ammonium hydroxide (26%) and the solution of 1 g of OPP dissolved in 200 mL of water was added rapidly and sequentially. The pH of the reaction medium was adjusted to 10. The mixture was stirred at 80 °C for 30 min and then cooled to room temperature. The black precipitate Fe_3O_4-OPP (MNP-OPP) was collected by filtering, washed to neutral with water, dried at 50°C for 24 h and finally stored for further use. The bare MNP was prepared in a similar way except that no OPP was added.

2.3.2 Characterization of Adsorbents

All the adsorbents were characterized with respect to their physical and chemical parameters. The standard methods for analysis were adopted [4-8]. The properties, explored in the physical characterization are (i) density, (ii) porosity, (iii) surface area; calculated by the Brunauer-Emmett-Teller (BET) method (iv) structure of the adsorbent material; with X-ray diffraction studies (v) surface morphology; with scanning electron microscope (SEM) images and (vi) magnetization with Vibrating Sample Magnetometer (VSM). Chemical characteristics of the adsorbents explored are (i) chemical composition of adsorbent material through Carbon hydrogen nitrogen sulphur analyzer (CHNS) and through Energy Dispersive X-Ray (EDX) and (ii) surface functionality by FT-IR.

For pH_{pzc} determination, 0.01M NaCl was prepared and its pH was adjusted in the range of 2–12 by adding NaOH or HCl. 50mL of 0.01M NaCl each was put in three different conical flasks and then 0.25 g of the adsorbent was added to these solutions. These flasks were kept for 48 h and the final pH of the solution was measured by using pH meter (Model Cyberscan 510, Singapore). Graphs were then plotted for pH_{final} versus $pH_{initial}$.

The results obtained are discussed in characterization part of succeeding chapters and also compiled in Table 3.1, 4.1, 6.1, for RTAC, CTRTAC and $RTAC_{ox}$ respectively.

2.3.3 Quantitative Analysis of Adsorbates

The concentration of the adsorbate in the residual solutions at equilibrium adsorption was subsequently analyzed using UV-Vis spectrophotometric, GC-MS and AAS methods.

2.3.3.1 UV-Vis Spectrophotometric Method

Among the various types of adsorbates studied, dyes (Acid Blue 113) and aromatic amines (aniline, p-toluidine, p-chloroaniline, p-anisidine) were analyzed spectrophotometrically. The λ_{max} values of Acid Blue 113 were 580 nm whereas the λ_{max} of aromatic amines was 280nm, 295nm, 290nm and 286nm for aniline, p-anisidine, p-chloroaniline, p-toluidine respectively. The concentration of humic Acid was determined at a wavelength of 254 nm.

2.3.3.2 GC-MS Method

The residual concentration of the studied pesticides was analyzed with GC-MS due to low detection limit and high efficiency of GC-MS in comparison to UV-Vis spectrophotometer. GC analyses were performed using Clarus 500 GC Mass spectrophotometer. The pesticides were extracted from aqueous solutions (obtained from batch and column experiments) using 10mL of n-hexane. The *n*-hexane layer was separated, concentrated to 1.0 mL and used for determination of the pesticides by gas chromatography. A Hewlett-Packard HP-5 MS fused silica capillary column (30 m × 0.25 mm I.D., 0.25 μm film) was used with Helium as carrier gas, at a flow rate of 1.0 ml/min min with 25 mL/min as make up gas flow. A 1 μL sample was injected under split mode (split ratio 10:1). All the gas chromatographic experiments were carried out with the temperatures of the column, injector and detector as 260, 230, and 310 °C, respectively. The GC column temperature program was as follows: an initial temperature 100 °C, held for 3 min, and then ramp 10°C/min to 280 °C held for 5 min. The retention time for methoxychlor, atrazine and methyl parathion were observed 13.8, 12.7 and 10.1 min respectively.

2.3.3.3 AAS Method

The metal ion concentration was determined on an atomic absorption spectrophotometer model Z-7000 (Hitachi, Japan) at a wavelength of 283.3 nm for Pb^{2+}, 232 nm for Ni^{2+} and 228.8 nm for Cd^{2+}.

2.3.4 Adsorption Experimental Method

Several experimental techniques have been investigated by many researchers in order to make an intimate contact between adsorbate and adsorbent for the maximum uptake of pollutants from water. Both batch and column techniques were used for investigations. Adsorption isotherms were determined by batch method which is simple and easy to perform. Further, it permits convenient evaluation of parameters that influence the adsorption process. Column studies were also carried out to know the feasibility of the process in practice. These batch and column experimental technologies are discussed below.

2.3.4.1 Batch Adsorption Method

The development of batch adsorption process involves the plotting of isotherm; a typical isotherm plot is shown in Figure 2.1. This is an equilibrium graph plotted between adsorbate concentrations on per gram of adsorbent (q_e) and in aqueous phase respectively at equilibrium (C_e). Basically, maximum adsorption of adsorbate on a particular adsorbent can be achieved by optimizing various parameters of adsorption. The parameters affecting the adsorption process and considered for study were pH, adsorbent dose, and particle size, initial concentration of adsorbate, contact time and temperature.

For the optimization purpose, the first experiment was indented to determine the effect of contact time and minimum time to reach equilibrium condition by adsorbate-adsorbent system. A fixed amount of the adsorbent was added to 100 mL of adsorbate (dyes/pesticides/metal ions/amines) solution of a fixed concentration in a number of 250 mL stopered Erlenmeyer flask, which were placed in thermostat shaking assembly. The solutions were after agitated at constant temperature on an orbital shaker at 100rpm and Erlenmeyer flasks were taken out from shaker after a regular period of time. The solution was filtered with 0.2 µm rated nylon membrane. The filtrate was analyzed to determine the remaining concentration of adsorbate in solution. Remaining Erlenmeyer flasks were analyzed similarly until two successive Erlenmeyer flasks showed nearly equal adsorption and results so obtained were enabled to draw a progressive extent of adsorbent with the passage of time. The contact time after which adsorbent showed no noticeable adsorption is termed as equilibrium contact time. This optimized time period is generally employed in the succeeding experiments to study the effect of other factors.

To study the effect of particle size of adsorbent on the extent of adsorption, three particles size i.e. 100-150, 150-200 and 200-250 BSS were used in three different series of Erlenmeyer flasks; each series contains a range of adsorbate solution. The experiments were carried out upto the optimum contact time and at fixed temperature. The samples were analyzed and results were plotted in terms of isotherms, which showed comparative performance of various particle size. The finest particle size (200-250 BSS) shows maximum adsorption capacity among them, due to larger surface area.

Likewise, similar sets, containing a range of adsorbate concentration, with different adsorbent dose were analyzed. The isotherms obtained from results were helpful to determine the optimized dose for maximum removal.

pH of solution can alter the surface properties of adsorbent and adsorbate and therefore, affect the adsorption behavior and extent of adsorption. In view of this phenomenon adsorption experiments were carried out at various pH values. For this purpose a series of Erlenmeyer flasks containing fixed adsorbate solution at different pH, depending on the physicochemical stability of adsorbent or adsorbate at certain pH; were used. pH of solution was adjusted with the use of 0.1 M HNO_3 and 0.1 M NaOH as per requirement. These experiments are useful especially to explore the adsorption mechanism. The results were plotted as the extent of adsorption against pH of solution.

Similarly, temperature is also an important factor which influences the adsorption process. To observe the effect of solution temperature on the extent of adsorption, three sets of experiments are conducted at different solution temperatures. The results showed the adsorption process as endothermic (increases with increase in temperature) or exothermic (decrease with increase in temperature). The resulting data were plotted as isotherms which were very useful in predicting the adsorption characteristics of adsorbent. The adsorbate uptake qe (mg/g) was determined as follows:

$$q_e = (C_0 - C)\frac{V}{W} \quad (1)$$

Where, C_0 and C are the initial and final adsorbate concentrations (mg/L), respectively, V is the volume of solution (L) and W is the weight of adsorbent (g).

2.3.4.1.1 Modeling of Adsorption Isotherms

To analyze the validity of the adsorption data Freundlich, Langmuir and the Dubinin–Radushkevich isotherm adsorption models were used. Besides, linear regression analyses of the adsorption data were carried out to select the suitable adsorption model.

2.3.4.1.1.1 Langmuir Isotherm

Langmuir's model of adsorption [9] depends on the assumption that intermolecular forces decrease rapidly with distance and, consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. A linear expression of the Langmuir equation is:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \qquad (2)$$

where, q_e is the amount adsorbed (mgg^{-1}), C_e is the equilibrium concentration of the adsorbate (mgL^{-1}), Q_0 is the Langmuir constants related to maximum monolayer adsorption capacity (mgg^{-1}) and b is the constant related to the free energy or net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$). The plots of $1/q_e$ vs $1/C_e$ were drawn for three different temperatures and the values of Q_0 and b determined from intercept and slope respectively. The linear forms of the isotherms at all temperature and the correlation coefficients were used to predict if the adsorption data closely follow the Langmuir model of sorption.

Hereby, a dimensionless constant, commonly known as separation factor (R_L) defined by Webber and Chakkravorti [10] can be represented as:

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

Where b (L/mg) refers to the Langmuir constant and C_o is denoted to the adsorbate initial concentration (mg/L). In this context, lower R_L value reflects that adsorption is more favorable. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

2.3.4.1.1.2 Freundlich Isotherm

The Freundlich isotherm is derived by assuming an exponential decay energy distribution function inserted into the Langmuir equation [11]. It describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. When n=$1/n$, the Freundlich equation reduces to Henry's law. Hence, the empirical equation can be written

$$q_e = K_F C_e^{1/n} \qquad (4)$$

Where K_F is the Freundlich constant (L(mg$^{1-1/n}$ g)$^{-1}$) which is an indicative of relative adsorption capacity of the adsorbent, and $1/n$ is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of equation 4.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (5)$$

Therefore, plots of log q_e versus log C_e were drawn to calculate the values of K_F and $1/n$ from intercept and slope respectively. The linear forms of the isotherms at all temperature and the correlation coefficients were used to predict if the adsorption data closely follow the Freundlich model of sorption.

2.3.4.1.1.3 Dubinin–Radushkevich (D-R) isotherm

Dubinin–Radushkevich isotherm [12] is an empirical model initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism. It is generally applied to express the adsorption mechanism [13] with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

A linear expression of the D-R equation is:

$$\log q_e = \log q_D - 2B_D R^2 T^2 \log(1 + \frac{1}{C_e}) \qquad (6)$$

Where R = gas constant (J/molK), T = absolute temperature (K) and B_D is a constant related to the adsorption energy and q_D is the theoretical saturation capacity (mg/g).

The D–R model constant (B_D) however, gives an idea about the mean free energy of adsorption(E_D) which in turn gives information about the nature of the adsorption process. The value of E_D is computed using the relation [14].

$$E_D = \frac{1}{\sqrt{2B_D}} \qquad (7)$$

The magnitude of E_D may characterize the type of the adsorption as chemical ion exchange (E_D= 8–16 kJ.mol^{-1}), or physical sorption (E < 8 kJ.mol^{-1})

2.3.4.1.2 Thermodynamic Study

In order to study the feasibility of adsorption, three thermodynamic equations (8-10) were applied to equilibrium adsorption isotherms to calculate the related parameters (free energy, enthalpy and entropy) for the adsorption systems.

$$\Delta G^\circ = -RT\ln b \tag{8}$$

$$\ln\frac{b_2}{b_1} = -\left(\frac{\Delta H^\circ}{R}\right)\left[\frac{(T_2 - T_1)}{T_1T_2}\right] \tag{9}$$

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \tag{10}$$

Where b, b_1 and b_2 are Langmuir constants at different temperatures and other terms have their usual meanings. The negative value of free energy (ΔG°) reflects feasibility of adsorption system and vice-versa. The positive and negative values of enthalpy (ΔH°) show endothermic or exothermic nature of adsorption respectively. Similarly, positive or negative values of entropy (ΔS°) change give an idea about increase or decrease in randomness in adsorption process during adsorption.

2.3.4.1.3 Kinetic Study

In kinetic study two batches of different adsorbate concentrations but with similar adsorbent were taken. The extent of adsorption in these batches was recorded as a function of time. The data so obtained were further used to explore the kinetics of adsorption process. Pseudo first-order or pseudo second-order models were tried to investigate kinetic data.

2.3.4.1.3.1 Pseudo First-order Model

The pseudo-first order, rate expression of Lagergren's is given as [15]:

$$\log(q_e - q_t) = \log q_e \frac{k_{1,ads}}{2.303} t \qquad (11)$$

Where q_t (mg g^{-1}) is the amount adsorbed (adsorbate) on the adsorbent at time t and $k_{1,ads}$ (min^{-1}) is the rate constant of first-order adsorption, q_e the equilibrium sorption uptake, is extrapolated from the experimental data at time t = infinity. A straight line of log ($q_e - q_t$) versus t suggests the applicability of this kinetic model. q_e and $k_{1,ads}$ were determined from the intercept and slope of the plot, respectively.

2.3.4.1.3.2 Pseudo Second-order Model

The pseudo second-order kinetic model [16] in its integrated and linearized form has been used and given below.

$$\frac{t}{q_t} = \frac{1}{k_{2,ads} q_e^2} + \frac{1}{q_e} t \qquad (12)$$

Where $k_{2,ads}$ (g mg-min^{-1}) is the rate constant of second-order adsorption. If the plot t/q versus t give a straight line, it shows that, second-order kinetics is applicable and q_e and $k_{2,ads}$ are determined from the slope and intercept of the plot, respectively. It is important to note that for the application of this model the experimental estimation of q_e is not necessary.

2.3.4.1.4 Diffusion Mechanistic Study

The adsorption process involves particle diffusion or film diffusion. Three consecutive steps, which occur in the adsorption of an adsorbate by a porous adsorbent, are:

1. transport of the adsorbate to the external surface of the adsorbent (film diffusion);
2. transport of the adsorbate within the pores of the adsorbent (particle diffusion);
3. adsorption of the adsorbate on the interior surface of the adsorbent.

Step 3 is considered to be very rapid and does not represent the rate-determining step in the uptake of adsorbate. The following three distinct possibilities exist for the remaining two steps in the overall transport process:

Case I: External transport > Internal transport.

Case II: External transport < Internal transport.

Case III: External transport ≈ Internal transport.

In cases I and II, the rate is governed by particle and film diffusion, respectively. But in case III, the transport of ions to the boundary may not be possible at a significant rate, thereby, leading to the formation of a liquid film with the formation of a concentration gradient at the adsorbent particle

To investigate the actual process involved in the adsorption process, the mathematical treatment recommended by Boyd et al., Bangham model and the intra particle diffusion model were employed.

2.3.4.1.4.1 Boyd model

The mathematical treatment recommended by Boyd et al. [17] was employed to explore whether the adsorption process involves particle diffusion or film diffusion. A quantitative treatment of the sorption dynamics was employed with the help of the following expressions:

$$F = 1 - \frac{6}{\pi^2} \sum_{1}^{\infty} (1/n^2) \exp(-n^2 B_t) \qquad (13)$$

$$F = \frac{Q_t}{Q_\infty} \qquad (14)$$

$$B = \frac{\pi^2 D_i}{r_o^2} = \text{Time Constant} \qquad (15)$$

Where, F is the fractional attainment of equilibrium at time t, n is the Freundlich constant of the adsorbate and B_t is the time constant; Q_t and Q_∞ are the amounts adsorbed (mgg^{-1}) after time t and after infinite time, respectively; B is the time constant after time t, D_i is the effective diffusion coefficient of adsorbate and r_o is the radius of spherical adsorbent particle.

Based on the values of Fractional attainment, B_t values are derived from Reichenberg's table [18]. The linearity of the Bt vs time plots with straight lines passing through the origin will suggest that the rate determining process is particle diffusion where external transport of the adsorbate ions is much favoured than the internal transport.

2.3.4.1.4.2 Bangham's Equation

The applicability of the following Bangham's equation [19] to kinetic study was tested to learn about the slow step occurring in the adsorption process:

$$\text{Log}\log\left(\frac{C'_0}{C'_0 - q'm'}\right) = \log\left(\frac{k_0 m'}{2.303V}\right) + \alpha \log t \qquad (16)$$

Where C'_0 is initial concentration of adsorbate in solution (mgL^{-1}), V the volume of solution (mL), m′ the weight of adsorbent used per liter of solution ($g\ L^{-1}$), q′ ($mg\ g^{-1}$) the amount of adsorbate retained at time *t* and α (< 1) and k_0 are constants. log log $[C'_0/(C'_0 - q'm')]$ values were plotted against log *t* in Bangham's plot. The linearity of these plots confirms the applicability of Bangham's equation and indicates that diffusion of adsorbate molecules into pores of the adsorbent mainly controls the adsorption process rather a film diffusion controlled process.

2.3.4.1.4.3 Intra Particle Diffusion

In a well-agitated batch adsorption system, there can also be a possibility of intraparticle pore diffusion [20] of adsorbate ions, which can be the rate-limiting step.

$$q_t = k_i\, t^{0.5} \qquad (17)$$

Where k_i is the constants of the intra-particle diffusion model

The linearity of the plots of q_t versus $t^{0.5}$ with straight lines passing through the origin will imply that although intraparticle diffusion is involved in the adsorption process, it is not the sole rate- controlling step and that some other mechanisms may play an important role.

2.3.4.2. Column Adsorption Method

Column-type continuous flow operations have many distinct advantages over batch studies. The main objective of flow through column experiments is to provide a more sensible simulation of how the adsorbent material adsorbs the colour contaminant. Column experiments also provide a much closer approximation of the physical conditions and chemical processes rather than the batch experiments. Hence, the practical applicability of the product for column operations has also been studied to obtain some parameters necessary for a factual design model. In this method, a column of adsorbent is loaded, saturated and effluent is allowed to pass through it at a definite rate. The adsorbent has to be granular with sufficient particle size; otherwise the column becomes choked in no time. The effluent from column is taken and analyzed for the concentration of the adsorbate and breakthrough curves are obtained. These investigations provide information regarding the optimum mass, height and area of the column and the rate of the effluent flow which will permit best treatment of the wastewater. In the present work, a glass column (30 × 2.5 cm) is fully loaded with adsorbent on a glass-wool support. A schematic diagram of column, used in the experiments, is given as Figure 2.2. Double distilled water was used to rinse the adsorbent and to remove any bubbles present. A dye/pesticide/metal ion/amines solution was poured into the column and the column effluent was allowed at a flow rate of 1.5-2.5 mL min^{-1}. A definite amount of the column effluent was taken and the concentration of the solute (pollutants under investigation) determined from time to time by spectrophotometric/GC-MS/AAS method is required. This process is continued till the concentration in the column effluent becomes constant. The plots of concentration of the adsorbate in the column effluent and volume of the effluent provide breakthrough curves.

2.3.4.2.1. Breakthrough Curve

The efficiency of column operations is understood in terms of breakthrough curve. A breakthrough curve is obtained by plotting column effluent concentration versus volume treated or the time of treatment or the number of bed volumes (BV) treated. A typical breakthrough curve is shown in Figure 2.3. Some important features of a breakthrough curve are breakthrough capacity, exhaustion capacity and degree of column utilization. The breakthrough capacity is defined as the mass of the adsorbate removed by the adsorbent at breakthrough concentration, which in turn defined as maximum acceptable (desired) concentration. When, effluent concentration attains this value, the adsorbent needs to be replaced. The degree of column utilization is defined as the mass adsorbed at breakthrough point divided by the mass adsorbed at complete saturation i.e. when effluent concentration becomes equal to or nearly equal to influent concentration. The exhaustion capacity is defined as the mass of the adsorbate removed by unit weight of the adsorbent at saturation. Various factors influence the breakthrough curves such as nature of the adsorbate and adsorbent, the column geometry and operating conditions. Favorable adsorption isotherms and extremely high adsorption rates result in virtually coinciding of breakthrough point and exhaustion point, the breakthrough curves approaching a straight vertical line. As the mass transfer rates are decreased, breakthrough curves become less sharp. Since mass transfer rates are finite, the breakthrough curves are diffuse and exhibit an S shape.

Weber [21] explained the relationship between the nature of breakthrough curves and the fixed bed absorber as shown in Figure 2.4. When the feed water is introduced through the inlet of the column, the solute is adsorbed most rapidly and effectively by the upper few layers of the fresh adsorbent during the initial stages of operations. These upper layers are; of course; in contact with the solution at its highest concentration level, C_o (concentration of the influent). The small amounts of solute which escape adsorption in the first few layers of the adsorbent are then removed from the solution in the lower strata of the bed, and essentially no solute escape from the adsorbent initially (effluent concentration, C=0). The primary adsorption zone is concentrated near the top or influent end of the column. As the polluted feed water continues to flow into the column, the top layers of the adsorbent become practically saturated with the solute and become less effective for further adsorption. Thus, the primary adsorption zone now moves downward to regions of fresher adsorbent. The wave like movement of this zone, accompanied by a movement of the C_o concentration front, occurs at a rate which is generally much slower than the linear velocity of the feed water. As the primary adsorption zone moves downwards, more and more solute tends to escape in the effluent, as indicated in the Figure 2.4. The plots of C/C_o versus time or volume, for a constant flow rate, depict the increase in the ratio of effluent to influent concentration as the zone moves through the column.

The breakpoint on the curve has been adopted by various workers differently to determine the breakthrough capacity of the column [22, 23]. The calculation [24] of breakthrough capacity, exhaustion capacity and degree of column utilization have been evaluated from breakthrough curves as per equations 10 to 12 and figure 2.3 using a Excel work sheet, developed to calculate curve area.

$$\text{Breakthrough capacity} = \text{area } 1 \times C_o \tag{18}$$

$$\text{Exhaustion capacity} = (\text{area } 1 + \text{area } 2) \times C_o \tag{19}$$

$$\text{Degree of column utilization } (\%) = [\text{area } 1 / (\text{area } 1 + \text{area } 2)] \times 100 \tag{20}$$

Another method of calculating the various experimental parameters was as follows:

$$q_{tot}\ (\text{mg}) = t_s \times F \times (C_o\text{-}C_s) / 1000 \tag{21}$$

$$q_b\ (\text{mg}) = t_b \times F \times (C_o\text{-}C_b) / 1000 \tag{22}$$

$M_{tot}\,(mg) = t_s \times F \times (C_o) / 1000$ (23)

$\% \, RM = q_{tot}/M_{tot} * 100$ (24)

Where q_{tot} and q_b are the adsorbate adsorbed by the column at saturation and breakpoint respectively, t_s and t_b are time at saturation and breakpoint respectively, F is flow rate (mL/min), C_o and C_s are the concentration of metal ion (mg/L) at saturation and breakpoint respectively. M_{tot} is the total adsorbate supplied to the column and RM is the adsorbate removal rate by the column.

2.3.5. Desorption and Regeneration Experiments

Desorption studies help to elucidate the mechanism of adsorption as to recover the pollutants from the spent adsorbent apart from protecting the environment from solid waste disposal problem. After the column is exhausted by the studied adsorbate, acidic or basic solution or buffers or organic solvents were used for desorbing the adsorbate depending on the type of pollutants adsorbed on the adsorbent. The desorbing medium is passed through the column at a constant flow rate 1.5 mL/min. Once complete elution of the adsorbate from the column had taken place the columns were washed properly with distilled water. The amount of pollutant desorbed from the adsorbate is thereby calculated.

Regeneration of the adsorbent for repeated use is of crucial importance in industrial practice for pollutant removal from wastewater. This fulfills an important criterion for advanced adsorbents. Reusability study of adsorbent was carried out by following the adsorption-desorption study for 5 cycles. The adsorption efficiency in each cycle was analyzed. Both the adsorption and desorption experiments were followed as described above.

2.3.6. Test with Simulated and Real Industrial Effluents

Since the ultimate objective of the adsorption technology is removal of pollutants from the industrial or real wastewaters that often contain varied types of pollutants simultaneously, column adsorption experiments were conducted with actual industrial waste-waters. Urban wastewater from IIT Roorkee campus was collected and was spiked with the studied dyes, pesticides and metal ions to obtain wastewater which simulated an actual textile, pesticides metal plating and electroplating industry effluent. The characterization of water samples were carried out using standard methods [25]. The pollutant removal was carried out in the laboratory column set up filled with the studied adsorbent having bed depth of 15cm and flow rate of 1.5mL/min.

2.3.7. Quality assurance/Quality control

Inorder to establish the accuracy, reliability and reproducibility of the collected data, all the batch isotherm tests are replicated thrice and the experimental blanks are run in parallel. Check standards and blanks are run. Multiple sources of National Institute of Standard and Technology (NIST) traceable standards are used for instrument calibration and standard verification. All jars, conical flasks, and containers used in the study are prepared by soaking in 5% HNO_3 solution for a period of 3 days before being doubly rinsed with distilled, deionized water and oven dried. In different experiments, blanks are run and corrections made wherever necessary. All observations are recorded in triplicate and average values are reported.

Table-2.1: Physico-Chemical Properties of dye Acid Blue 113

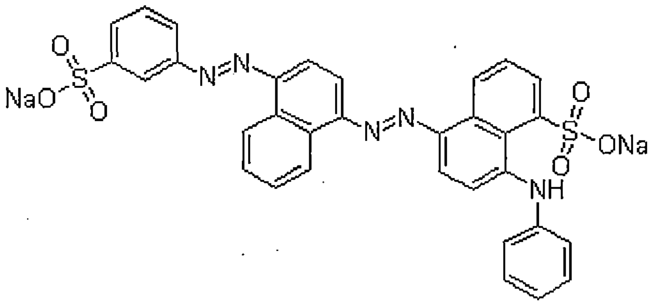
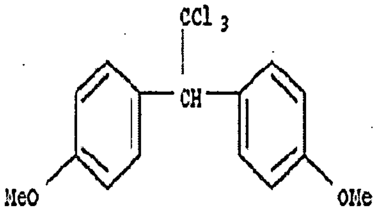
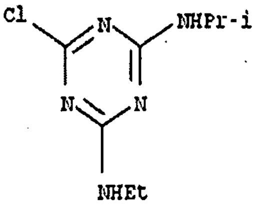
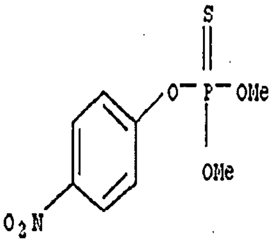
1	Molecular Structure	
2	Molecular Formula	$C_{32}H_{21}N_5O_6S_2Na_2$
3	IUPAC Name	Disodium8-anilino-5-[[4-(3-sulfonatophenyl)azo-1-naphthyl]azo]naphthalene-1-sulfonate
4	Synonyms	1-Napthalenesulfonic acid,8-(phenylamino)-5-[[4-[(3-sulfophenyl)azo]-1-napthalenyl]azo]-disodium salt, Acid Blue 113,Acid Fast Blue 5R
5	Molecular Weight	681.65g
6	Solubility in water	40g/L
7	Absorption Maxima(λmax)	580
8	Colour index	CI 2630
9	Appearance	Dark blue powder
10	Nature	Was purple when dissolved in water, violet blue when dissolved in ethanol, did not dissolve in organic solvents.
11	Uses	Used for dyeing wool, nylon and silk fabric rayon blended fabric and leather; Also used for biological coloring of paper.

Table 2.2:
Physico-Chemical & Toxicological Properties of Pesticides

Pesticide	Methoxychlor	Atrazine	Methyl parathion
Molecular Structure			
Molecular Formula Molecular Weight	$C_{16}H_{15}Cl_3O_2$ 345.65	$C_8H_{14}ClN_5$ 215.69	$C_8H_{10}NO_5PS$ 263.23
Chemical family	Organochlorine	Organochlorine	Organophosphate
Pesticide type	Insecticide	Insecticide	Insecticide
Solubility in water (25°C)	0.045ppm	33.0ppm	60.0ppm
Log octanol-water partition co-efficient	4.68-5.08	2.34	1.83-3.43
Environmental fate	Highly persistent, non-mobile, high bioaccumulation potential	Moderately persistent & mobile, low bio-accumulation potential	Moderately persistent & mobile, low bio-accumulation potentia
Carcinogen class	Class D	Class C	Class A
LC_{50}	0.052mg/L	<0.1mg/L	0.163mg/L
Toxicity Category	III (moderately toxic)	I (Highly toxic)	I (Highly toxic)
Use classification	Restricted & banned	Restricted & banned	Restricted & banned
EPA limit in drinking water	20ppb	3ppb	2ppb

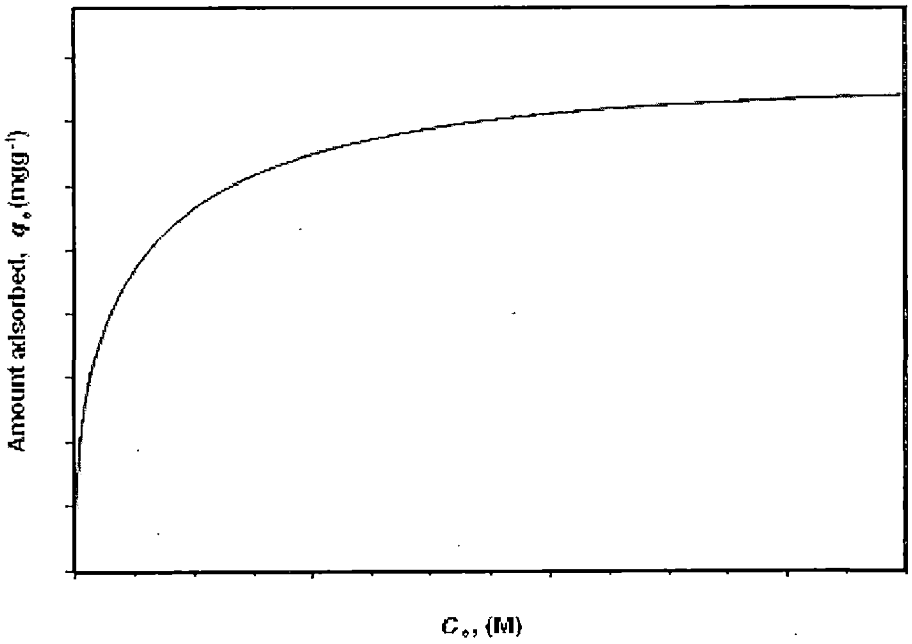


Figure 2.1:
Adsorption isotherm from a batch experiment.

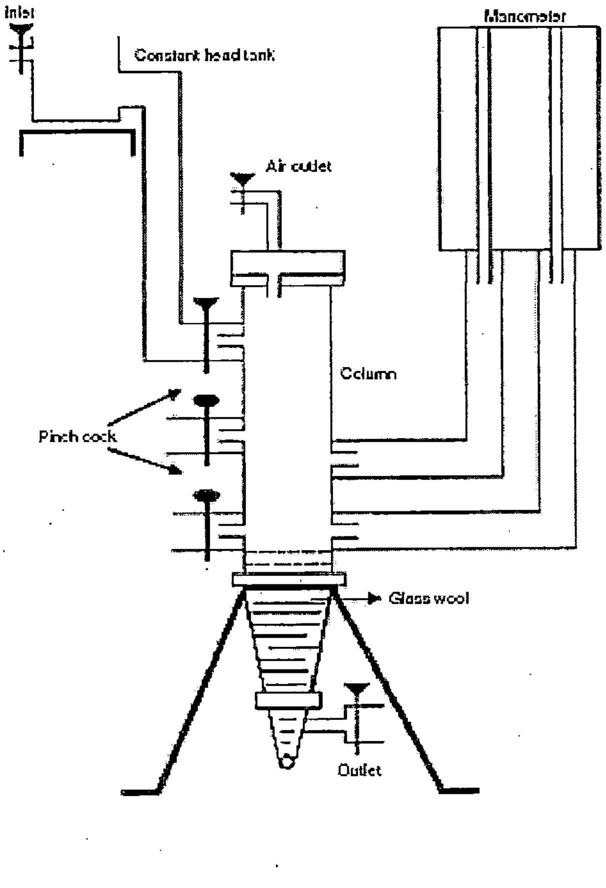


Figure 2.2:
A schematic diagram of column used for adsorption experiments.

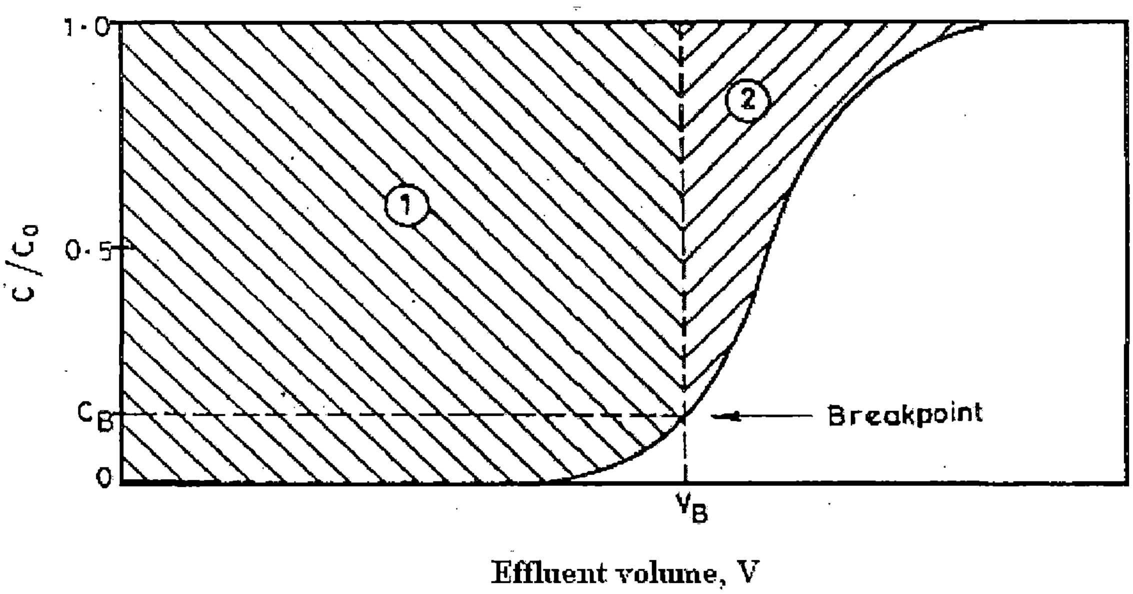


Figure 2.3:
Breakthrough curve. (C_o: Concentration of influent; C: concentration of effluent)

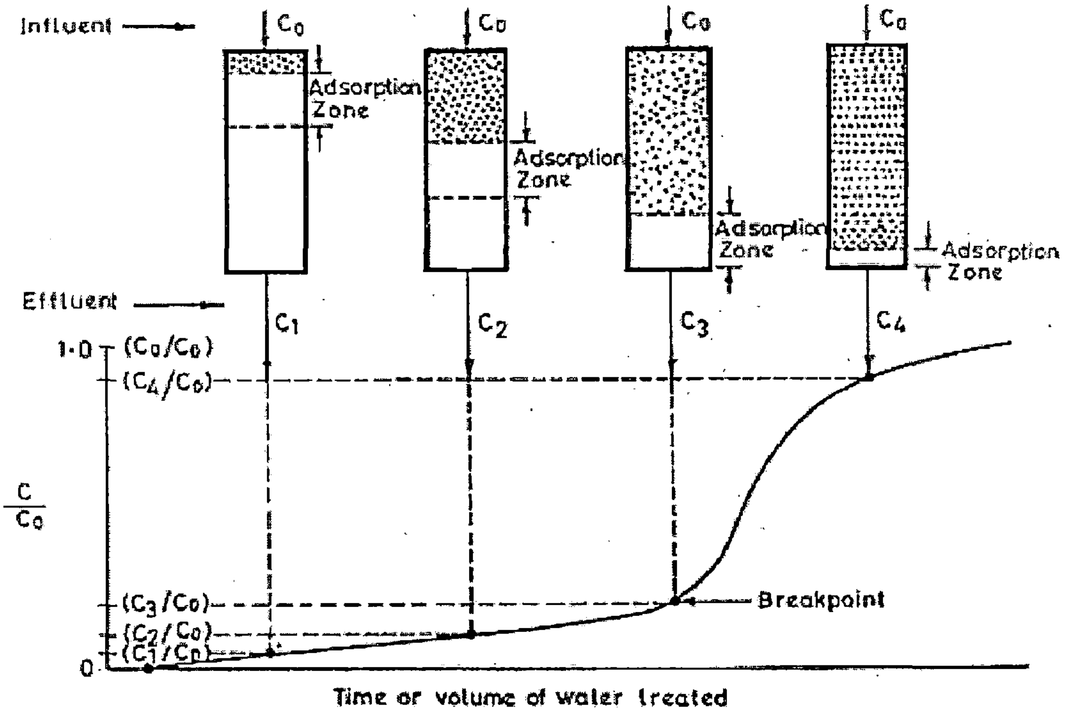


Figure 2.4:
Representation of the movement of the adsorption zone and the resulting breakthrough curve

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Chapter 3

RUBBER TIRE ACTIVATED CARBON FOR THE REMOVAL OF DYES

3.1. INTRODUCTION

One of the important classes of the pollutants is dyes, and once they enter the water it is no longer good and sometimes difficult to treat as the dyes have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be biodegraded [1, 2]. Mankind has used dyes for thousands of years [3] and the earliest known use of a colorant is believed to be by Neanderthal man about 1,80,000 years ago. However, the first known use of an organic colorant was much later, being nearly 4000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs [4]. Till the late nineteenth century, all the dyes/colorants were more or less natural with main sources like plants, insects and mollusks, and were generally prepared on small scale. It was only after 1856 that with Perkin's historic discovery [5, 6] of the first synthetic dye, mauveine, that dyes were manufactured synthetically and on a large scale.

Dye molecules comprise of two key components: the chromophores, responsible for producing the colour, and the auxochrome, which not only can supplement the chromophore but also can render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers. Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified [5] both by their chemical structure and their application to the fiber type. Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. It is worthwhile to note that the azo dyes are the one most widely used and accounts 65–70% of the total dyes produced.

Overall at present there are more than 100,000 commercial dyes with a rough estimated production of $7x10^5$–$1x10^6$ tons per year [7-11]. Of such a huge production the exact data on the quantity of dyes discharged to the environment is not available. However, it is reported that 10–15% of the used dyes enter the environment through wastes [12, 9]. The big consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities. Dyes are considered an objectionable type of pollutant because they are toxic [13, 7, 14, 15] generally due to oral ingestion and inhalation, skin and eye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity [7, 8, 2]. They impart colour to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which inturn cause the destruction of aquatic communities present in ecosystem [16, 17]. Further, the dyes have a tendency to sequester metal and may cause micro toxicity to fish and other organisms [17]. As such it is important to treat colored effluents for the removal of dyes.

Previous research efforts have focused on the adsorption technology for the dye remediation from waste water [18]. It has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. In addition, this technique can handle fairly large flow rates, producing a high-quality effluent that does not result in the formation of harmful substances, such as ozone and free radicals [19]. Although the adsorption technique is versatile and is easy to adopt in practical forms, the adsorbent materials are either costly or cannot be regenerated for large-scale applications. Hence research of the recent past mainly focused on utilizing low cost waste materials as alternatives to activated carbon for large scale waste water treatment. A number of natural materials, agricultural waste/by-products and industrial waste have been studied in the literature for their capacity to remove dyes from aqueous solutions such as wood [20], coal [21], orange peel waste [22], banana pith [23], rice husk [24], deoiled soya [25], fly ash [26], blast furnace slag [27], red mud [28], bottom ash [29]etc.

Discarded tires are an interesting and inexpensive medium for the adsorption of toxic and large molecular weight dyes from aqueous solutions. Currently over 4 million tires are discarded annually throughout the world representing near to 15,000 tires per day, which makes the problem of solid waste management difficult to handle [30, 31]. These huge numbers of waste tires represent not only an enormous environmental problem but also a cheap source for the preparation of adsorbent materials that may be useful for the removal of pollutants from aqueous solutions. According to Williams and Bessler [32], rubber tire is composed of a mixture of polymers of styrene butadiene rubber, natural rubber and butadiene rubber plus other additives like carbon black, sulphur and zinc oxide. Approximately 32% by weight of the waste tire [33] is mainly constituted of carbon black in which the carbon content is as high as 70-75 wt. %. [34]. This carbonaceous adsorbent is rather similar to activated carbon and the only apparent physical difference is that carbon black has much less internal surface area [35]. Carbon black obtained by untreated rubber tire pyrolysis may be heated in air, carbon dioxide or steam atmosphere to develop its surface area and porosity [36-49] and hence to improve its adsorption behavior. Conversion of waste rubber tire into activated carbon will thus demonstrate a double benefit by utilizing waste tire as a feedstock for inexpensive, quality activated carbon production, enabling both material recovery and reuse and waste water pollution abatement. Usually, during the tertiary waste water treatment, in certain applications, larger pollutants cannot easily penetrate into the micropores to adsorb onto the adsorbents [50]. So the produced activated carbons should posses not only micropores but also interconnecting mesopores [51]. In this regard, waste tires give an important source of raw material because highly mesoporous activated carbons can be produced from waste tyres rubber [52]. Micropores with interconnecting mesopores activated carbon are one of the most important characteristics in the liquid phase adsorption. Moreover, owing to the high surface areas (ranging from 164 to 1260 m^2/g) and pore volumes (up to 1.62 cm^3/g), tire carbon are considered as a potential adsorbent in water treatment for the purpose of removing organic pollutants.

We hence attempt to use waste rubber tire as adsorbent which is also cheap and easily available waste material for the removal of Acid Blue 113 from aqueous solution. The dye "Acid Blue 113" chosen as a model compound for the present study finds vast applications as a coloring agent in the textile industry. The various physico-chemical characteristics of the model dye are given in Table-2.1. Because it is highly colored, it is readily visible in the effluent water and is the focus of significant environmental complaint. Exposure to this dye and dye metabolite has potential for toxic effect to environment and humans. IARC [53] has identified Acid Blue 113 as a potential carcinogenic agent. Due to large degree of organics present and stability of the dye, conventional physicochemical and biological treatment methods are ineffective for its removal.

The objective of this work is to evaluate and to compare the adsorptive efficiency of waste rubber tire for the removal of Acid Blue 113 with that of a commercial activated carbon. This study provides a systematic investigation of the adsorption characteristics exhibited by activated carbons produced from waste rubber tire. The results can be used to determine the potential use of these carbons in industrial applications that require the removal of a range of dyes from solution. Rubber-derived carbons were investigated for their porosity, surface characteristics and chemistry. Subsequently, the carbons were investigated for their aqueous adsorption characteristics using Acid Blue 113 dye. Experimental data were modeled to the various adsorption isotherms to determine the adsorption capacities. Adsorption and porosity results were compared with those obtained from a commercial activated carbon inorder to elucidate the adsorption mechanism. The efficiency of the prepared adsorbent for dyes removal has been compared with other low cost adsorbents discussed in this chapter. Column operations have also been carried out on the rubber tire activated carbon which was found to be efficient and effective for the removal of dyes. The results of these investigations are reported in this chapter.

3.2. RESULTS AND DISCUSSION

3.2.1. Characterization of RTAC

Table 3.1 summarizes some of the textural characteristics and surface area of the RTAC obtained along with the CAC. The table shows that the volume of mesopores (dimension in the 2 to 50 nm range) in RTAC is 0.69 cc/g (71.13 % of total pore volume) thereby demonstrating that RTAC is a mesoporous activated carbon and that the activation process is responsible for the mesoporous structure and high surface area exhibited by RTAC as compared to that in unactivated rubber tire sample. On the other hand CAC has a microporous structure and the micropore volume found is 0.48cc/g (70.60 % of total pore volume).

Table 3.2 demonstrates that carbon is the major constituent of RTAC and is present to the extent of 78.76 % indicating the carbonaceous nature of the adsorbent. The heteroatoms present are derived from the starting material.

(1g) was stirred with 100 mL deionized water maintained at pH 6.4 at left for 24hrs. A decrease in pH of the water to 3.5 was observed. This indicates that RTAC is a carbonaceous adsorbent as per Steenberg classification and comes under “L” type carbon [54]. RTAC was found to be stable in water, dilute acids, dilute bases, salt solutions and organic solvents at temperature of 25-45°C and in the pH range of 1-11.

Scanning Electron Micrograph (SEM) images of adsorbent prior to activation (Figure 3.1a), after activation and before adsorption (Figure 3.1b) and finally after activation and after adsorption (Figure 3.1c) clearly indicate the surface texture and porosity of the rubber tire adsorbent. Carbon being the prominent component indicates the carbonaceous nature which in turn imparts porosity to the RTAC as observed in the SEM results.

Table 3.3 showing the IR spectrum of the RTAC sample, indicates the presence of a prominent band at 3434.78 cm^{-1} which can be inferred to the presence of an OH group. It was observed from the table that after adsorbing dye, there were distinct and significant changes in the absorption peak frequencies of hydroxyl group, suggesting a binding process of dye has taken place on the surface of the RTAC.

3.2.2. Preliminary Adsorption Studies

To optimize the effect of various parameters on adsorption of Acid Blue 113 by RTAC and CAC, batch experiments were run under different conditions. The results of the experiments are discussed below.

3.2.2.1. Effect of Contact Time

In order to determine the equilibration time for maximum uptake of Acid Blue 113 dye, its adsorption at fixed concentration (12×10^{-5} M) on RTAC and CAC was studied as a function of contact time. The uptake of dye on RTAC and CAC depicts that the sorption is quite rapid initially, gradually slows down and then reaches the equilibrium. In both the systems nearly 50 to 60% of the ultimate adsorption occurred within 15 mins of contact for RTAC and 28 mins of contact for CAC. Equilibrium was attained at 40 mins for RTAC-Acid Blue 113 (Figure 3.2) and 60 mins for CAC-Acid Blue 113 systems. The uptake of dye molecules by the adsorbents, and the time required for establishment of equilibrium suggest the effectiveness of these materials for wastewater treatment. The decrease in amount of dye adsorbed with time may be due to aggregation of dye molecules around the adsorbent particles. This aggregation may hinder the migration of adsorbate, as the adsorption sites become filled up, and also resistance to diffusion of dye molecules in the adsorbents increases. The difference in the equilibrium time between the two adsorbents might be due to differences in the surface properties of the adsorbents.

3.2.2.2. Effect of Particle Size

The adsorption of Acid Blue 113 was studied at different particle sizes of RTAC and CAC viz. 100-150,150-200 and 200-250 μm. Table 3.4 and Figure 3.3 show that with increasing mesh size the adsorption capacity were found to increase from 2.28 mg/g to 9.72 mg/g for RTAC and 2.19mg/g to 7.84 mg/g for CAC. This leads to the conclusion that amount adsorbed increases with decreasing particle size. This may be due to the fact that the smaller adsorbent particles have shortened diffusion paths, such that the ability of adsorbate to penetrate all internal pores of the adsorbent is higher. For further studies, particle size of 200-250 μm was chosen for both adsorbents based on the adsorption capacity and availability of the adsorbent.

3.2.2.3.Effect of Adsorbent Dose

The effect of adsorbent dose on removal of Acid Blue 113 was studied by varying the dose of adsorbent from 1 to 20 g/L for both RTAC and CAC. The experiment was carried out at fixed dye concentration of $12\text{x}10^{-5}$M and at a fixed temperature of 25°C and at pH of 5 for RTAC and pH of 2 for CAC. From Table 3.5 and Figure 3.4, it is evident that adsorbent dose significantly influences the amount of dye adsorbed. Initially the amount of dye adsorbed was found to be rapid from 1 to 10 g/L which then slowed down as the dose increased from 10 to 20 g/L for RTAC. In case of CAC, dye adsorbed increases as the dose of adsorbent increases from 1 to 5g/L, which then decreases as the dose increased from 5 to 20 g/L. The initial rise in adsorption with adsorbent dose is probably due to a stronger driving force and larger surface area. With a rise in adsorbent dose, there is a less commensurate increase in adsorption resulting from lower adsorptive capacity utilization of adsorbent [55, 56]. Also, larger surface area and a microporous structure have resulted in lower adsorbent dose for CAC. But, a mesoporous structure of RTAC has resulted in larger adsorptive dye capacity as compared to that for CAC.

3.2.2.4. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The effect of pH on the adsorption was studied by varying the pH of the medium from 1 to 11 at fixed dose of 10 g/L for RTAC and 5 g/L for CAC and fixed dye concentration of 12×10^{-5} M and the results are depicted in Figure 3.5. The amount of dye adsorbed for RTAC increases with increase in pH from 1 to 2 and thereafter it decreases with increase in pH from 2 to 11 whereas the dye adsorbed for CAC increases with increase in pH from 1 to 5 and thereafter decreases. Optimum pH of 2 and 5 for RTAC and CAC respectively was selected for further studies as maximum adsorption of dye was obtained. The higher adsorption of the dye at lower pH is apparently due to greater accessibility of the dye to the active sites and more facile diffusion.

3.2.2.5. Effect of initial concentration

To determine the effect of initial dye concentration on the adsorption process, the initial concentration of Acid Blue 113 was varied from 1×10^{-5} to 12×10^{-5} M at a fixed pH and at fixed temperatures of 25°C. The amount of dye adsorbed per unit mass of adsorbent increases from 0.84mg/g to 9.72 mg/g for RTAC and from 0.67 to 7.93 mg/g for CAC. Figure 3.6 shows a direct relationship between initial dye concentration and amount of dye adsorbed for both adsorbents. This suits the findings which have been quoted by the other researchers [57-59]. The increase in the adsorption capacity is probably due to greater interaction between adsorbate and adsorbent. The higher amount of dye adsorption at higher concentrations is probably due to increased diffusion and decreased resistance to dye uptake. However, increasing the dye concentration above $10x10^{-5}$M causes little increase in the amount of dye adsorbed, indicating saturation of the adsorption sites.

3.2.2.6.Effect of Temperature

Adsorption studies were carried out at 25, 35 and 45° C for RTAC and CAC. The sensitivity of the adsorption process towards temperature is exemplified in Table 3.6 and it is observed that in both cases, adsorption decreases with increase in temperature, indicating exothermic nature of the process. This may be due to the tendency of dye molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution.

3.2.3. Modeling of Adsorption Isotherms

To find out the most suitable adsorption model, the isotherm data thus obtained were analysed, by the well-known models of Langmuir and Freundlich. The values of regression coefficients obtained from these model's plots were also evaluated, which were used as a fitting criteria to find out suitable model. Values of resulting parameters and regression coefficients (R^2) are listed in Table 3.6.

The plots of Langmuir model at three different temperatures (Figure 3.7) were found to be linear over the whole concentration range studied. The correlation coefficients ranged from 0.9940 to 0.9994 for RTAC-Acid Blue 113 and from 0.9903 to 0.9955 for CAC-Acid Blue 113 as shown in Table 3.6. With Freundlich model, the plots of log q_e vs log C_e at three temperatures too exhibit linearity for the whole concentration range and correlation data were found to vary from 0.9467 to 0.9734 for RTAC and ranged from 0.8572 to 0.9734 for CAC. By comparing the results presented in Table 3.6, it can be seen that the plots of Langmuir model showed higher correlation ($R^2 > 0.99$) than Freundlich models. Additionally, for RTAC-Acid Blue 113, the values of Q_o at 25, 35 and 45°C (9.89, 8.34 and 7.83 mg/g) calculated by Langmuir equation fitting were all close to those actually determined (9.72, 8.91 and 7.95) at the given temperatures. Similar results were obtained for CAC-Acid Blue 113 system with the theoretical and experimental values of Q_o at 25, 35 and 45°C being (7.19, 6.99 and 5.59mg/g) and (7.84, 6.94 and 5.53 mg/g) respectively. These facts suggest that the adsorption of Acid Blue 113 on RTAC and CAC involves the monolayer coverage of the dye on the surface of the adsorbent. Satisfactory fitting of the Langmuir model to the adsorption isotherms textile dye on waste rubber dye have been reported [60].

Further, it is clear from the Table 3.7 that all the values of R_L are less than unity, confirming thereby the favourable adsorption process in both cases of adsorbents. Similar findings have been reported in literature [61].

3.2.4. Thermodynamic Study

The values of the free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for adsorption process are summarized in Table 3.8. The enthalpy change ΔH° in case of both adsorbents is negative (exothermic) due to decrease in adsorption on successive increase in temperature. Further, negative ΔG° values for RTAC and for CAC dictate spontaneous process. The negative value of ΔS° for RTAC and CAC reveals the increased randomness at the solid–solution interface during the fixation of the dye on the active sites of the adsorbent. Since the adsorption process is exothermic, it follows that under these conditions the process becomes spontaneous because of the negative entropy change.

3.2.5. Kinetic Study

The process efficiency of the adsorption is controlled by kinetics and, hence, Lagergren's pseudo first-order or pseudo second-order models are applied to investigate kinetic data. The regression analysis of resulted plots was carried out to observe the suitability of any model.

A straight line of log (q_e-q_t) versus t suggests the applicability of this kinetic model as shown in Figure 3.8. q_e and $k_{1,ads}$ shown in Table 3.9 were determined from the intercept and slope of the plot. The pseudo-second-order kinetic parameters q_e and $k_{2,ads}$ were determined from the slope and intercept of the plot of t/q versus t respectively.

Table 3.9 lists the results of rate constant studies for different temperatures by the pseudo-first-order and pseudo-second-order models. The value of correlation coefficient R^2 for the pseudo-first-order adsorption model for both adsorbents is relatively high (>0.99), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo second-order model are not satisfactory. Therefore, it has been concluded that the pseudo-first-order adsorption model is more suitable to describe the adsorption kinetics of dye over either RTAC or CAC.

3.2.6. Mechanism of the adsorption process

The mathematical treatment recommended by Boyd et al. was employed to explore whether the adsorption process involves particle diffusion or film diffusion. The B_t vs time plots displayed linearity with straight lines passing through the origin in both the cases of RTAC and CAC (Figure 3.9). This suggests that the rate determining process is particle diffusion where external transport of the adsorbate ions is much favored than the internal transport.

From the slopes of the straight lines obtained from time versus Bt graph, the B (time constant) values were derived, which were then further applied to evaluate the effective diffusion coefficient of the adsorbate (Di) at 25, 35 and 45°C. Plot of 1/temperature versus log Di (graph not shown) shows that the values of Di increase with increasing temperature, indicating thereby a increase in the mobility of the ions with increase in temperature. The intercepts obtained on these graphs were used to derive the value of pre-exponential constant (D_o) analogous to the Arrhenius frequency factor, which was used to find out the value of activation energy E_a and entropy of activation $S^{\#}$ using the following equations:

$$D_i = D_o \exp(-E_a / RT) \quad (1)$$

$$D_o = (2.72d^2kT/h) \exp(\Delta S^{\#}/R) \quad (2)$$

Where d is the average distance between the two adsorption sites and has been taken as 5 Å for the particle sizes of the adsorbents chosen, k is the Boltzmann constant, h is the Plank constant and R is the Gas constant. The calculated values for D_i, D_0, E_a and $\Delta S^{\#}$ are listed in Table 3.10. The negative values of $\Delta S^{\#}$ obtained for both the systems reveal that the internal structure of the adsorbents do not go through any significant change during the adsorption of the dye.

3.2.7. Column Studies

Breakthrough capacity of the prepared column was determined by plotting C/C_o vs V (effluent volume) as given in Fig 3.10. It is seen that first 500mL of influent was totally adsorbed (100%). Eighty percent adsorption of the dye occurs in the next 0.5 to 1.5 mL influent followed by a rapid decrease of adsorption (80-1.7 %) for 1.5 to 4.5 mL The column was exhausted and no further adsorption of dye occurred. A breakthrough capacity of 8.60mg/g was obtained from the breakthrough curve which is relatively lower with the batch adsorption capacity (9.72 mg/g). This decrease is usually observed and generally attributed to relatively less time of interaction between sorbent and adsorbate surface in column method.

The length of the primary adsorption zone (d), total time involved for the establishment of primary adsorption zone (tx), time for the primary adsorption zone to move down its length (t_δ), time for initial formation of primary adsorption zone (t_f), mass rate flow of the adsorbent (Fm) and fractional capacity of the column (f) was calculated from the breakthrough curves and is shown in Table 3.11 and Table 3.12.

3.2.8. Desorption studies

In order to recover the dye and regenerate the column, the spent column was eluted with sodium hydroxide solution (pH 13). The experiment was conducted under controlled conditions of flow rate through the column bed. The volume of eluent versus amount of dye recovered is graphed in Figure 3.11. A total 3L of 0.1M NaOH was found sufficient for regeneration of RTAC. The first 400 mL of the eluent was found to be sufficient for 50% removal of the adsorbed dye from RTAC. The total percentage recovery of the dye was 99.53%.

3.2.9. Removal of Dyes from Wastewater

10 mL of Acid blue 113 dye (1.0×10^{-3} M) was spiked with 70 mL of wastewater; collected from Roorkee city, India to get a final volume of 100 mL with dye concentration of 1.0×10^{-4} M. Column experiment, within optimized flow rates (1.5 mL min^{-1}) was carried out with 18g of RTAC as adsorbent of particle of size 200-250 mesh. Despite the presence of competitive effect of metal ions and dyes, about 85% reduction in dye concentration was achieved as a result of treatment with the developed adsorbent. In view of these results, it is clear that the developed method is very suitable and efficient for removing the reported dye from wastewater at large scale economically.

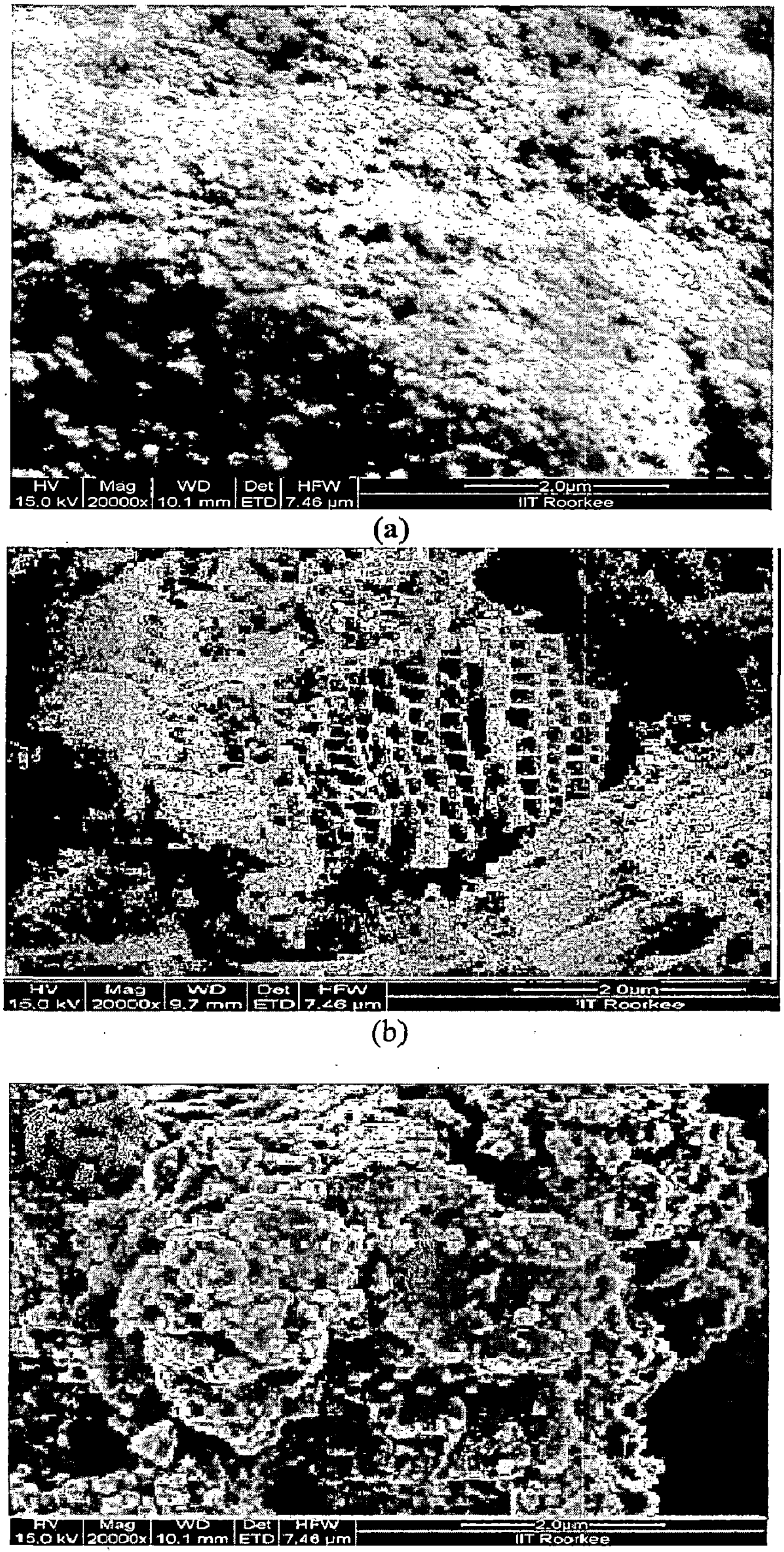
3.2.10. Comparison with other reported absorbents

A comparative assessment of RTAC with various other adsorbents reported in literature reveals the efficacy of the developed adsorbent for Acid Blue 113 dyes removal from waste water as revealed in Table-3.13 [62-64]. Besides, very few workers have optimized column condition with these dyes on low cost adsorbent. In view of this, the present study could be a better means to investigate the possibility of RTAC for the removal of reported dyes.

3.3. CONCLUSION

Mesoporous activated carbon with high surface area was prepared from waste rubber tire through physical activation method and its potential for dye adsorption capacity was studied and compared with that of a commercial activated carbon. Larger mesopore volume accounts for higher adsorption capacity of the prepared activated carbon than its commercial counterpart even though the commercial activated carbon has a higher micropore volume and a higher surface area. These facts reveal that the dye adsorption depends on both the surface properties as well as the porous properties. Also for bulky adsorbate like Acid Blue 113, mesopore volume of the activated carbon plays an important role in the adsorption phenomena.

The liquid phase batch adsorption studies reveal the effectiveness of the developed system with respect to its adsorption capacity i.e. 9.72 mg/g at 12×10^{-5} M dye concentration and its superiority over the commercial activated carbon. Equilibrium and thermodynamic studies reveal the system is exothermic, spontaneous, and favourable and follows the Langmuir isotherm model. The value of rate constants derived from the pseudo first order kinetics specifies that RTAC adsorbs Acid Blue 113 at a faster rate and also removes more amount of the dye than CAC. The kinetic study further reveals that rate determining step of the adsorption process is particle diffusion with increased mobility of adsorbate with increasing temperature and the rate follows. Column studies with a breakthrough capacity of 8.60 mg/g as well as 85% dyes removal from simulated real waste water revealed the practical utility of the developed adsorbent. Regeneration of the adsorbent was also possible due to 99.53% desorption of the dye; thereby fulfilling an important criteria for advanced adsorbents. The proposed adsorbent “waste rubber tire” in other words, the adsorbent-adsorbate system is cost effective, environment friendly with no generation of secondary pollutant, efficient and fast for the removal of dyes from contaminated waste water. It can be concluded to be a promising advanced adsorbent in environmental pollution cleanup.



(c)

Figure 3.1:
SEM micrograph (a) unactivated rubber tire (b) RTAC before adsorption (c) RTAC after adsorption

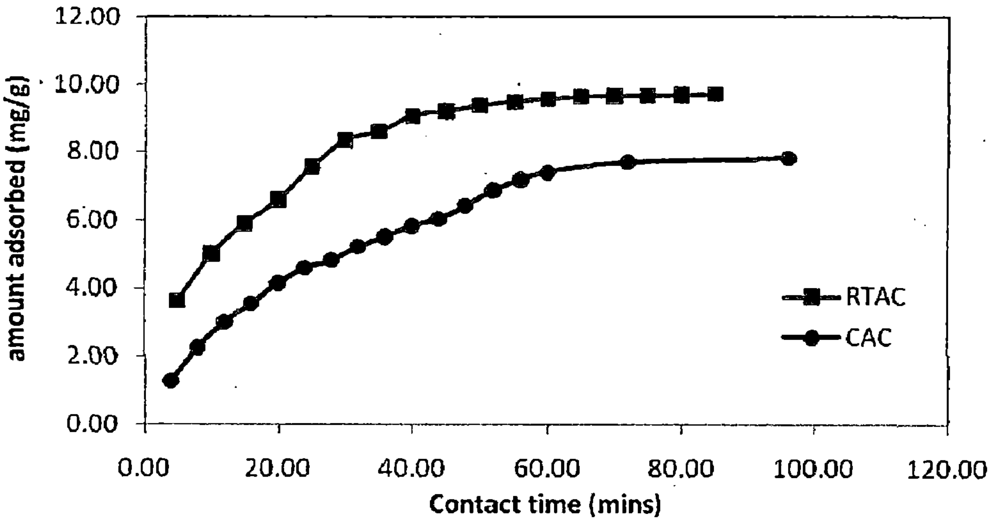


Figure 3.2:
Effect of contact time on the adsorption of Acid Blue 113 dye on to RTAC and CAC
[dye conc. 12x10^{-5}M; temperature 25°C; RTAC dose 10g/L, pH 2; CAC dose 5g/L, pH 5]

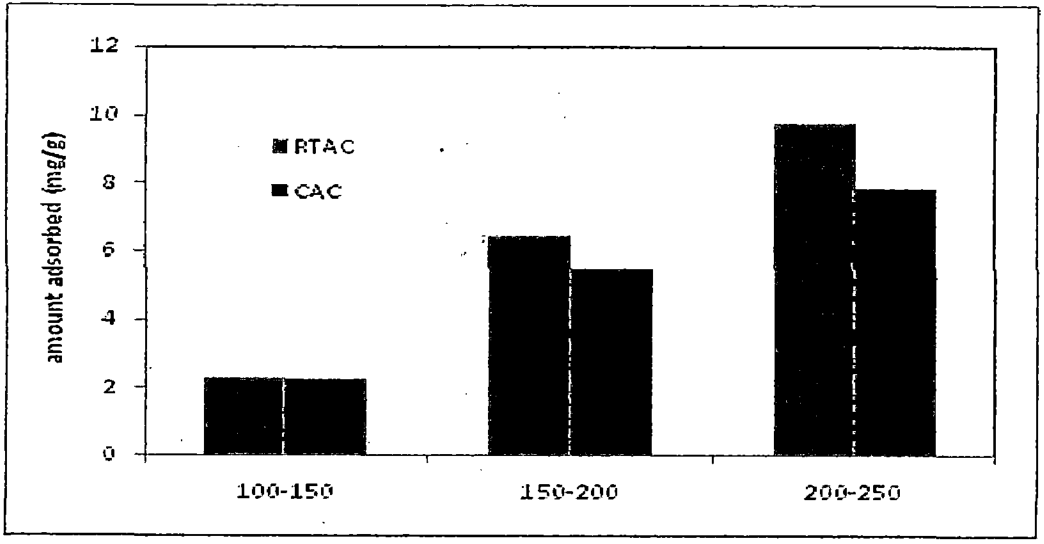


Figure 3.3:
Effect of particle size on the adsorption of Acid Blue 113 onto RTAC and CAC
[Dye conc. 12x10^{-5}M; temperature 25°C; RTAC dose 10g/L, pH 2; CAC dose 5g/L, pH 5]

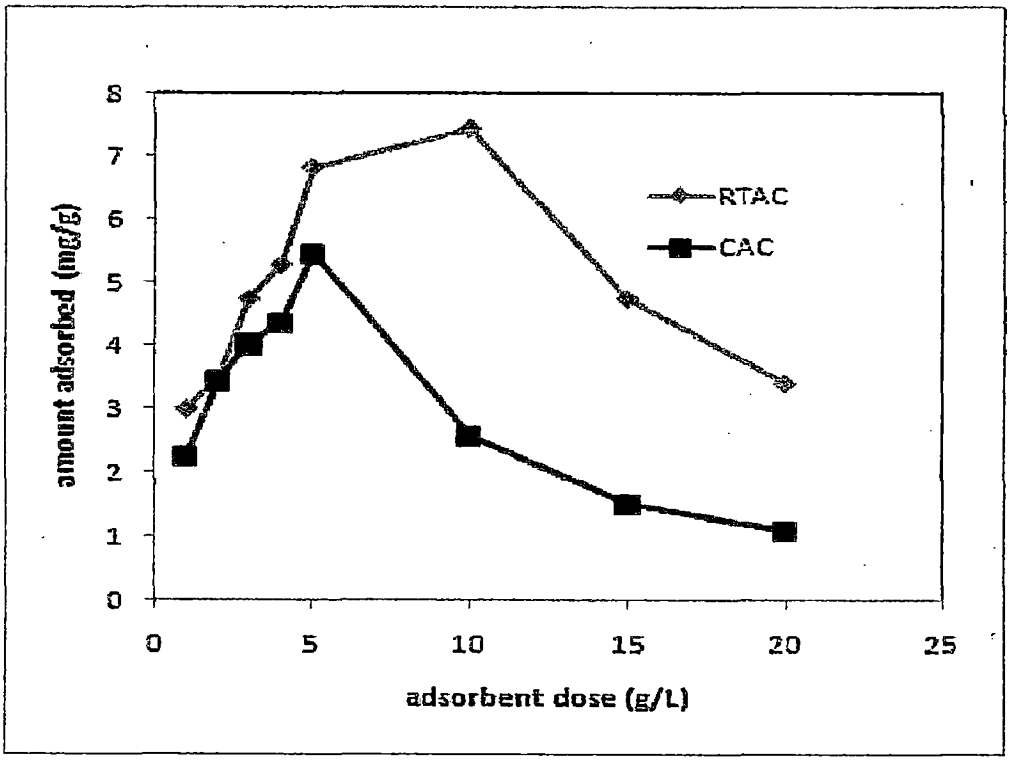


Figure 3.4:
Effect of adsorbent dosage on the adsorption of Acid Blue 113 onto RTAC and CAC
[Dye conc. $12x10^{-5}$M; temperature 25°C; RTAC: pH 2; CAC: pH 5]

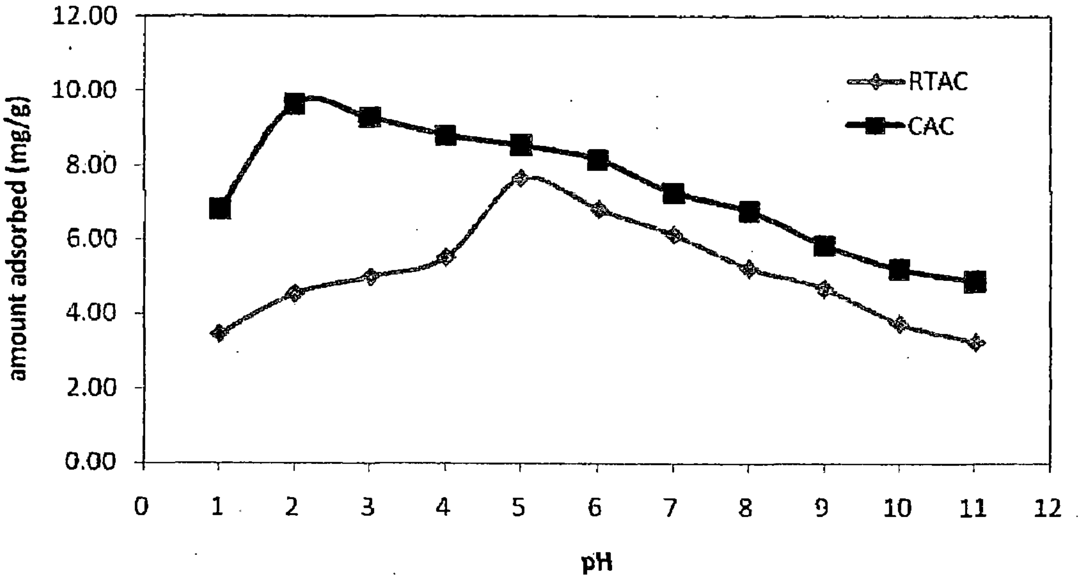


FIGURE 3.5:
Effect of pH on the adsorption of Acid Blue 113 dye on the two adsorbents RTAC (dose 10g/L) and CAC (dose 5g/L) dye conc. $12x10^{-5}$M; temperature 25°C

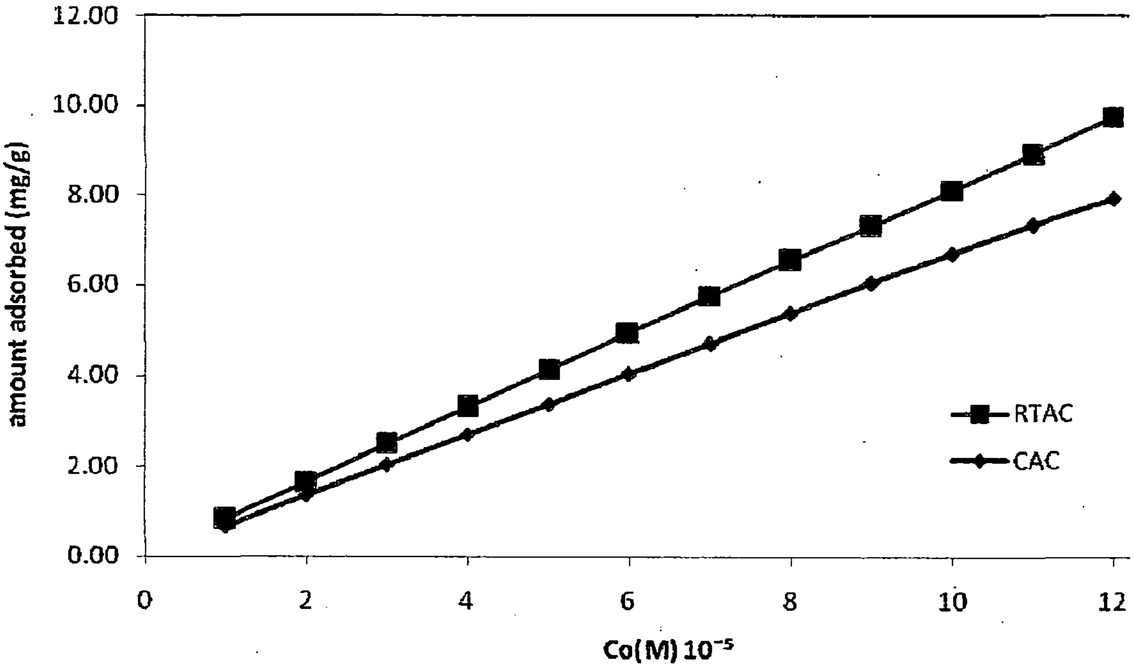
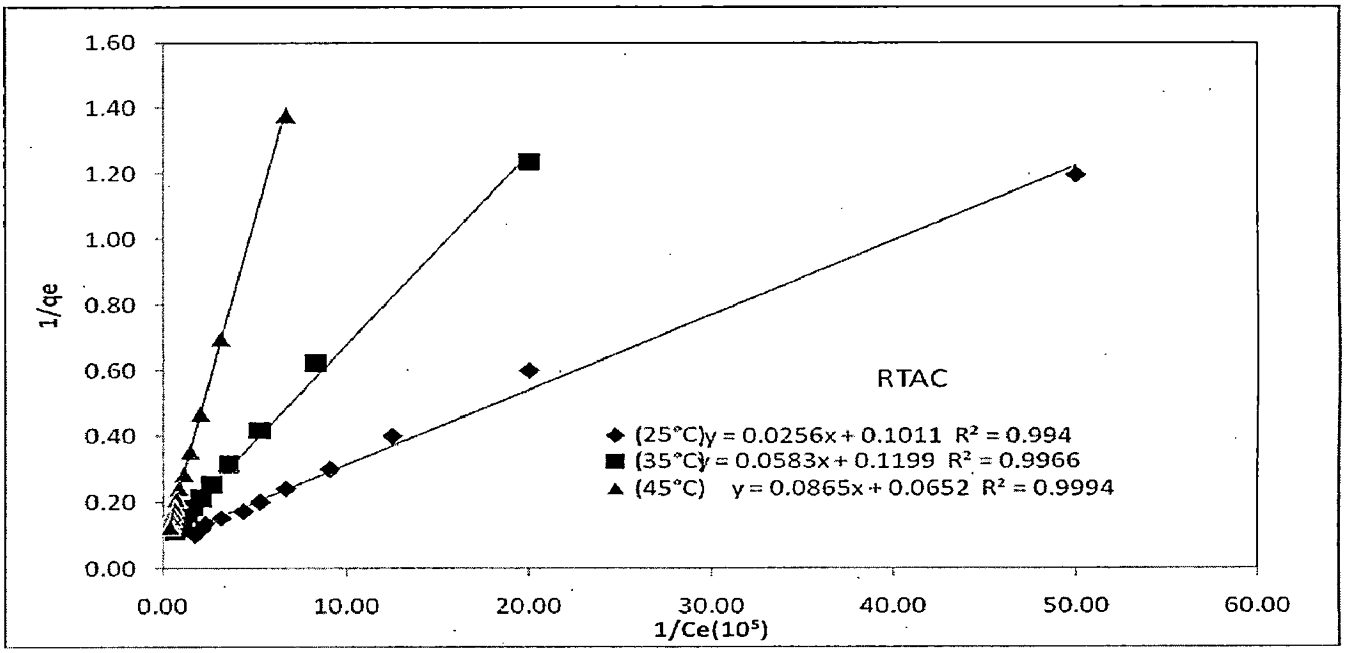
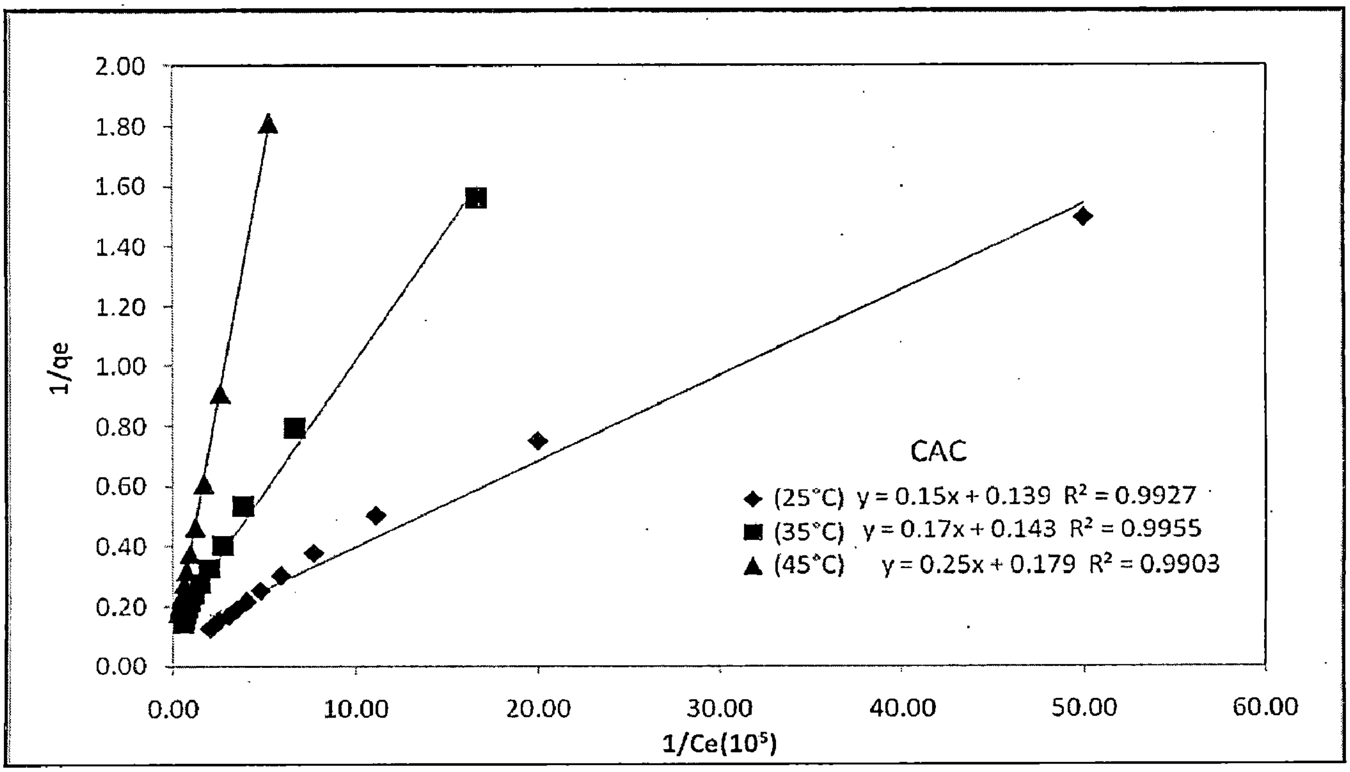


FIGURE 3.6:
Effect of initial concentration on the extent of adsorption of Acid Blue 113 dyes at 25°C on RTAC
(pH=2, adsorbent dose =10g/L) and on CAC (pH=5, adsorbent dose = 5g/L)

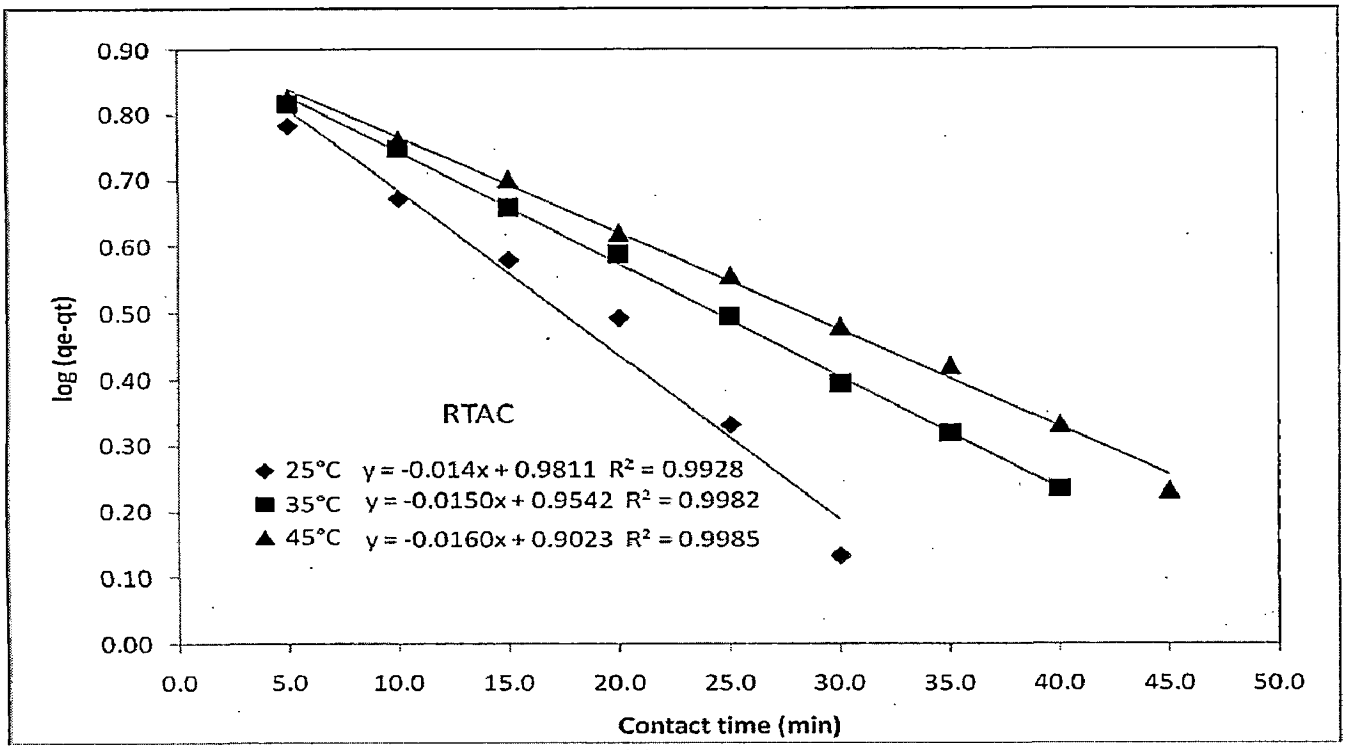


(a)

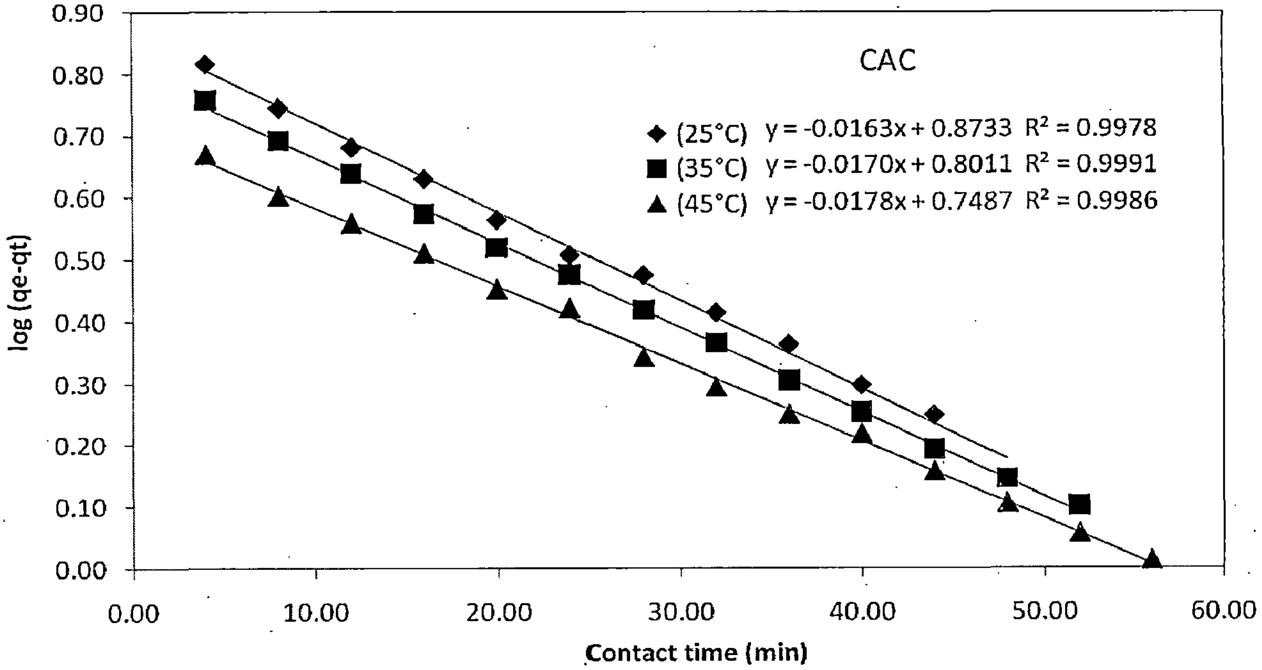


(b)

FIGURE 3.7:
Langmuir adsorption isotherms at three different temperatures for adsorbents (a) RTAC and (b) CAC

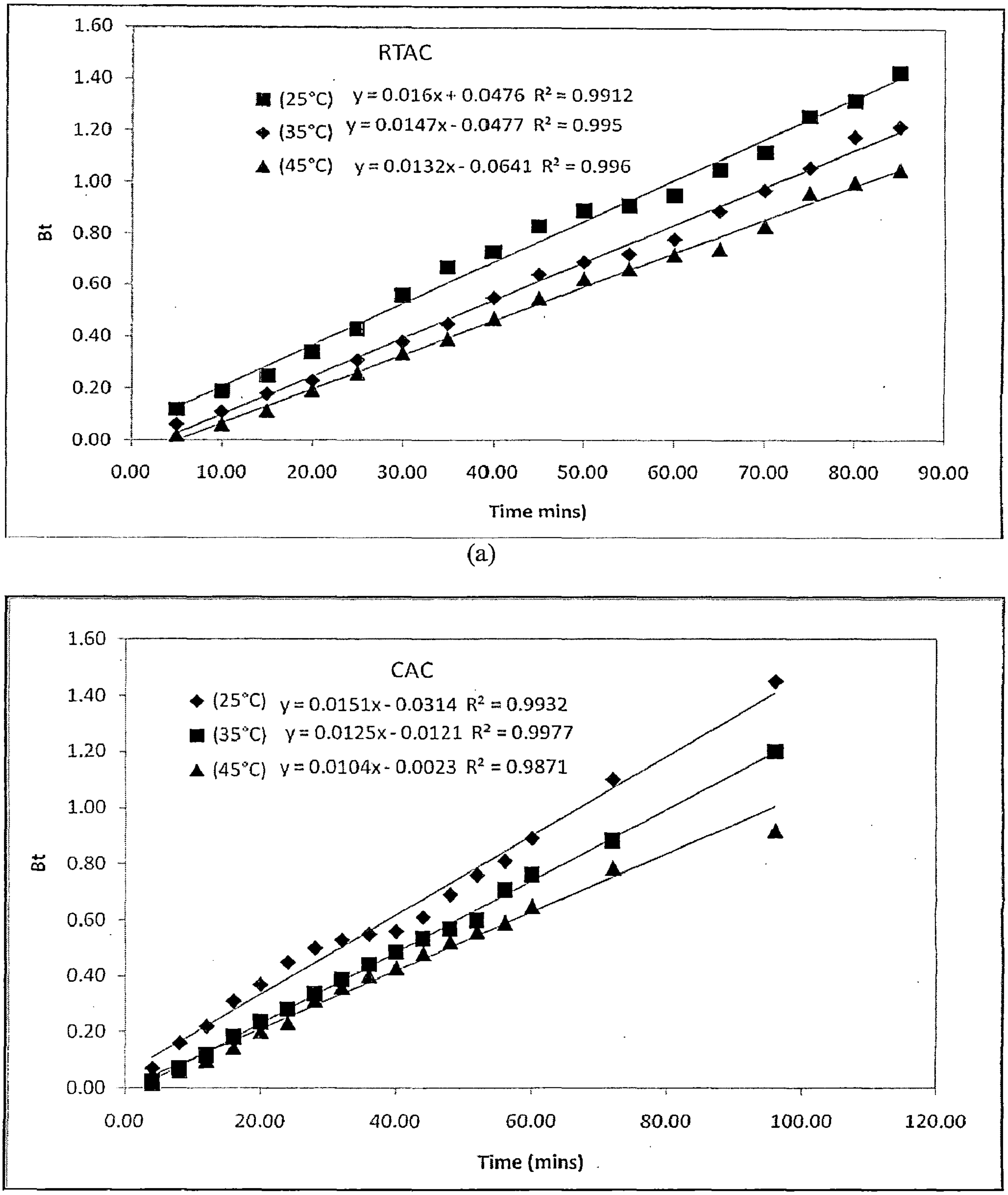


(a)



(b)

FIGURE 3.8:
Lagergren's pseudo first order plot at three different temperatures for adsorbents (a) RTAC and (b) CAC



(a)

(b)

FIGURE 3.9:
B_t vs t plot at three different temperatures for adsorbents (a) RTAC and (b) CAC

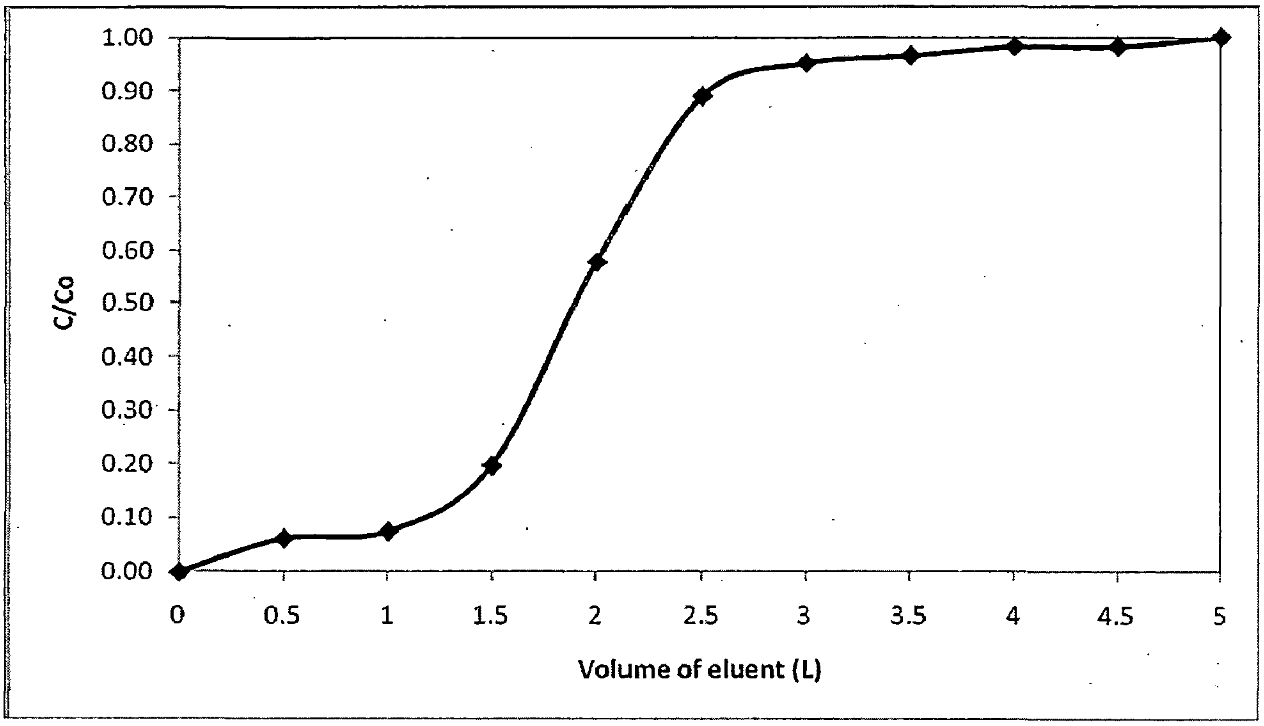


FIGURE 3.10:
Breakthrough curve for RTAC- Acid Blue 113 system

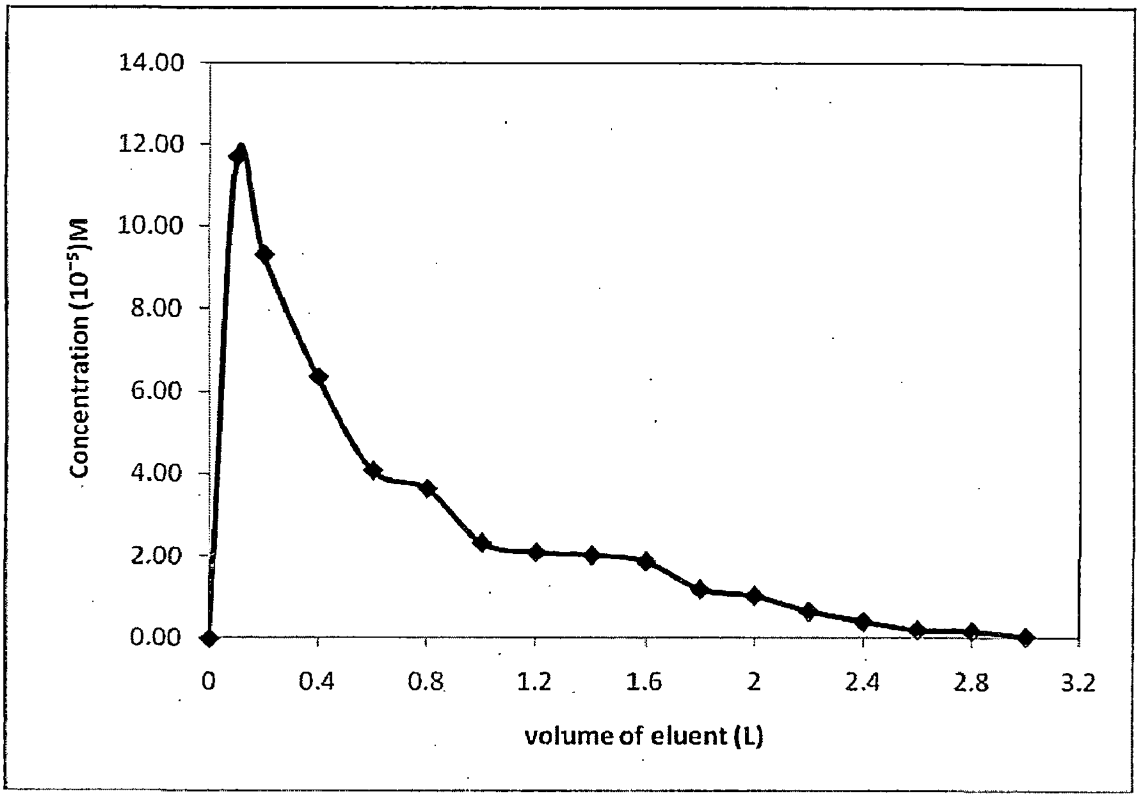


FIGURE 3.11:
Regeneration plot for Acid Blue 113-RTAC column

Table-3.1:
Physical parameters of adsorbents RTAC and CAC

	RTAC	CAC
Particle density (g/cc)	1.40	0.523
Porosity (%)	72.49	86.67
BET surface area (m^2/g)	562	1168
Total pore volume (cc/g)	0.97	0.68
Micro-Pore volume (cc/g)	0.28	0.48
Meso-Pore volume (cc/g)	0.69	0.20

Table-3.2:
Elemental analysis of RTAC

	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (%)
RTAC	10.89	78.76	1.06	0.29	1.96	7.04

Table-3.3:
FTIR Spectra of RTAC before and after adsorption

RTAC	O-H	C-H	P-H	C-F	C=C	C=C(aromatic
before adsorption	3434.78	2926.09	2352.17	1021.74	1630.43	1460.87
after adsorption	3382.09	2925.08	2344.89	1024.66	1631.09	1456.89

Table-3.4:
Effect of particle size on the uptake of Acid Blue 113 dye (Adsorbent dose 10g/L for RTAC, 5g/L for CAC; adsorbate concentration 12x10^{-5}M; pH 2 for RTAC and 5 for CAC; temperature 25°C)

Particle Size (μm)	100-150	150-200	200-250
qe (mg/g) for RTAC	2.28	6.43	9.72
qe (mg/g) for CAC	2.19	5.45	7.84

Table-3.5:
Effect of adsorbent dose on the uptake of Acid Blue 113 dyes (adsorbate concentration 12x10^{-5}M; pH 2 for RTAC and 5 for CAC; temperature 25°C)

Adsorbent dose (g/L)	1	2	3	4	5	10	15	20
qe (mg/g) for RTAC	3.00	3.48	4.73	5.28	6.82	7.43	4.75	3.41
qe (mg/g) for CAC	2.25	3.44	4.02	4.35	5.45	2.58	1.51	1.10

Table-3.6:
Isotherm model parameters for uptake of Acid Blue 113 onto RTAC and CAC

Isotherm model	Parameter	25°C		35°C		45°C	
		RTAC	CAC	RTAC	CAC	RTAC	RTAC
Langmuir	b(L/mol)x10^5	3.95	0.93	2.06	0.84	1.48	0.72
	Q°(mg/g)	9.20	7.19	8.50	6.99	7.74	5.59
	R^2	0.9968	0.9927	0.9967	0.9955	0.9937	0.9903
Freundlich	K_f	75.03	0.0001	57.67	0.007	50.42	0.02
	n	1.79	2.06	1.75	2.11	1.71	2.42
	R^2	0.9617	0.8572	0.9734	0.9734	0.9467	0.8824

Table-3.7:
R_l values obtained at different temperatures for adsorption of Acid Blue 113

Temperature	25°C	35°C	45°C
RTAC	0.021	.041	0.056
CAC	0.090	0.099	0.116

Table-3.8:
Thermodynamic Parameters for the adsorption of Acid Blue 113

Adsorbent	-ΔG°(kJ/mole)			-ΔH°(kJ/mole)	-ΔS°(kJ/ K. mole)
	25°C	35°C	45°C		
RTAC	31.91	30.30	29.48	27.05	0.19
CAC	28.32	28.08	27.69	13.11	0.14

Table-3.9:
Kinetic Parameters for the adsorption of Acid Blue 113 onto RTAC and CAC

Adsorbent	(exp) qe(mg/g)	Temp (°C)	*Pseudo First Order*			*Pseudo Second Order*		
			qe(mg/g) (theo)	k_1(min^{-1})	R^2	qe(mg/g) (theo)	k_2 (g/mg/min)	R^2
RTAC	9.72	25	9.57	0.032	0.9928	9.89	0.0103	0.8925
	8.91	35	8.99	0.034	0.9982	7.46	0.0082	0.9134
	7.95	45	7.99	0.036	0.9985	6.38	0.0067	0.8545
CAC	7.84	25	7.47	0.037	0.9978	10.65	0.0033	0.9016
	6.94	35	6.33	0.039	0.9991	9.50	0.0034	0.9240
	5.33	45	5.61	0.040	0.9986	7.63	0.0043	0.8906

Table-3.10:
Values of B, Di, Do, ΔS and Ea for Acid Blue-113-adsorbent system

Adsorbent	C_o (10^{-5})M	C_x (10^{-5})M	C_b (10^{-5})M	V_x (mL)	V_b (mL)	V_x-V_b (mL)	F_m (mg/cm²/min)	D (cm)
RTAC	12	10.68	2.38	2500	1500	1000	0.4204	30

Table-3.11:
Fixed Bed Adsorber Calculation

Adsorbent	B			D_i(10^{-15})(m²/sec)			D_o(10^{-12}) (m²/sec)	-ΔS (JK⁻¹mole⁻¹)	Ea (kJ/mole)
	25°C	35°C	45°C	25°C	35°C	45°C			
RTAC	0.016	0.015	0.013	2.80	2.87	2.94	4.51	190.89	18.29
CAC	0.015	0.012	0.010	3.40	3.80	4.40	0.014	231.89	3.464

Table-3.12:
Parameters for Fixed Bed Adsorber

Adsorbent	t_x mins	t_δ mins	t_f mins	f	δ (cm)	% saturation
RTAC	5946.4	2378.6	56.0	0.9765	12.11	99.049

Table 3.13:
Comparison of RTAC with other low cost adsorbents, used in literature for Acid Blue 113 dyes removal

Adsorbent	**Adsorption Capacity (mg/g)**	**Ref.**
Activated Red Mud	3.86	62
Carbon xerogel	0.268	63
Carbon slurry	219	64
RTAC	9.20	In this study
CAC	7.19	In this study

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Chapter 4

RUBBER TIRE ACTIVATED CARBON FOR THE REMOVAL OF PESTICIDES

4.1. INTRODUCTION

Water pollution by pesticides from various sources such as discharges from pesticide industry, agricultural runoff, municipal wastes, and from other non point sources has been recognized in agricultural areas of the world for many years, and considerable evidence suggest that many water resources are contaminated by such organic pesticides [1-5]. Pesticides are used worldwide in agriculture to control pests and to increase crops yields. The extensive use of pesticides on one hand improved the agricultural productivity many folds, but on the other hand, they are posing a severe persistent thereat to the ecology and environment with widespread pollution. Pesticides are known for their severe toxicity and bioaccumulation in aquatic organisms [6, 7]. The real hazard setting aside aesthetic considerations is exacerbated when pesticide agents interfere with the transmission of light through water, retard photosynthetic activities, inhibit the growth of biota terrestrial, affect the symbiotic process, damage the quality of the irrigation channels and impede the propagation of algae, thus upsetting biological processes within streams, resulting in food chains and ecological imbalance [8, 9]. Increasingly acute exposure to pesticide substances causes vulnerability to a wide spectrum of immune suppression, neurobehavioral disorders as allergy, autoimmune disease, reproductive abnormalities, multiple myeloma, leukemia, malignant lymphoma etc. [10-12]. In view of their high toxicity and bioaccumulation, stringent limits have been enforced on pesticides by various international organizations. The Bureau of Indian Standards (BIS) requires that the pesticides should not be present in the natural waters.

Methoxychlor, atrazine, and methyl parathion are the most widely used toxic pesticides in the third world countries and are widely detected in surface and ground waters in different countries of the world. The toxicity and EPA limit in drinking water supplies are reported in Table-2.2. Although the application of these chemicals has been banned or restricted in many countries especially the developed ones, some developing countries are still using these compounds because of low cost and versatility in industry, agriculture and public health.

The selection of a suitable technique for pesticide removal is a complex problem because of the wide variety of their chemical structures. Treatment technologies (precipitation, coagulation–flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange) with varying levels of success has accelerated a dramatic progress in the scientific community [13-18]. Adsorption process by activated carbon is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes [19-24]. But this process is not cost effective especially for developing countries where there is a significant demand for agricultural pesticides while there is a lack of sophisticated wastewater treatment technologies. Hence, exploitation of newer, cheaper, and indigenous waste materials for the removal of pesticides from wastewater has currently become focus of intense research. Materials investigated till date, as adsorbents for pesticides include: charcoal from agro waste [25, 26, 27], coal fly ash [28], wood charcoal [29], bark [30], sal wood charcoal [31], watermelon peel [2], chestnut shell [33], oil shale ash [34], olive stone [5], baggasse fly ash [36, 37], carbon slurry [38, 39]. Their lower cost, easier availability and no complicated regeneration processes has further stressed on their exploitation as sorbents.

Waste tires represent another interesting source of raw material because highly mesoporous activated carbons can be prepared from waste tires rubber with suitable application to waste water treatment [40, 41, 42]. Since the production of activated carbon from waste tires transforms hard-to dispose waste to pollution-cleaning adsorbent, it is considered a doubly effective solution for environmental pollution. In some waste water treatment applications involving macromolecules like pesticides and dyes which cannot easily penetrate into the micropores and adsorb onto them, the activated carbons should possess not only micropores but also mesopores [43, 44]. A detailed perusal of literature reveals little research on mesoporous activated carbon from waste rubber tire for pesticide adsorption and this line of research has provided limited insight into the factors affecting the pesticide removal capacity of waste rubber tire. Therefore, the present study aims to prepare activated carbons from tire char for pesticide adsorption. Keeping in consideration of the fact that pesticides are bulky and have complex chemical structures, a combination of chemical and physical treatment viz. chemical treatment of tire char prior to physical activation has been adopted in an attempt to develop surface porosity as well as to incorporate desired functional groups on the surface of the resultant activated carbons. The adsorption capacity of the carbons was further evaluated for pesticides removal from waste water. Methoxychlor, atrazine, and methyl parathion are model pesticides selected for study; they are toxic and their applications have been banned but despite this, are most widely used in the third world countries because of low cost and versatility in industry and agriculture (USEPA). Factors that are likely to affect the adsorption capacity of tire rubber were studied; in addition, adsorption isotherms and kinetic models have been determined and analyzed.

4.2. RESULTS AND DISCUSSION

4.2.1. Characterization of CTRTAC

Since adsorption is a surface phenomenon, the rate and extent of adsorption specific to a given adsorbent are influenced by the physicochemical characteristics of the adsorbent such as surface area, pore size, surface chemistry, and elemental composition [45]. The carbonaceous nature of the CTRTAC is evident from data of CHNS analysis shown in Table-4.1 which reveals the carbon content as 78.43%. Surface texture and porosity developed as a result of the thermal and chemical treatment is clearly evident from the SEM images. Figure 4.1b reveals that the thermally and chemically treated sorbent is highly porous as compared to the untreated adsorbent (Figure 4.1a). Surface texture of the CTRTAC after adsorption of pesticide (methoxychlor) is depicted in Figure 4.1c. Table 4.2 summarizes the textural characteristics and surface area of the adsorbent before and after thermal and chemical treatment. The surface area of untreated rubber tire was found to be $22m^2/g$ where as that of CTRTAC showed an increase, and was found to be $981m^2/g$. The table shows that the volume of mesopores (dimension in the 2 to 50 nm range) in CTRTAC is 0.86 cc/g (56.96% of total pore volume) The activation process is thereby responsible for the development of a mesoporous and a microporous activated carbon as well as a higher surface area.

The X-ray diffraction spectrum pattern of the CTRTAC sample did not show any peak, thereby, indicating the amorphous nature of the product (Figure 4.2). However, FTIR spectrum of the CTRTAC after treatment (Figure 4.3b, Table 4.3) indicates the presence of two prominent bands lying at 1624 and 3413.03 cm^{-1} which may be assigned to the presence of carbonyl group and hydroxyl group respectively. In the activation of KOH-impregnated samples for 2 hr at 800-900 °C, the large amount of unstable oxygen groups (e.g. carboxylic ester) decomposes and only hydroxyl and carbonyl groups remain [46].

Successive physical and chemical treatment has helped in transforming a non-porous rubber tire sample to a well developed mesoporous adsorbent with a high surface area and favorable surface chemistry.

4.2.2. Preliminary Adsorption Studies

To optimize the effect of various parameters on adsorption of the studied pesticides by CTRTAC, batch experiments were run under different conditions. The results of the experiments are discussed below.

4.2.2.1. Effect of Contact Time and Concentration

The rate of uptake of pesticides on CARTAC as evident from Figure 4.4 depicts that the sorption is quite rapid initially, gradually slows down and then reaches the equilibrium Equilibrium was attained at 60 mins for CTRTAC-pesticide system An increase in adsorption was observed from 41.1 to 112.0 mg/g for methoxychlor, 36.9 to 104.9 mg/g for atrazine and 28.8 to 88.9 mg/g for methyl parathion with 5 mg/L and 12 mg/L initial concentration of the pesticides. The time of equilibration adsorption (maximum adsorption) was unaffected with initial concentration, but the amount adsorbed increased by increasing concentration of the pesticides.The uptake capacity of pesticides molecules by the adsorbent, and the time required for establishment of equilibrium suggest the effectiveness of these materials for wastewater treatment.

4.2.2.2. Effect of Adsorbent Particle Size

The adsorption of pesticides was studied at different particle sizes of CTRTAC of 100-150,150-200 and 200-250 BSS. The batch experiments were conducted at a fixed pesticide concentration of 12 mg/L, at a fixed temperature of 25°C and fixed pH of 2. By increasing mesh size from 100-150 BSS to 200-250 BSS (Figure 4.5), the adsorption capacity of methoxychlor was found to increase from 64.90 mg/g to 111.90 mg/g. Similar results are observed for atrazine (50.20 mg/g at 100-150 BSS to 104.0 mg/g at 200-250

BSS) and for methylparathion (41.80 mg/g at 100-150 BSS to 88.0 mg/g at 200-250 BSS). This leads to the conclusion that the amount adsorbed increases with increasing mesh size which is indeed true as decreasing mesh size has a decreasing particle size which in turn has a higher surface area. This may be due to the fact that the smaller adsorbent particles have shortened diffusion paths, such that the ability of adsorbate to penetrate all internal pores of the adsorbent is higher. Particle size of 200-250 BSS was, hence, chosen for further studies.

4.2.2.3.Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of pesticides was studied by varying the dose of adsorbent from 0.02 to 0.14 g/L. The experiment was carried out at fixed pesticide concentration at 12 mg/L, at a fixed temperature of 25°C and pH 2. From Figure 4.6 and Table-4.4, it is evident that adsorbent dose significantly influences the amount of pesticide adsorbed. Initially, the amount of pesticide adsorbed was found to be rapid from 0.02 to 0.10 g/L. Further increase of adsorbent dose resulted in very less increase in adsorption, and hence, 0.1 g/L was considered the optimum dose (Table-4.4). The initial rise in adsorption with adsorbent dose is probably due to a stronger driving force and larger surface area. With a rise in adsorbent dose, there is a less commensurate increase in adsorption resulting from lower adsorptive capacity utilization of adsorbent [47].

4.2.2.4. Effect of pH

To observe pH effects, the adsorption of the pesticides was studied over a pH range of 2.0-11.0 and the results are plotted in Figure 4.7. Over the range of experimental pH, surface functional groups of CTRTAC (especially carbonyl, hydroxyl) become deprotonated and the extent of deprotonation increases with an increase in pH. This deprotonation results in a more negatively charged carbon surface at higher pH than at the lower pH values. The negative charge developed at the surface of the adsorbent as a result of deprotonation causes strong electrostatic repulsion for the pesticides in solution, thereby retarding diffusion and adsorption. While, with decrease in alkaline conditions or pH, deprotonation of adsorbent is reduced, thereby accelerating diffusion and adsorption [39]. An increase in pH from 2.0 to 11.0 resulted in decrease in adsorption from 112.0 to 56.8mg/g for methoxychlor, 104.9 to 42.5 mg/g for atrazine and 88.9 to 27.8 mg/g for methyl parathion. Maximum adsorption of all three pesticides occurs at pH 2 and hence was selected as the optimum and used throughout the study.

4.2.2.5. Effect of Temperature

The experiments were conducted at 25, 35, and 45 °C temperatures, and the results are shown in Figure 4.9 for methoxychlor with similar trend being observed for atrazine and methyl parathion. A perusal of these isotherms indicated that maximum adsorption decreased from 112 to 106.8 mg/g for methoxychlor, 104.9 to 93.0 mg/g for atrazine and 88.9 to 31.4 mg/g for methyl parathion respectively, with an increase in temperature; thereby indicating that the process was apparently exothermic for all the pesticides.

4.2.3. Modeling of Adsorption Isotherm

Adsorption isotherms of the pesticides on the rubber tire before and after treatment are plotted in Figure 4.8. It is evident from the figure that CTRTAC showed remarkable adsorption capacity for the pesticides. Untreated rubber tire showed negligible adsorption characteristics as compared to CTRTAC and hence was not shown in Figure 4.8. Thus it can be concluded that textural characteristics of CTRTAC was conducive to good adsorption capacities [48]; proving beyond doubt, that the adsorption process is a surface phenomenon and the nature of interaction between the adsorbent and adsorbate is, to some extent, physical in nature. This phenomenon is proved later in kinetic study.

Isotherm data was analyzed with Langmuir and Freundlich models as discussed earlier and the results of their linear regression were used to find out the fit model. Values of Langmuir constants Q^o and b, Freundlich constants K_F and n, as well as the regression coefficients (R^2) for all the pesticides are listed in Table 4.5. Langmuir model was found fit due to high correlation coefficients for CTRTAC-pesticides system. CTRTAC has maximum affinity for methoxychlor as indicated by the 'b' values. Figure 4.9 indicates the linear plots of 1/qe vs 1/Ce for methoxychlor adsorption showing the applicability of the Langmuir equation.

It is seen that the pesticides adsorbing onto CTRTAC follow the order: methoxychlor > atrazine > methyl parathion (Table-4.5). Also the log K_{ow} (octanol-water partition coefficient) of pesticides is of the order: methyl parathion > atrazine > methoxychlor. A direct relation is thus observed between the adsorptive capacity and log K_{ow} values of pesticides (Table 4.5). The log K_{ow}, or Octanol - Water partition coefficient, is simply a measure of the hydrophobicity (water repelling) of an organic compound. The more log K_{ow} value, the more hydrophobic a compound, the less soluble it is, therefore the more likely it will adsorb to an adsorbent [49]. Thus methoxychlor (having a log K_{ow} value of 4.68-5.08) being least soluble in water (least affinity for water) is adsorbed at the solid-liquid interface to the maximum extent. Methyparathion on the other hand shows least log K_{ow} value of 1.83-3.43 and hence is least hydrophobic thereby is the least adsorbed onto CTRTAC.

4.2.4. Thermodynamic Study

The free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using equations described in our earlier work [42]. The values of these parameters summarized in Table 4.6 indicate the sensitivity of the adsorption process towards temperature. The enthalpy change, ΔH°, is negative (exothermic) due to the decrease in adsorption with successive increase in temperature. Negative ΔG° values dictate spontaneous process, revealing increased randomness at the solid–solution interface during the fixation of the pesticides on the active sites of the adsorbent. Since the adsorption process is exothermic, it follows that under these conditions the process becomes spontaneous because of the negative entropy change.

4.2.5. Kinetic Study

The Lagergren's pseudo-first-order and pseudo-second-order models were used to test adsorption kinetics data in order to investigate the mechanism of adsorption and were analyzed as discussed earlier. The values of the kinetic parameters as well as the regression coefficients (R^2) at two different concentrations of the pesticides are listed in Table 4.7.

The value of correlation coefficient R^2 for the pseudo-first-order adsorption model is relatively high (>0.99), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo second-order model are not satisfactory. Therefore, it has been concluded that the Lagergren's pseudo-first-order adsorption model is more suitable to describe the adsorption kinetics of the pesticides over CTRTAC. Figure 4.10 indicates the linear plots of log (qe-qt) vs time for pesticides adsorption on CTRTAC showing the applicability of the Lagergren's pseudo-first-order model.

Lower first-order rate constants for methoxychlor may be due to its larger size, which would not facilitate its approach through pores to adsorbent surface. As the sizes of atrazine and methyl parathion are nearly same, their rate constants should also be similar, and the experimental rate constants are found nearly same as evident from Table 4.7.

4.2.6. Mechanism of the adsorption process.

The applicability of the following Bangham's equation was tested to learn about the slow step occurring in the present adsorption system.

Log log $[C_0/(C_0 - q_t m)]$ values were plotted against log t in Bangham's plot (Figure 4.11). The linearity of these plots confirms the applicability of Bangham's equation and indicates that diffusion of pesticide molecules into pores of the adsorbent mainly controls the adsorption process [50]. The micropores provides majority of the active sites for pesticide adsorption while mesopores act as transportation routes [51].

The values of E_a (energy of activation) are calculated from the following equation:

$$\log K_2/K_1 = E_a/2.303\ R(T_2-T_1)/T_2T_1 \qquad (1)$$

Where K is the 1st order rate constant, T is the temperature in Kelvin and R is the gas constant. The value of E_a calculated from the slope (slope = $-E_a/2.303R$) of the graph plotted between log K vs 1/T was 2.05, 2.71 and 3.84 kJ/mol respectively. Thus, it is confirmed that the nature of interaction between the adsorbate and adsorbent is physical in nature involving weak Van der Waals forces.

4.2.7. Column Studies

The application of the results obtained from adsorption batch experiments were used to remove the pesticides-methoxychlor, atrazine and methyl parathion of fixed concentration of 12 mg/L by column experiments. The flow rate was varied to achieve maximum removal of pesticides. It was observed that the maximum removal of the pesticides (91% for methoxychlor, 82% for atrazine and 71% for methyl parathion) was achieved at the flow rate of 1.5 ml/min (Figure 4.12). The breakthrough curves (Figure 4.13) were used to calculate the column capacity (breakthrough capacity, exhaustion capacity and column utilization) and the results are tabulated in Table 4.8. Relatively lower adsorption capacity than batch capacity has been observed, which is generally attributed to relatively less time of interaction between the adsorbent and the adsorbate surface with column method.

4.2.8. Cost evaluation and Comparison of adsorption efficiency

The adsorption capacity values of the rubber tire were compared with the pesticide adsorption capacities reported for other adsorbents, namely, activated carbon, oil shale ash, baggasse fly ash, olive stone, carbon slurry and coal fly and the findings are tabulated in Table 4.9. The pesticide removal capacity of rubber tire was found remarkably higher than that of the reported adsorbents. Another advantage of using waste rubber tire as adsorbent is its lower cost and its economic feasibility in comparison to commercial carbon available in India (US $285.0 per ton) [38]. The waste rubber tire granules costs US$ 10.0 per ton and considering the cost of transport, chemicals, electrical energy used in the process and labor, the finished product would cost approximately US$ 25.0 per ton.

4.3. CONCLUSION

This study has investigated the adsorption of pesticides onto activated carbon developed from thermal and chemical treatment of waste rubber tire. Chemical treatment prior to activation facilitated in the development of not only a well developed porous adsorbent but also incorporation of carbonyl and hydroxyl functional groups onto the adsorbent surface; these ultimately helped in the adsorption process. Batch adsorption studies revealed maximum adsorption occurring at a contact time of 60mins, particle adsorbent size of 200-250 μm, low pH and at a lower temperature. CTRTAC offered admirable adsorption capacities for the removal of methoxychlor, atrazine and methyl parathion which were 112.0 mg/g, 104.9 mg/g and 88.9 mg/g respectively from an initial concentration of 12 mg/L signifying 93.3%, 87.4% and 74.1% removal of pesticides. These promising results were confirmed with the removal of 91%, 82.1% and 71.78% methoxychlor, atrazine and methyl parathion respectively by column experiments. Both textural as well as surface chemistry of the developed adsorbent was conducive for the enhanced adsorption capacity of bulky adsorbates like the pesticides. The decreasing trend of the adsorptive capacity of the CTRTAC is indicative of the influence of the pesticide solubility.

The developed system is feasible and spontaneous as revealed from thermodynamic studies. Kinetics study indicates that the rate determining step of the adsorption process is pore diffusion of pesticides onto the adsorbent. Finally, a cost analysis study of CTRTAC and commercial activated carbon concludes that CTRTAC is a more effective, efficient, economic adsorbent and can be used for the removal of reported and other pesticides from wastewater.

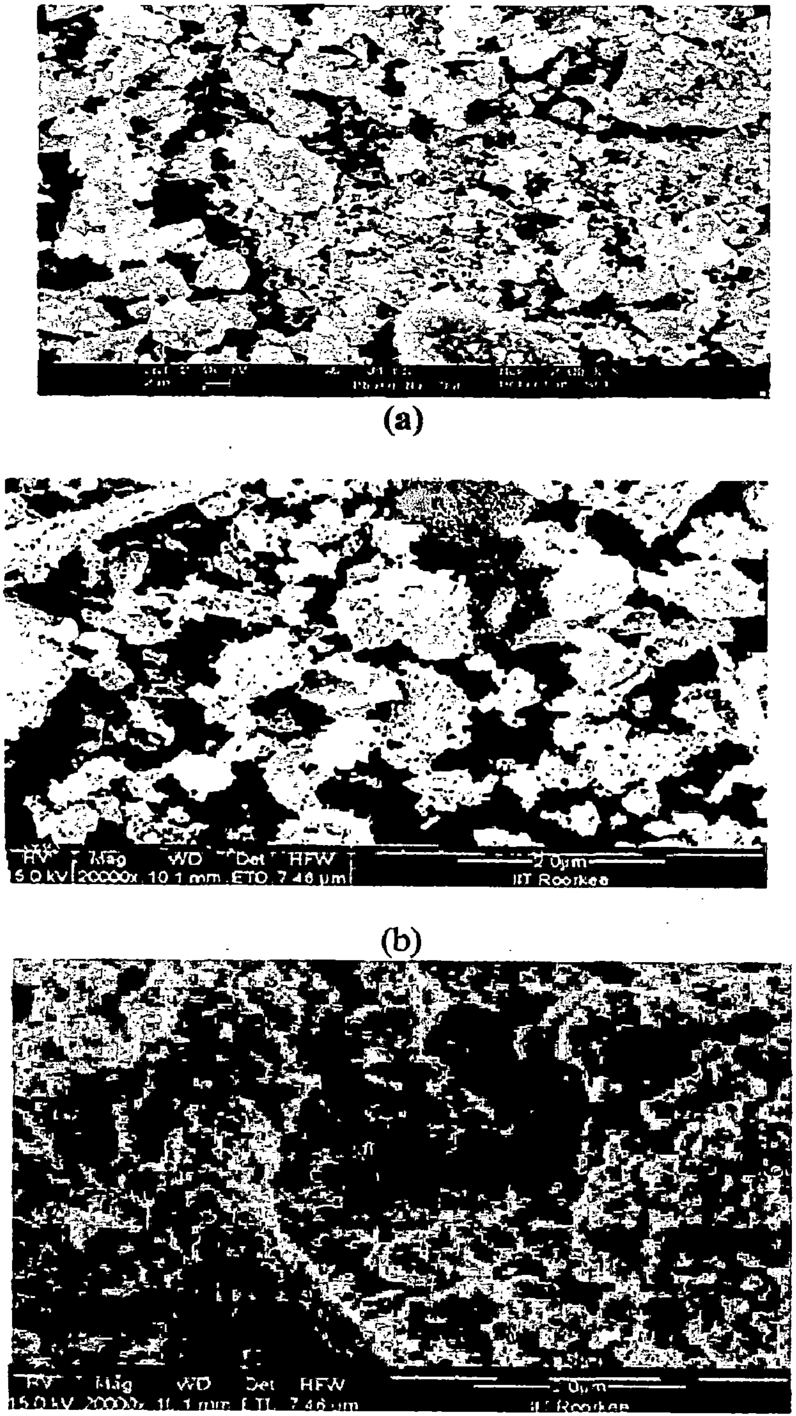
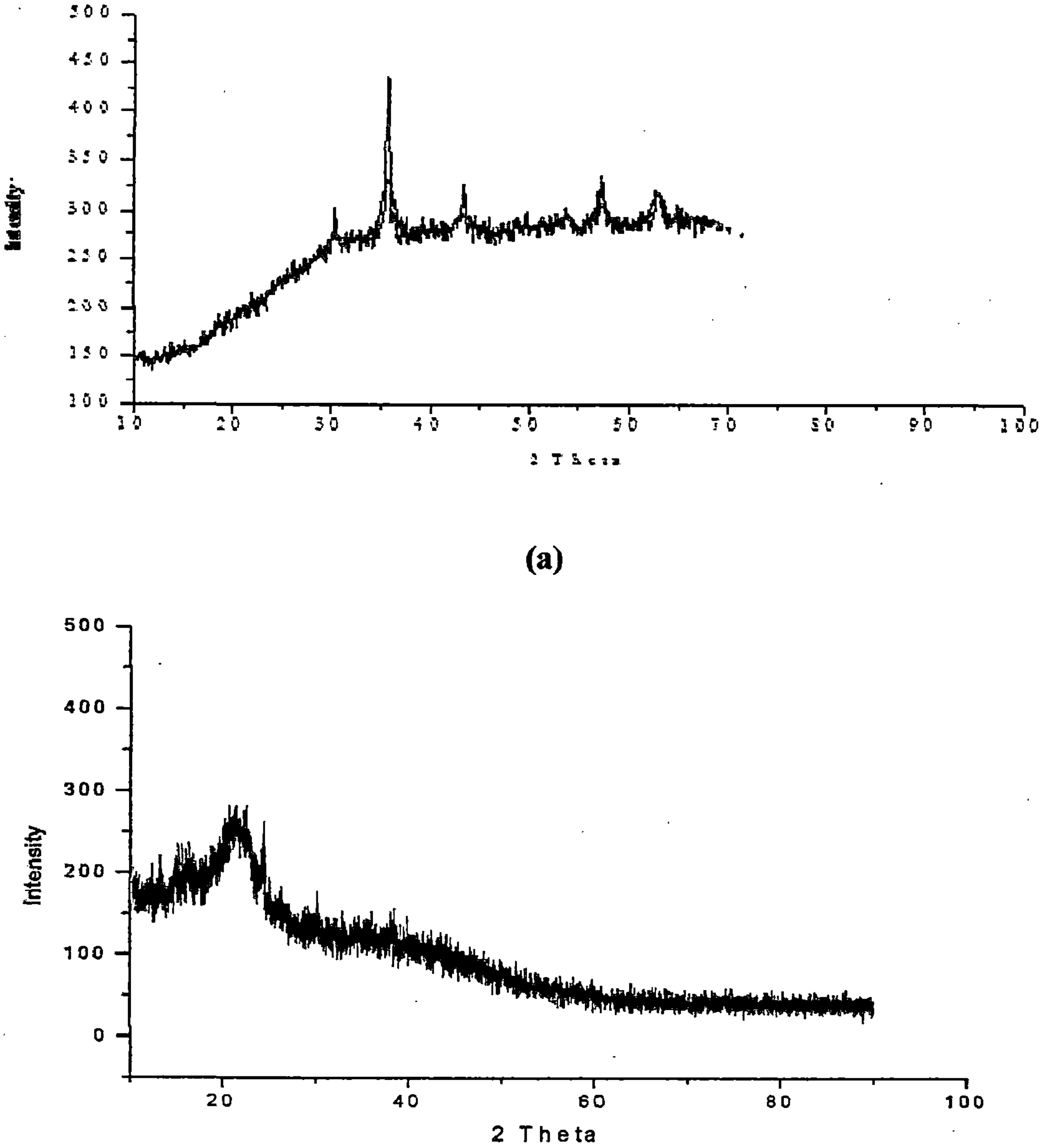


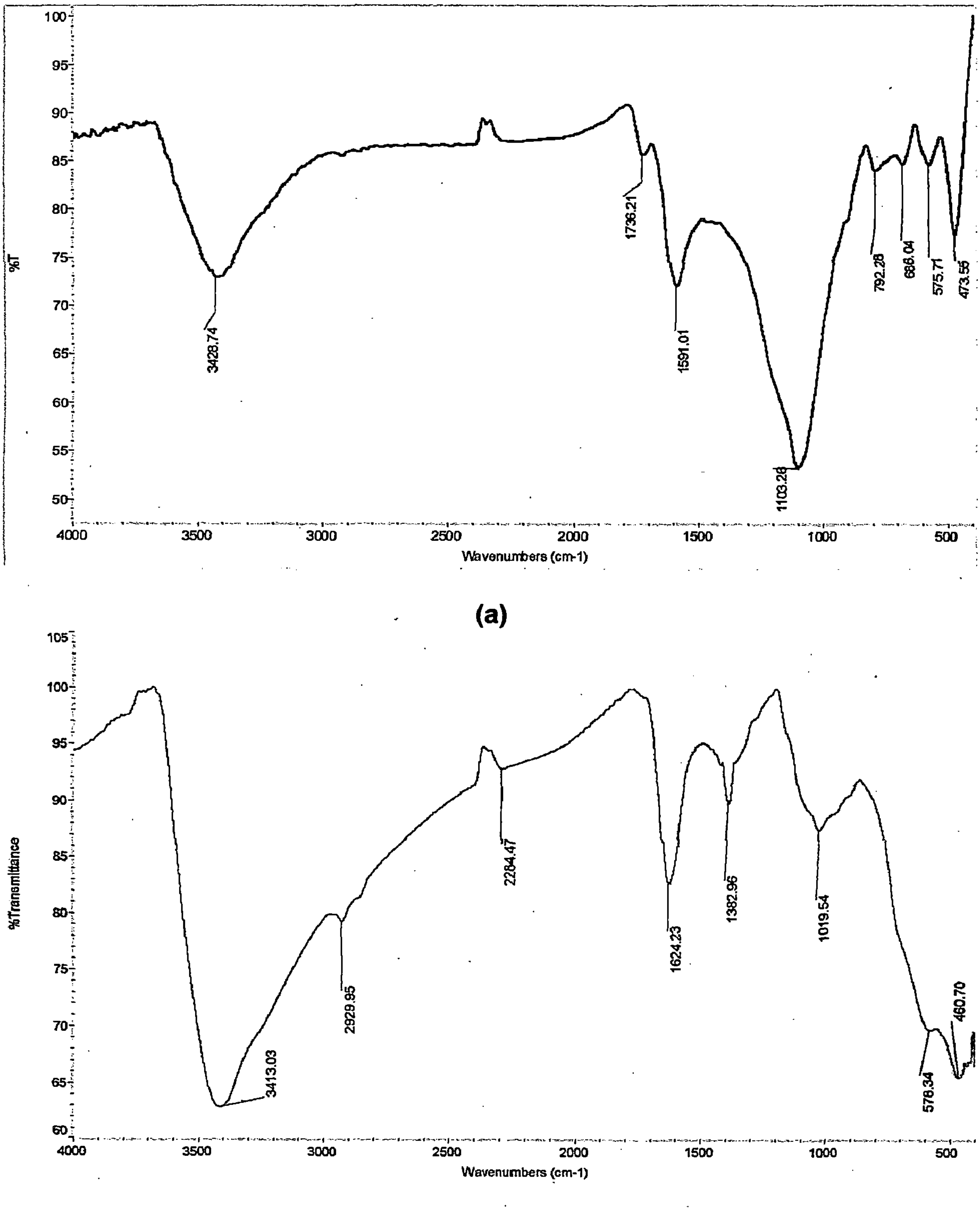
Figure 4.1:
SEM micrograph (a) unactivated rubber tire (b) CTRTAC before adsorption (c) CTRTAC after adsorption of methoxychlor pesticide.



(a)

(b)

Figure 4.2:
XRD of (a) unactivated rubber tire (b) CTRTAC



(a)

(b)

Figure 4.3:
FTIR spectra of (a) unactivated rubber tire (b) CTRTAC

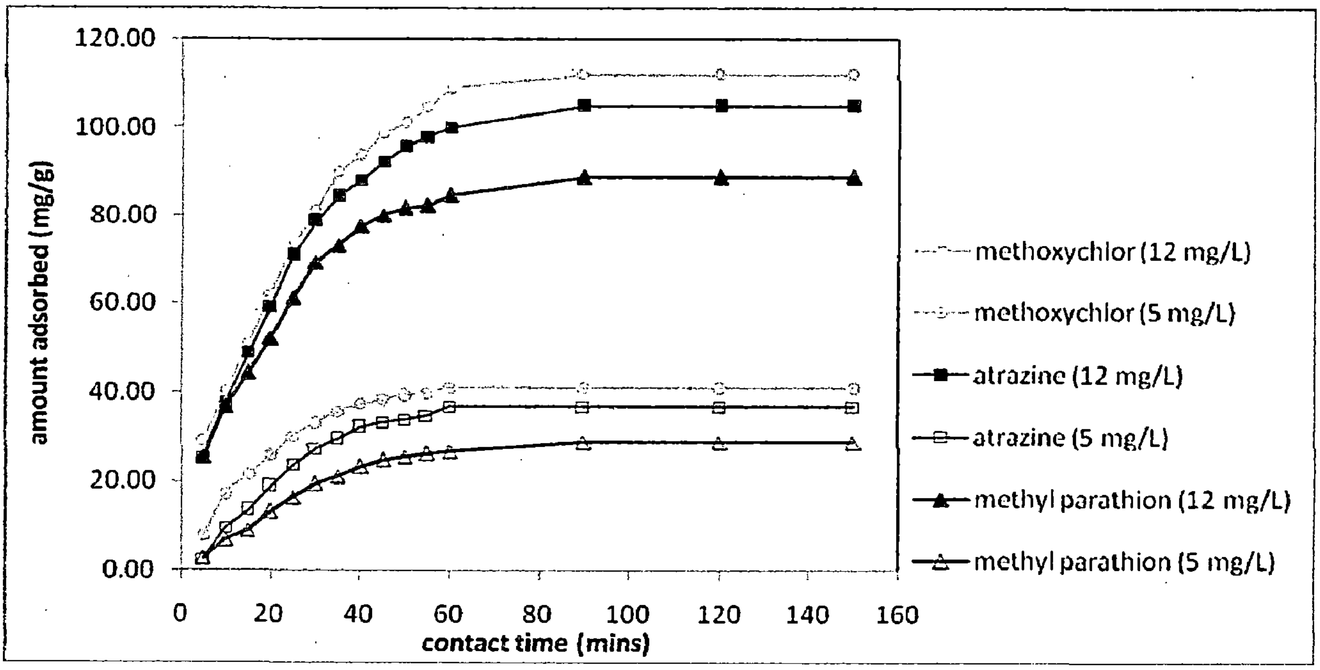


Figure 4.4:
Effect of contact time on the uptake of pesticides at two different initial concentrations (temperature: 25°C, particle size: 200- 250μm, pH: 2).

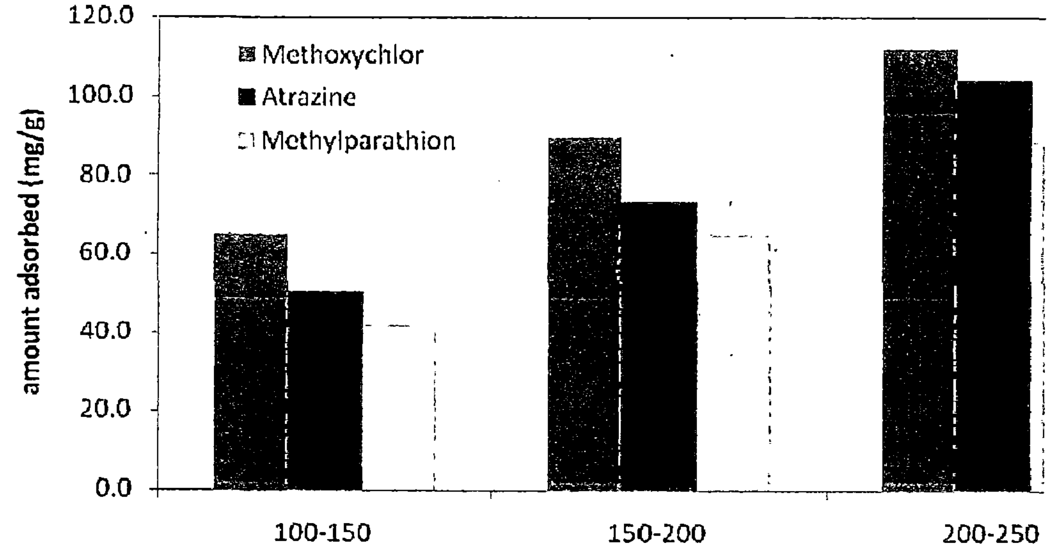


Figure 4.5:
Effect of particle size on the adsorption of pesticides onto CTRTAC (pesticide concentration: 12 mg/L, temperature: 25°C, Particle size: 200- 250μm, pH: 2).

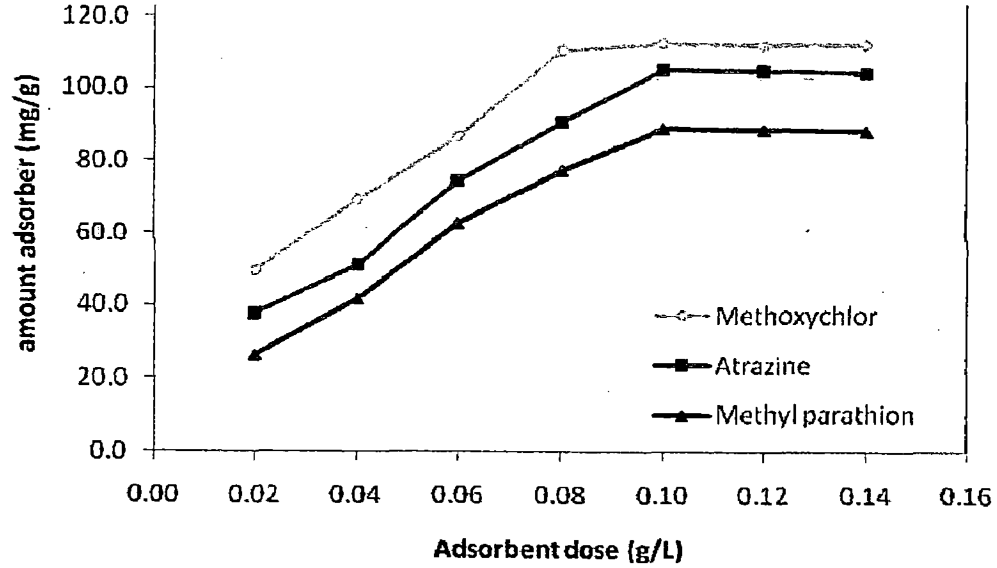


Figure 4.6:
Effect of adsorbent dosage on the adsorption of pesticides onto RTAC (pesticide concentration: 12 mg/L, temperature: 25°C, Particle size: 200- 250μm, pH: 2).

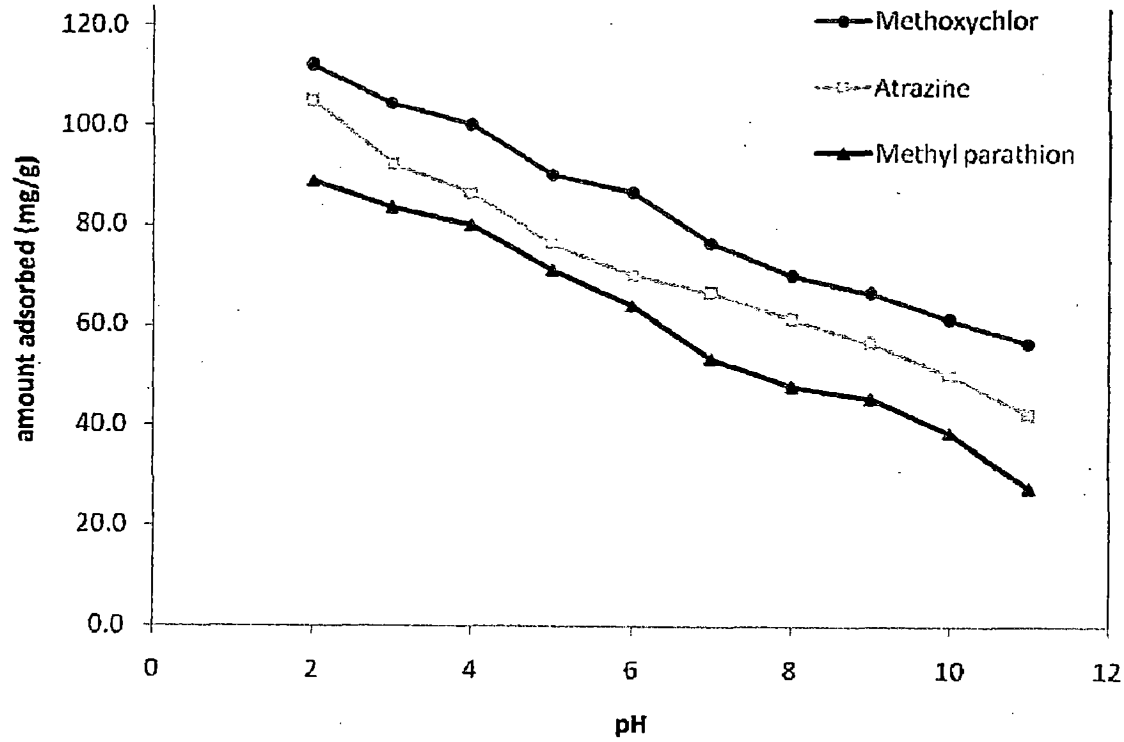


Figure 4.7:
Effect of solution pH on the uptake of pesticides (temperature: 25°C, particle size: 200-250μm, initial concentration: 12mg/L; pH: 2)

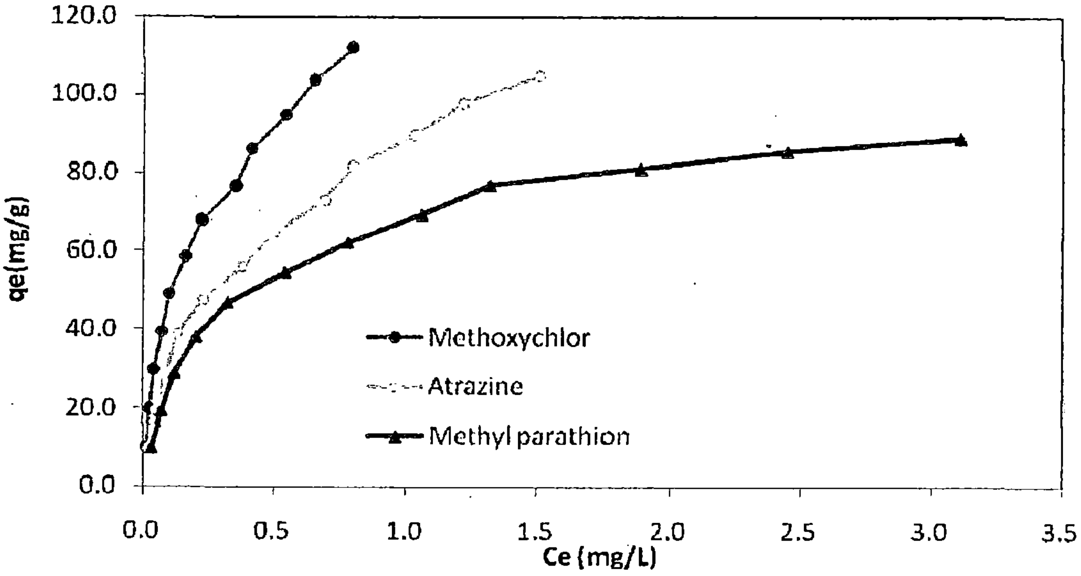
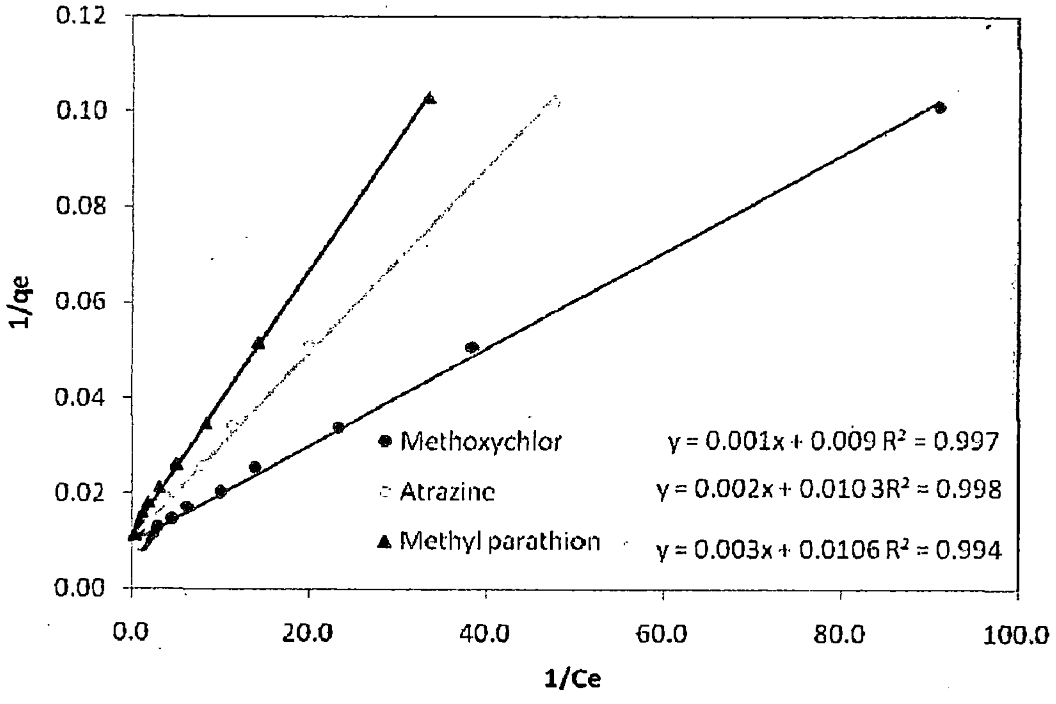


Figure 4.8:
Adsorption isotherm of pesticides on CTRTAC at 25°C



. Figure 4.9:
Langmuir adsorption isotherm of methoxychlor on CTRTAC at different temperatures

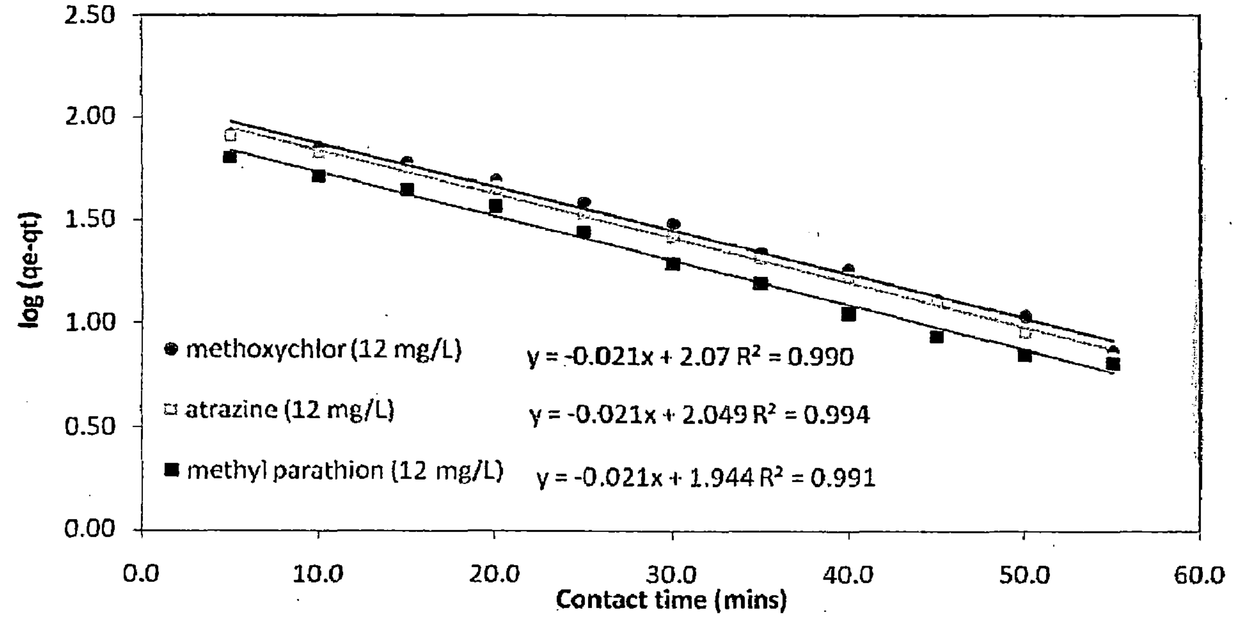


Figure 4.10:
Lagergren's Pseudo 1st order plot of pesticides on CTRTAC at 12mg/L initial concentration

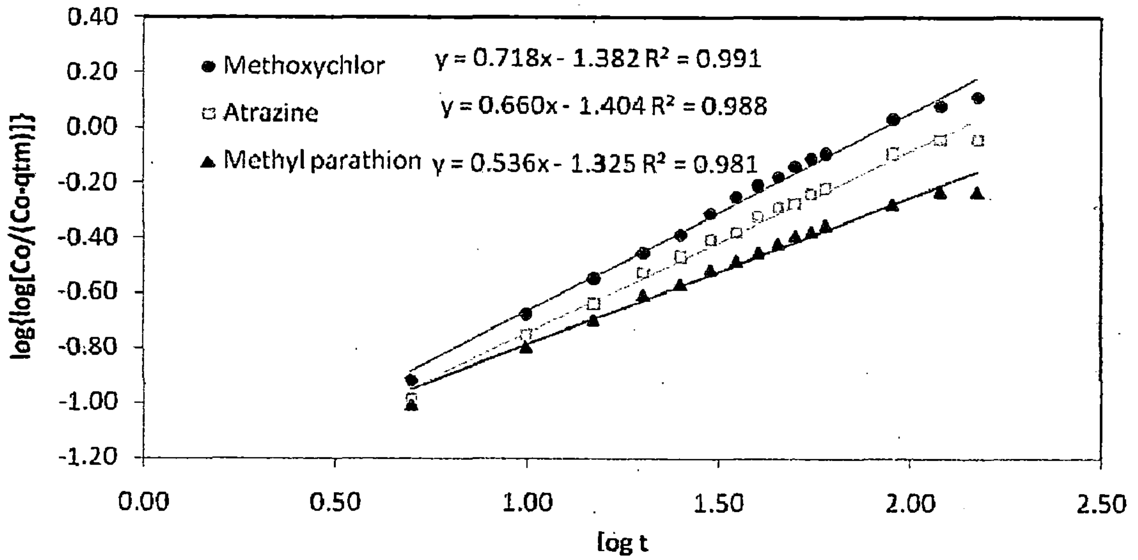


Figure 4.11:
Bangham plot of pesticides on CTRTAC at 12 mg/L initial concentration.

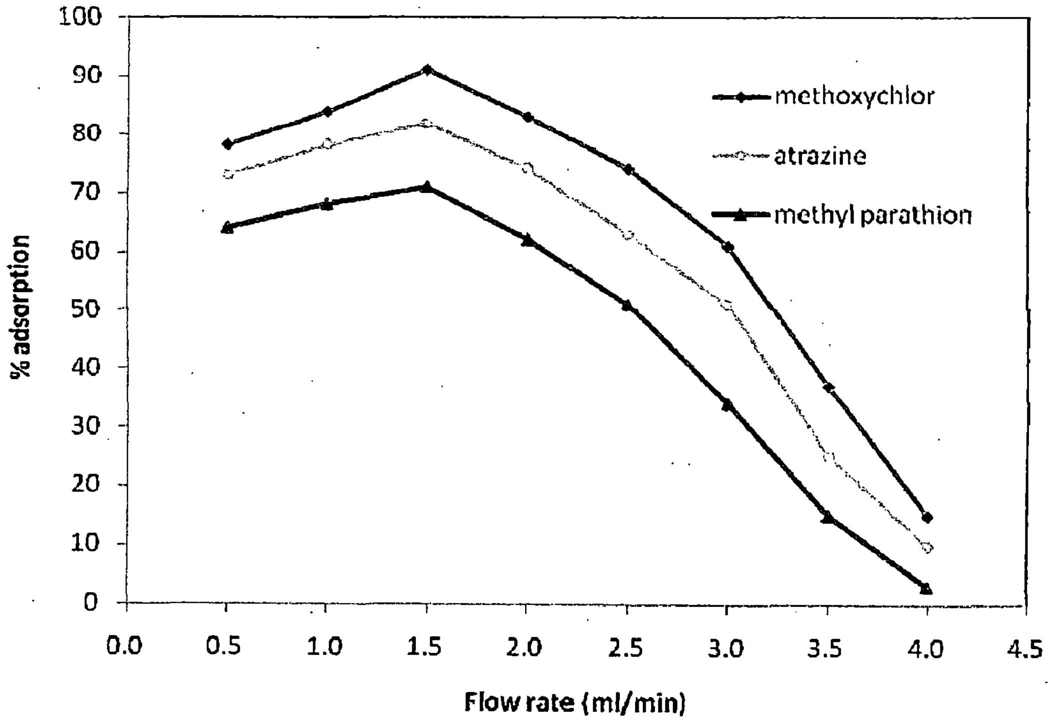


Figure 4.12:
Effect of flow rate on removal of pesticides on CTRTAC

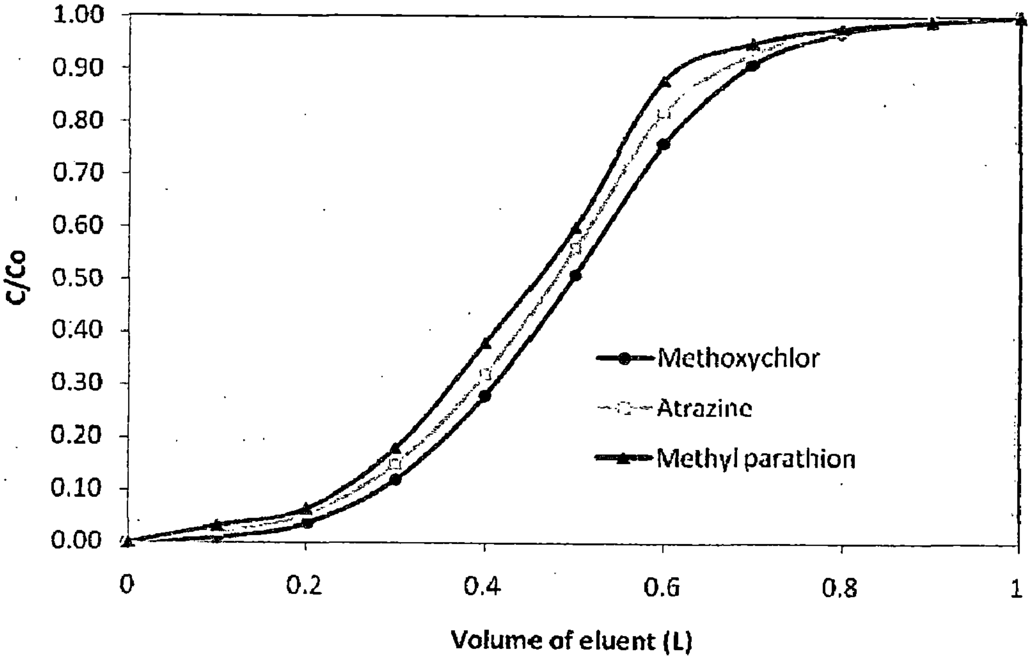


Figure 4.13:
Breakthrough curves of pesticides on CTRTAC

Table-4.1:

Table-4.1:

Elemental analysis of treated and untreated waste rubber tire

Elements	Before treatment	After treatment
C (%)	22.21	78.43
H (%)	2.39	1.05
N (%)	0.65	0.76
S (%)	1.65	0.06
O (%)	6.98	12.04

Table-4.2:

Surface textural data of CTRTAC adsorbent

		Before treatment	After treatment
BET surface area	(m²/g)	22	981
Porosity	(%)	2.39	89.34
Total pore volume	(cc/g)	0.32	1.51
Micro-Pore volume	(cc/g)	0.32	0.65 (43.04%)
Meso-Pore volume	(cc/g)	--	0.86 (56.96%)
Average pore diameter	(nm)	1.17	3.12

Table-4.3:

FTIR Spectra of CTRTAC before and after treatment

CTRTAC	O-H	C=O(stretch)	C-O (stretch)	C-H (stretch)	C=C(aromatic)
before treatment	3428.74	1736.21(ester)	1103.26(ester)	-	1591.01
after treatment	3413.03	1624.23(carbonyl)	-	2929.95	1382.96

Table 4.4:

Effect of adsorbent dosage on the uptake of pesticides onto CTRTAC

(temperature: 25°C, initial concentration: 12mg/L; pH: 2)

Adsorbent dose (g/L)	CTRTAC/Methoxychlor	CTRTAC/Atrazine	CTRTAC/Methylparathion
	qe (mg/g)	qe (mg/g)	qe (mg/g)
0.02	49.60	37.90	26.40
0.04	68.90	51.20	41.80
0.06	86.60	74.40	62.70
0.08	100.20	90.70	77.40
0.10	112.00	104.90	88.90
0.12	111.80	104.60	88.40
0.14	111.90	104.00	88.00

Table 4.5

Adsorption Isotherm model parameters for the pesticides at different temperatures

Pesticides	Log K_{ow}	Temp (°C)	Langmuir isotherm			Freundlich isotherm		
			Q^0 (mg/g)	b	R^2	K_f	n	R^2
Methoxychlor	4.68-5.08	25	111.11	9.10	0.997	140.28	1.88	0.972
		35	97.09	5.15	0.998	130.02	1.62	0.971
		45	94.34	2.65	0.994	99.08	1.36	0.988
Atrazine	2.34	25	100.00	5.00	0.996	92.05	1.92	0.978
		35	95.24	2.63	0.995	75.16	1.54	0.981
		45	83.33	2.00	0.996	44.57	1.59	0.953
Methyl parathion	1.83-3.43	25	90.91	3.67	0.998	65.01	2.24	0.946
		35	66.67	1.50	0.995	57.28	2.16	0.957
		45	50.00	1.00	0.996	47.86	1.98	0.978

Table 4.6:

Thermodynamic Parameters for pesticide adsorption

Pesticide	ΔG°(kJ/mole)			ΔH°(kJ/mole)	ΔS°(J/ K. mole)	R^2
	298K	308K	318K			
Methoxychlor	-34.27	-27.59	-20.92	-233.15	-667.37	0.989
Atrazine	-17.15	-13.09	-9.02	-138.27	-406.44	0.999
Methyl parathion	-6.93	-3.83	-0.74	-99.022	-309.05	0.989

Table 4.7:

Kinetic Parameters for pesticides on CTRTAC

Adsorbate	qe (mg/g)	C_0	**Pseudo First Order**			**Pseudo Second Ord**		
	(exp)	(mg/L)	qe(mg/g) (theo)	k_1 (min^{-1})	R^2	qe (mg/g) (theo)	k_2 $(gmg^{-1}min^{-1})$	
Methoxychlor	112.0	12	117.5	0.0484	0.99	125.0	0.0003	
	41.1	5	40.93	0.0815	0.991	55.56	0.0012	
Atrazine	104.9	12	111.9	.0609	0.994	111.1	0.0008	
	36.8	5	35.48	0.0932	0.993	45.45	0.0007	
Methyl parathion	88.9	12	87.9	.0605	0.991	45.45	0.0033	
	28.8	5	27.8.	0.930	0.993	40.00	0.0007	

Table 4.8:

Comparison of batch and column capacities and degree of column utilization

Pesticide	Initial concentration mg/L	Batch capacity mg/g	Column capacity: Breakthrough capacity mg/g	Column capacity: Exhaustion capacity mg/g	Column capacity: Degree of column utilization (%)
Methoxychlor	12	112.00	95.54	104.87	91.1
Atrazine	12	104.90	81.62	99.41	82.1
Methyl parathion	12	88.90	59.13	82.38	71.78

Table 4.9:

Comparison of CTRTAC with other low cost adsorbents, used in literature for pesticides removal

Adsorbent	**Pesticide**	**Adsorption Capacity**	**Ref.**
Used tires	Paraquat dichloride	27.8mg/g	41
Oil shale ash	Delta methrin, Lambda-cyhalothrin	8.60mg/g, 11.4mg/g	52
Baggasse Fly ash	DDD,DDE	7.69µg/g, 6.67µg/g	36
Baggasse Fly ash	Lindane, Malathion	2.51mg/g, 2.08mg/g	37
Olive stone	Aldrin, Dieldrin, Endrin	9.75mg/g, 5.27mg/g, 3.31mg/g	53
Carbon Slurry	Endosulfan, methoxychlor	34.11mg/g, 36.06mg/g	39
Coal Fly ash	Metribuzin, Metachlor, atrazine	0.20mg/g, 0.28mg/g, 0.38mg/g	54
CTRTAC	Methoxychlor	112mg/g	this study
CTRTAC	Atrazine	104.9mg/g	this study
CTRTAC	Methyl parathion	88.90mg/g	this study

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Chapter 5

RUBBER TIRE ACTIVATED CARBON FOR THE REMOVAL OF METAL IONS

5.1. INTRODUCTION

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. The Agency for Toxic Substances and Disease Registry, Atlanta, Georgia [1] in co-operation with the U.S. Environment Protection Agency has compiled a list of highly hazardous heavy metals of which arsenic, lead, mercury, cadmium, chromium, nickel and copper are the most likely encountered in our daily environment. Various industrial processes are responsible for the release of these metals into the environment through their wastewaters [2, 3]. As a result of industrial activities and technological development, heavy metals released into the environment have been continuously on the increase, posing a significant threat to environment and public health because of their toxicity, accumulation in the food chain and persistence in nature [4, 5, 6]. These heavy metals easily enter the human body through food, water, air or absorption through skin when they come in contact with humans in agriculture, in manufacturing, pharmaceutical, industrial or residential settings. At high exposure levels, heavy metals result in damaged or reduced mental and central nervous function, lower energy levels and damage to blood compositions, lungs, kidneys, liver and other vital organs [7]. Long term exposure may result in slowly progressing physical, muscular and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy and multiple sclerosis. Allergies are not uncommon and repeated long term contact with these metals or their compounds can even cause cancer [1]. The importance of controlling the concentration of toxic metal ions in waters for human use became apparent after the Four Big Pollution Diseases of Japan, a group of manmade diseases all caused by environmental pollution due to improper handling of industrial wastes by Japanese corporations [8]. Two of the Four Big Pollution Diseases of Japan, Minamata (1932-1968) and Niigata disease (1965), were due to mercury poisoning. The third among these is the

"Itai-Itai" disease due to cadmium contamination in Jintsu river of Japan [9, 10]. The Chisso-Minamata disease, as is referred to, is a neurological disease whose symptoms include ataxia, numbness in the hands and feet, general muscle weakness, narrowing of the field of vision and damage to hearing and speech [11, 12]. All these severe injuries made the public opinion ecologically sensitive and extremely aware of environmental problems.

Widespread concern over the toxicity and the environmental impact of the toxic heavy metals has led to extensive research into developing effective technologies for the removal of these potentially damaging substances from effluents and industrial wastewater. The last decade has seen adsorption technology evolving as an efficient and universal method of water treatment as per the guidelines of WHO and EPA [13]. Its wider applicability and greater momentum is due to its cost effectiveness and environmental-friendliness. The cost effectiveness of this technology is due to the use of effective adsorbents from solid industrial [14-17] and agricultural/municipal wastes [18]. Conversion of such negative–valued solid waste to value-added products finding use in environmental applications has further boosted its demand. Research is ongoing in the search of more efficient adsorbent development from solid waste products.

Discarded tires are an interesting and inexpensive medium for the adsorption of toxic pollutants from aqueous solutions. As the biggest share amongst waste polymers in world, waste rubber tire does not decompose easily owing to its crosslinked structure and presence of stabilizers and other additives and hence, traditionally they are being disposed by incineration or landfilling [19]. However, this poses two problems: wasting of valuable rubber and environmental pollution. As a means of reuse, conversion of waste tires to activated carbon for potential use in waste water treatment for adsorption of toxic pollutants is rapidly becoming an important social subject. This not only provides a way for waste disposal and solid waste management but also their reuse lowers the cost for adsorbent production. Approximately 32% by weight of the waste tire is mainly constituted of carbon black in which the carbon content is as high as 70-75 wt. %. [20]. This carbonaceous adsorbent is rather similar to activated carbon and the only apparent physical difference is that carbon black has much less internal surface area [21]. Carbon black obtained by untreated rubber tire pyrolysis may be heated in air, carbon dioxide or steam atmosphere to develop its surface area and porosity [22, 23] and hence to improve its adsorption behavior. Based on the literature review, it is possible to conclude that there has been little research on nickel adsorption onto tire rubber, and this line of research has provided limited insight into the factors affecting the nickel removal capacity of rubber tire activated carbon. Also, many such single metal studies have limited value because industrial effluents contain several metal ions simultaneously.

In the present chapter, hence, attempts have been made to use waste rubber tire as adsorbent for the removal of two model toxic metal ions lead and nickel from aqueous solution. In addition, the study has been extended to a commercial activated carbon with the purpose of undergoing a comparative study.

The model pollutants selected are a potential threat to the environment because of their toxicity, persistent and bioaccumulation in the food chain [24]. Their toxicity leading to adverse health effect even when present in trace amounts are a source of environmental concern. WHO [25] has identified such metal ions to cause widespread health effects in humans as a consequence of exposure through drinking-water when present in excess.

The objectives of this study are: (1) synthesis of rubber tire activated carbon (RTAC) by physical activation and their characterization with respect to FE-SEM, XRD, pH_{PZC} and FTIR (2) comparative batch adsorption study of RTAC and CAC for Pb^{2+} and Ni^{2+} wrt various environmental parameters (3) isotherm, kinetic and thermodynamic study (4) optimization of column adsorption parameters, (5) desorption and reusability study to investigate the practical utility of the developed adsorbent and (5) to assess the performance of the RTAC in removing different metal ions from actual electroplating industrial effluents.

5.2. RESULTS AND DISCUSSION

5.2.1. Characterization of RTAC

The RTAC was found to be stable in water, dilute acids, dilute bases, salt solutions and organic solvents at temperature of 25-45°C and in the pH range of 1-11. A summary of the textural characteristics of the rubber tire activated carbons and of the CAC is outlined in Table-5.1 which reveals that the volume of mesopores in RTAC is 0.69cc/g and the micropore volume in CAC is 0.48cc/g. The carbon is present to the extent of 78.76% indicating the carbonaceous nature of the adsorbent. The thermal treatment has resulted in the development of high surface area (562 m^2/g) and mesoporous RTAC (71% volume).

SEM micrographs of CAC and RTAC present the morphological characteristics favorable for metal adsorption. Figure 5.1a shows a heterogenous, porous surface morphology of CAC having a mean particle diameter of 20 μm. Figure 5.1b shows morphology of a RTAC particle with much bigger pores. Adsorption of metal ions onto RTAC shows a changed morphology as evident from Figure 5.1c. EDAX confirms the carbonaceous nature of the activated carbons which is responsible for imparting porosity to the carbons as observed in the SEM results. The EDAX of Figure 5.1c further establishes the adsorption of lead and nickel on the RTAC surface.

The IR spectrum of the RTAC sample (Figure 5.2a) indicates the presence of a prominent band at 3428.74 cm^{-1}, 1736.21 cm^{-1}, 1591 cm^{-1} and 1103.28 cm^{-1} which can be inferred to the presence of a OH group of phenols and C=O group of esters; Similar peaks at 3379.04 cm^{-1}, 1703.52 cm^{-1}, 1594.69 cm^{-1} and 1259.56 cm^{-1} on CAC (Figure 5.2b) indicate the presence of similar functional groups thereby corroborating the similarity of pH_{PZC} values of both adsorbents.

5.2.2. Comparison of batch adsorption efficiency

Figure 5.3 reveals the following observations:

a. The adsorbents show the following order of efficiency: RTAC > CAC although the surface areas show a reverse trend as evident from Table-5.1. Since the pH_{PZC} of both adsorbents are nearly similar, obviously surface porosity plays an important role in determining the adsorption capacity.
b. Also, the RTAC and CAC show a similar trend for the adsorption of the studied metal ions: $Pb^{2+} > Ni^{2+}$

Micropores are the major adsorption sites, and adsorption on activated carbon usually proceeds through diffusion of adsorbates from the bulk liquid phase through the mesopores and then into the micropores [26]. While diffusing into the micropores, pore blockage may occur due to aggregation of adsorbate molecules or in some cases, the micropore cross sectional area may be too small for the adsorbate to penetrate [27]. So in the absence of mesopores as in the case of CAC, the adsorbates take a longer time to diffuse into the micropores causing greater pore blockage and resulting in lesser adsorption capacity [28]. In RTAC, the mesopores help in accelerating the diffusion of the adsorbates into the micropores and the probability of pore blockage gets reduced thereby increasing the adsorption capacity.

A glance at the possible interactions between the adsorbent-adsorbate will help in understanding the adsorptive trend as observed for the RTAC and CAC. Since the adsorption experiments of this work were performed at pH 7.5 well above the pH_{PZC} of RTAC and CAC (see Table 5.1) the surface charge of the adsorbents was predominantly negative. Now, taking into account the metal ion speciation, lead is known to exist in $PbOH^+$ form at pH 6-9 and nickel exits in Ni^{2+} form in aqueous solution, it is expected that at this pH, electrostatic adsorbate/adsorbent interactions are dominant in the adsorption processes [29]. Also, as evident from the FTIR studies, since similar functional groups are present on RTAC and CAC, similar metal-adsorbent interactions are evident.

Higher uptake for Pb^{2+} than Ni^{2+} is attributed to the larger ionic radii (0.133nm) and higher electronegativity (2.33 Pauling) of Pb^{2+} in comparison to that of Ni^{2+} (ionic radii=0.069nm, electronegativity=1.91 Pauling) [30, 31] (Table-5.1). The smaller the ionic radius, the greater is the tendency to be hydrolyzed resulting in lesser tendency for adsorption [32]. Higher electronegativity of Pb^{2+} will allow it to be more strongly attracted to the adsorbent surface. Also, Pb^{2+} and Ni^{2+} ions are well hydrated in aqueous solutions; their hydration sheath has to be denuded before their sorption onto RTAC. Thus, metal cations having lower hydration energy as for example Pb^{2+} are easily adsorbed onto RTAC in comparison to Ni^{2+} which has a higher hydration energy [30].

Summarily, the mesoporous properties of RTAC are responsible for enhanced metal sorption as compared to that of CAC.

5.2.3. Preliminary Adsorption Studies

5.2.3.1. Effect of pH

Solution pH is related to the adsorption mechanism and reflects the various adsorbent-adsorbate physico-chemical interactions [33, 34].

The uptake of Pb^{2+} and Ni^{2+} increased significantly with increasing pH from 1 to 8 (Figure 5.4). (Higher pH values were not studied because of the possibility for precipitation to occur). At pH values greater than 7, the metal uptake increased with increasing solution pH values. From pH 7 to pH 2, the amount of metal adsorption onto RTAC displayed the trend of decrease with decreasing solution pH values. These observations are in agreement with the expectations from pH_{PZC} studies of the adsorbents. Hence, from an electrostatic interaction point of view, the adsorption of lead and nickel on RTAC can be enhanced at pH > 7, due to the negative surface charge of RTAC attracting the positively charged lead hydroxides ($PbOH^+$) and nickel ions (Ni^{2+}) and on the other hand, lead transport and attachment to RTAC may be affected at pH < 7, due to the positive surface charge possessed by both RTAC and metal ion species (Pb^{2+} and Ni^{2+}).

5.2.3.2. Effect of contact time and initial concentration

The adsorption of Pb^{2+} and Ni^{2+} onto RTAC as a function of contact time and the simultaneous effect of initial metal ion concentration is depicted in Figure 5.5. Irrespective of the initial metal concentration, the adsorption efficiency increased in the first 120 mins of contact time after which the capacity leveled off and thus the optimum contact time selected was 120 mins. Obviously, the adsorption capacity showed an increase with increasing metal ion concentration, a probable reason being that concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases [35].

5.2.4. Adsorption Isotherm Modelling

Isotherm data were applied to the Langmuir and Freundlich adsorption models and the results of their linear regression as listed in Table-5.2 were used to find out the fit model among them. The parameters and correlation coefficients obtained from the plots of Langmuir ($1/q_e$ vs $1/C_e$), Freundlich (log q_e versus log C_e) and D-R [log q_e vs log(1+1/Ce)] are listed in Table 5.2.

Figure 5.6 as well as Table-5.2 show that the regression coefficients at three different temperatures for Pb^{2+} and Ni^{2+} are higher than 0.99, indicating the applicability of the Langmuir model with the metal ions getting adsorbed onto the adsorbent surface to form a monolayer. The value of Q_o for Pb^{2+} and Ni^{2+} was 312.50 and 131.58 mg/g at 298K and at pH 7.5. The values b (Table-5.2) is seen to be higher for Pb^{2+} as compared to Ni^{2+} indicating higher affinity of RTAC for Pb^{2+}. This can be attributed to the higher ionic radii and higher electronegativity exhibited by Pb^{2+} as explained earlier.

The D–R model constant (B_D) however, gives an idea about the mean free energy of adsorption (E_D) which in turn gives information about the nature of the adsorption process. E_D was found to be < 8 kJ mol^{-1} at all temperatures (Table 5.2) implying that adsorption of the studied metal ions onto RTAC is a physisorption process.

5.2.5. Thermodynamic study and the Effect of temperature

Table 5.2 amply demonstrates the sensitivity of the adsorption process towards temperature and it is observed that in all cases, adsorption increases with increase in temperature [36]. The values of these parameters, summarized in Table 5.2 indicate the sensitivity of the adsorption process towards temperature. A positive $\Delta H°$ suggests endothermicity; a possible explanation is that the metal ions are well hydrated and will require breaking of the hydration sheath so as to proceed for adsorption; this inturn requires high energy. High temperature hence favours the dehydration process and ultimately the adsorption phenomenon too [37].

The negative $\Delta G°$ values indicate that the developed RTAC-metal ion system to be thermodynamically feasible and spontaneous. The positive values of $\Delta S°$ reflect the affinity of RTAC towards Pb^{2+} and Ni^{2+} in aqueous solutions and may suggest the degree of freedom increases at the solid–liquid interface during the sorption of metal ions onto RTAC.

5.2.6. Kinetic Study

The Lagergren's pseudo-first-order and pseudo-second-order models were used to test adsorption data in order to investigate the kinetics of adsorption. Table 5.3 lists the results of the kinetic parameters of the two models as well as their regression coefficients (R^2) at two different concentrations of the Pb^{2+} and Ni^{2+} ions. The value of correlation coefficient R^2 for the pseudo-second-order adsorption model for both metal ions is comparatively high (>0.99), and the adsorption capacities calculated by the model are also close to those determined by experiments. Figure 5.7 indicates the linear plots of t/q_t vs. t for Pb^{2+} and Ni^{2+} showing the applicability of the pseudo-second-order model and thus can be concluded to be more suitable to describe the adsorption kinetics of both metal ions onto RTAC.

5.2.7. Mechanism of the adsorption process.

Prediction of the rate-limiting step is an important factor to be considered in the adsorption process. For solid–liquid adsorption process, the solute transfer process is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. In the present study, intra particle diffusion plots of q_t versus $t^{0.5}$ (Figure 5.8) were plotted for both metal ions. From Figure 5.8, the adsorption process tends to be followed by two phases. It was found that an initial linear portion was followed by a second linear portion and the plots do not pass through the origin. The two phases in the intraparticle diffusion plot suggests that the adsorption process proceeds by surface adsorption and the intraparticle diffusion. The initial curved portion of the plot indicates boundary layer effect while the second linear portion is due to intra-particle or pore diffusion [38].

5.2.8. Column Studies

The breakthrough curves (C/C_o vs Volume) for the effect of flow rate (1.5, 2.5mL/min), influent Ni^{2+} concentrations (100, 200 mg/L), bed depth (5, 10, 15 cm) are depicted in Figures 5.9 a, b, c respectively and the experimentally determined parameters are tabulated in Table-5.4.

Figure 5.9a reveals that the breakthrough and saturation time (and volume) decreased with increasing influent flow rate for both the test metals resulting in a lesser adsorption column capacity. It is generally considered that metal sorption capacity of column packed adsorbent is actually less when the flow rate is high, because at a high flow rate, the residence period of metal ions in the column is very short which cannot lead to the equilibrium of sorption process and metal ions run away from the column before achievement of the equilibrium [39].

For the effect of influent metal concentration, Figure 5.9b reveals that the breakthrough and saturation were attained early at a high influent metal ion concentration. At higher metal concentration, sorption of metal ions by the RTAC is faster than that at a lower concentration, thus resulting in quick attainment of breakthrough and saturation [40]. Also, the metal sorption capacity at breakthrough and at saturation was greater at higher influent metal concentration because higher concentrations provided better driving force to metal sorption process during continuous column run.

Figure 5.9c shows the breakthrough or saturation time increased with increase in bed height. Similarly, volume treated till breakthrough and saturation increased with increasing bed height. The column having greater bed height contains a larger amount of RTAC and thus provides a greater number of sites for the binding of metal ions, which resulted in a longer time for reaching breakthrough and saturation. Consequently, a larger volume of metal solution could be treated using higher bed height. However, columns with short bed height saturated quickly due to lesser availability of sorbent and hence the metal binding sites [41].

Thus under optimized conditions of lower flow rate of 1.5mL/min, increased metal ion concentration of 200mg/L and higher bed depth of 15cm, the column RTAC capacity for Ni^{2+} ions was found to be of 138.29 mg/g with a 98.43% metal removal.

5.2.9. Desorption and reusability studies

In order to assess the reusability of the RTAC -packed column, experiments were conducted in five successive cycles of sorption-desorption. The saturated RTAC was regenerated using 0.1 M HNO_3 and was further used as adsorbent for Ni^{2+}. Desorption experiments carried out showed that approx 98 % of the adsorbed Ni^{+2} was desorbed.

Results of the adsorption capacity of RTAC for five consecutive adsorption-desorption cycles are graphically illustrated in Figure 5.10. In all cycles, desorption was 97.27-98.00 %. A 10.96% decrease in adsorption efficiency occurred (Table 5.5) after five consecutive cycles of adsorption-desorption that demonstrates good reusability. This fulfills an important criterion for advanced adsorbents.

5.2.10. Testing under industry effluent simulation condition

Since the ultimate objective of the adsorption technology using RTAC as adsorbent is removal of metal ions from the industrial or real wastewaters that often contain several metal ions simultaneously, column adsorption experiments were conducted with actual industrial waste-waters. Urban wastewater from IIT Roorkee campus was collected and was spiked with nickel chloride, lead nitrate to obtain wastewater which simulated an actual electroplating industry effluent. The metal remediation was carried out in the laboratory column set up filled with RTAC having bed depth of 15cm and flow rate of 1.5mL/min. The results are revealed in Table-5.6. The results show that when the test column was performed at the native pH, metal removal was below satisfactory. However, lowering the pH to 7.5 helped in substantial metal removal from the waste water (87% Ni^{2+} removals and 96% Pb^{2+} removals). This is in accordance to the observation of batch and column studies carried out in the laboratory. Decreased metal removal was observed at further lowering of pH values to 2. This was apparently due to development of positive charge on the RTAC ($pH<pH_{PZC}$), owing to protonation of binding sites, and repulsion of the cationic metal species. The present study shows that the RTAC packed column is capable of removing a variety of heavy metals from real industrial waste water.

5.2.11. Comparison with other reported adsorbents

A comparative assessment of RTAC with various other adsorbents reported in literature reveals the efficacy of the developed adsorbent for the removal of lead and nickel ions as revealed in Table-5.7 [42-46]

5.3. CONCLUSION

This study focused on developing a mesoporous adsorbent in waste rubber tire and to further assess its adsorption efficiency for the removal of toxic lead and nickel ion from synthetic and real waste water. A commercial carbon was simultaneously used as an adsorbent for comparative study. The following conclusions are bulletined:

1. The higher mesoporosity and favourable surface chemistry of a modified rubber tire activated carbon has played a significant role in enhancing the adsorption capacity RTAC for liquid phase adsorption of lead and nickel removal.
2. The ionic properties of the studied metal ions have played an influencing role in determining their uptake trend by both RTAC and CAC.
3. Batch adsorption studies revealed the optimum levels of various environmental parameters for maximizing efficiency. Langmuir and D-R model helped in indicating the underlying mechanism of the adsorption process.
4. Kinetic modelling revealed the applicability of the pseudo-second-order model and intra particle diffusion to be more suitable to describe the adsorbate-adsorbent system.
5. Thermodynamic studies revealed the feasibility and endothermicity of the developed system.

6. Column studies with a metal removal capacity of 98.43% under optimized conditions as well as significant lead and nickel removals from an electroplating effluent simulated wastewater revealed the practical utility of the developed adsorbent.

7. The regeneration of RTAC and its subsequent use as adsorbent without significant loss in efficiency is of crucial importance in the economic development of adsorbate-adsorbent system for waste water treatment.

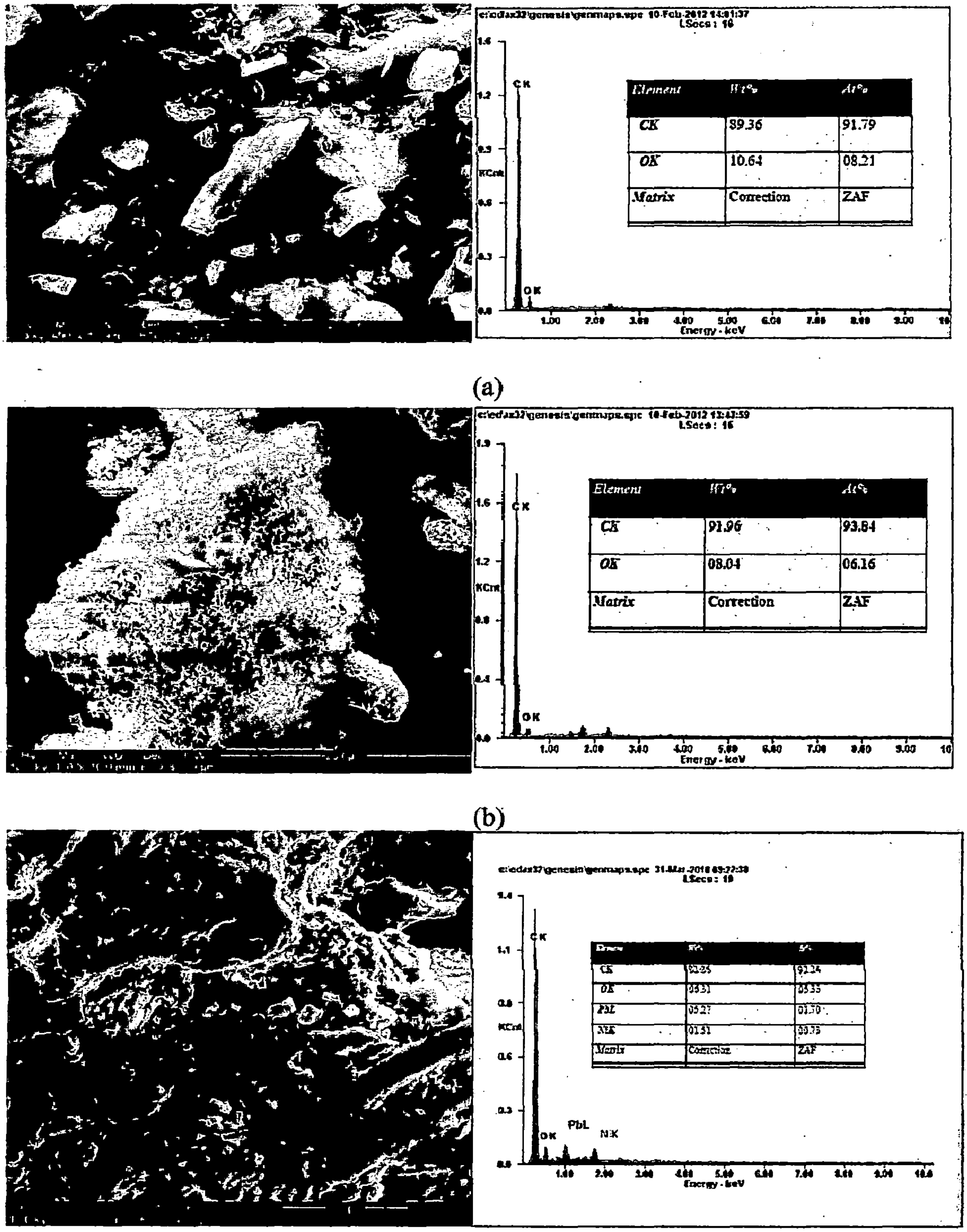


Figure 5.1:
SEM micrograph and EDX of (a) CAC (b) RTAC before adsorption (c) RTAC after adsorption of Pb^{2+} and Ni^{2+}

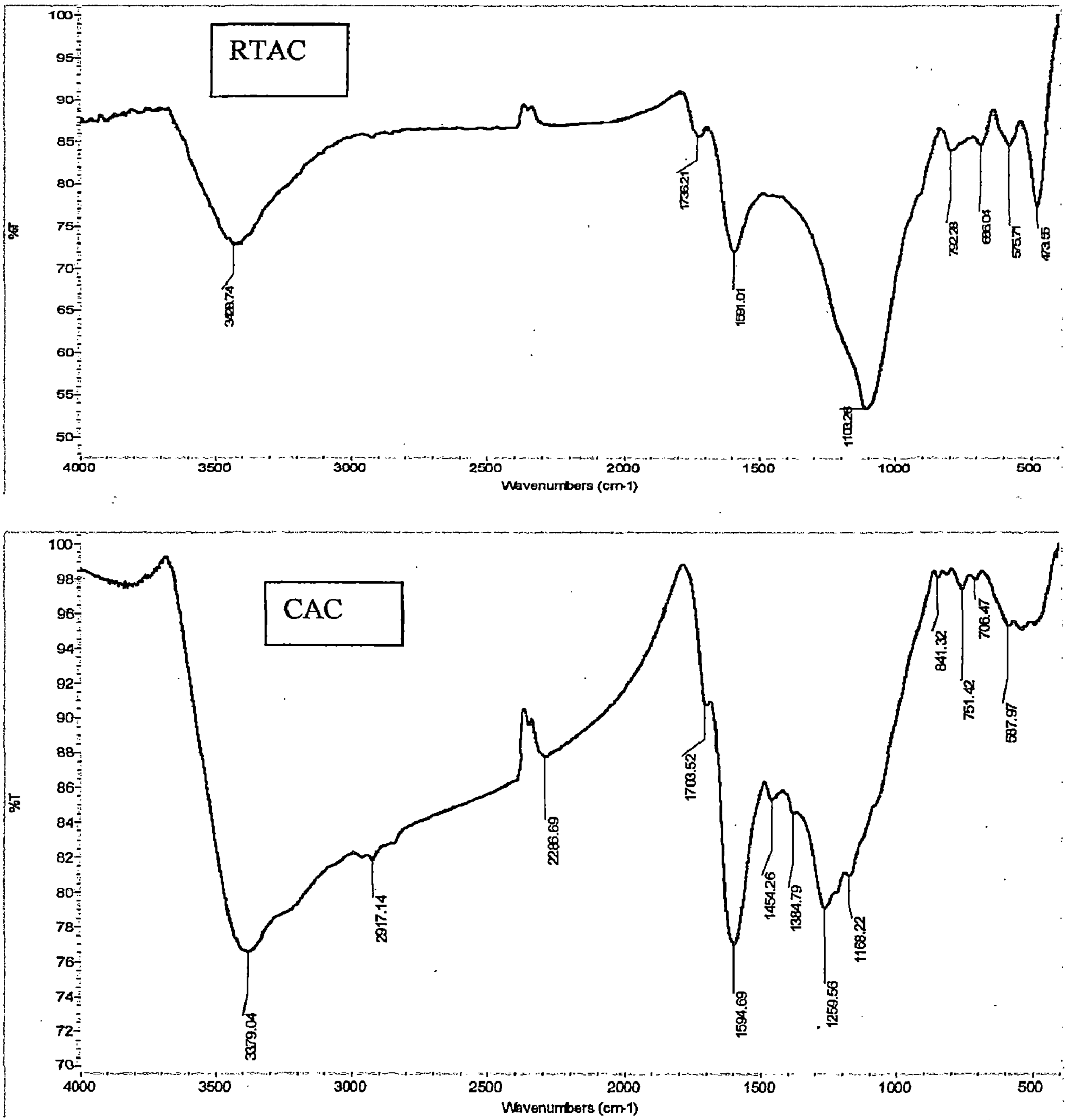


Figure 5.2:

FTIR spectra of (a) RTAC (b) CAC

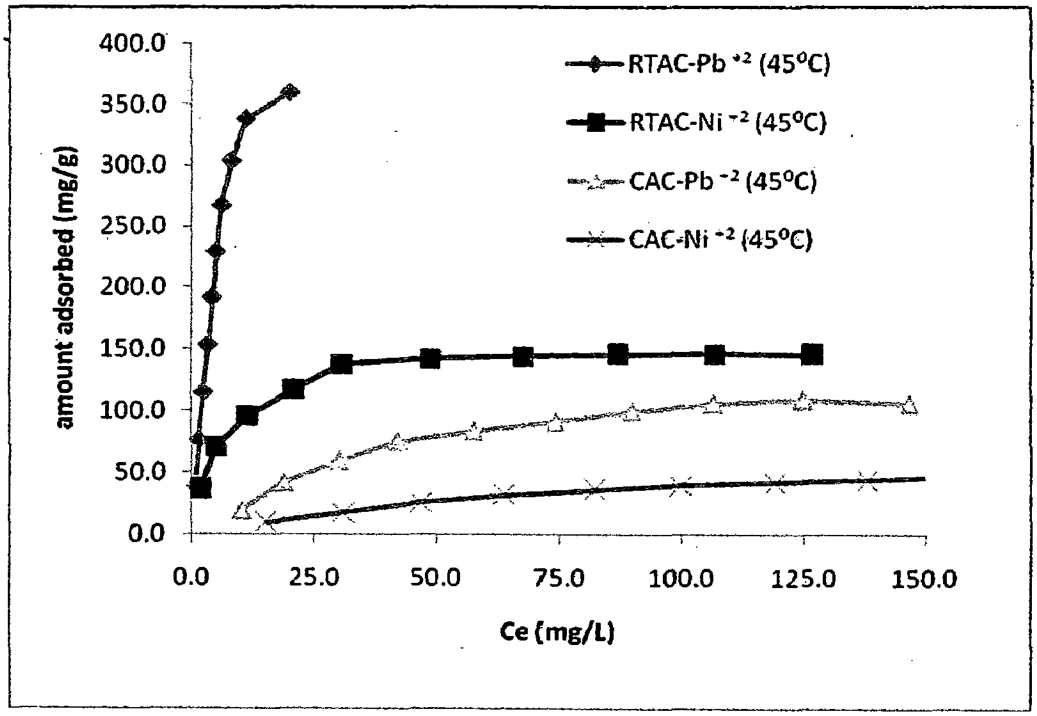


Figure 5.3:
Comparison of adsorption capacity of RTAC and CAC
(pH=7.5, adsorbent dose =50mg, C_0=200mg/L, particle size: 200-250BSS, temp-45°C, contact time- 120 mins)

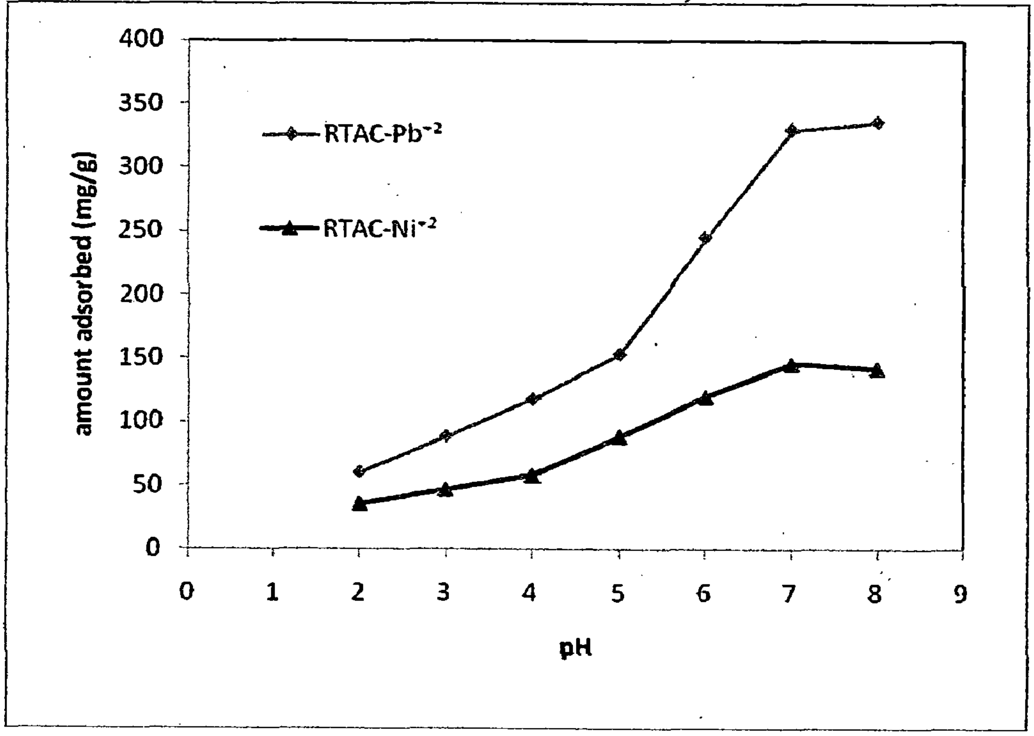
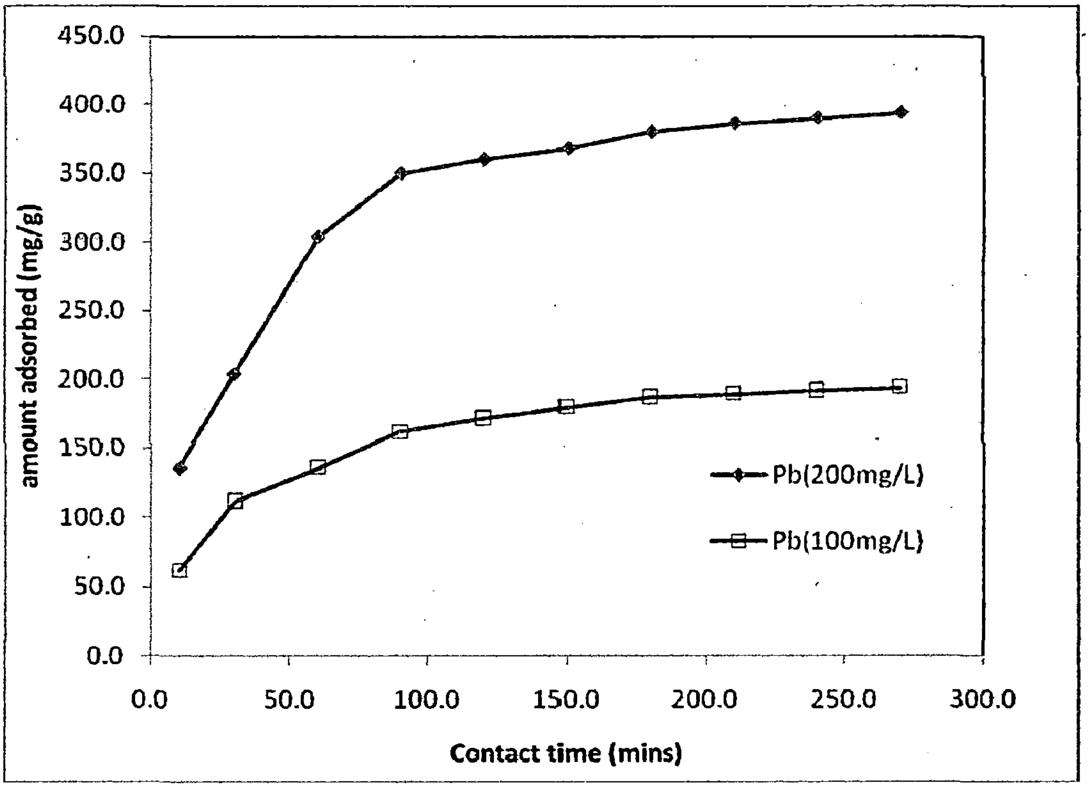
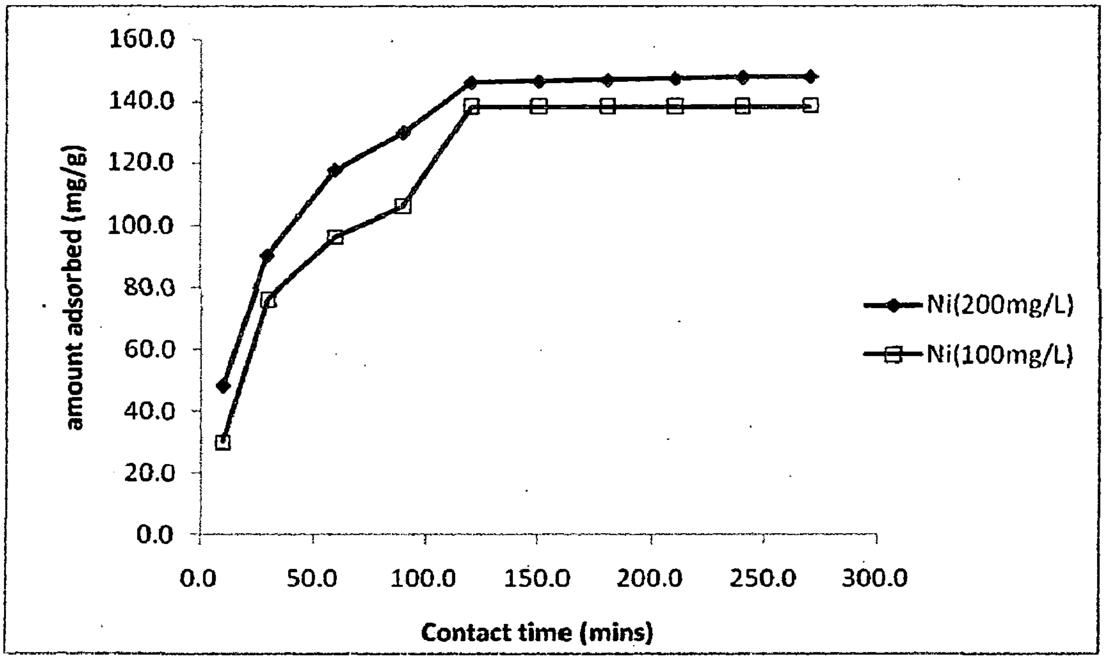


Figure 5.4:
Effect of solution pH on the uptake of metal ions on RTAC
(temperature: 45°C, adsorbent dose =50mg, particle size: 200-250BSS, initial concentration: 200mg/L).



(a)



(b)

Figure 5.5:
Effect of contact time on the uptake of (a) Pb^{2+} and (b) Ni^{2+} metal ions onto RTAC at two different initial concentrations
(temperature: 45°C, particle size: 200- 250BSS, adsorbent dose =50mg, pH: 7.5).

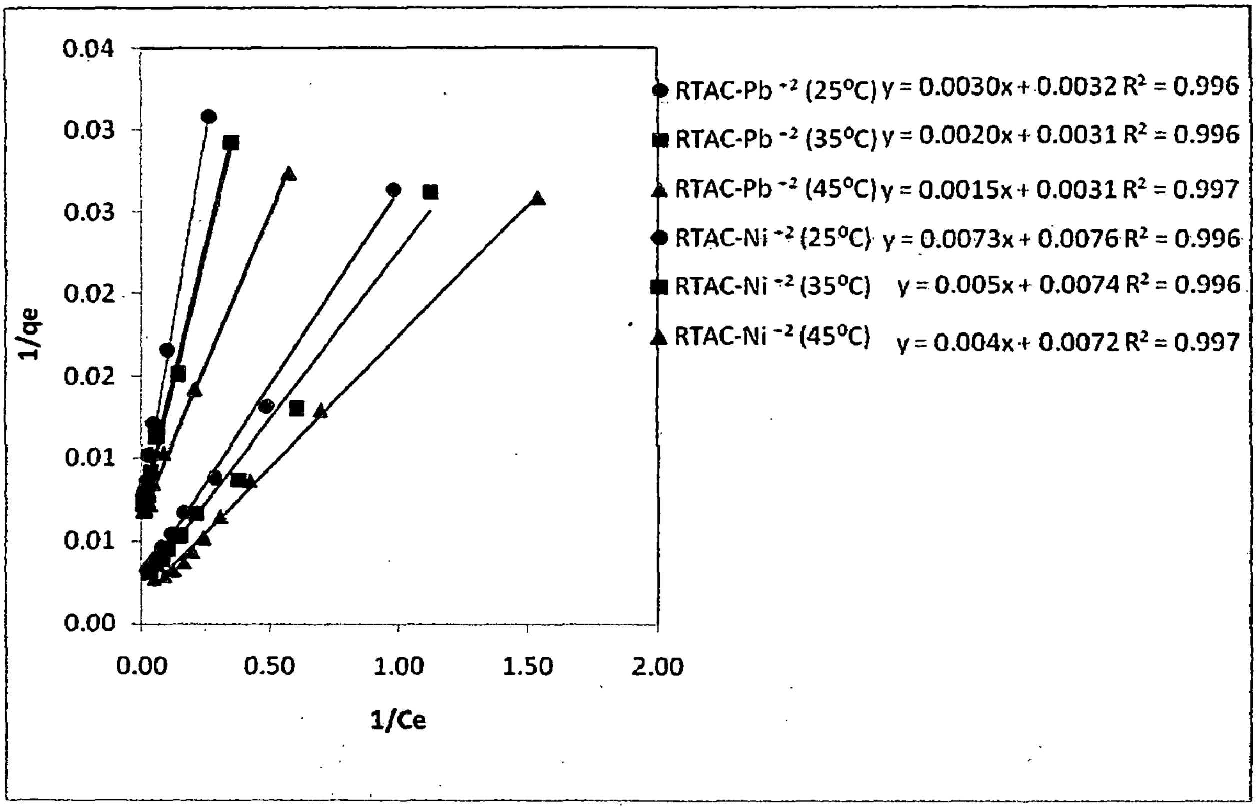


Figure 5.6:
Langmuir adsorption isotherm of metal ions onto RTAC at different temperatures

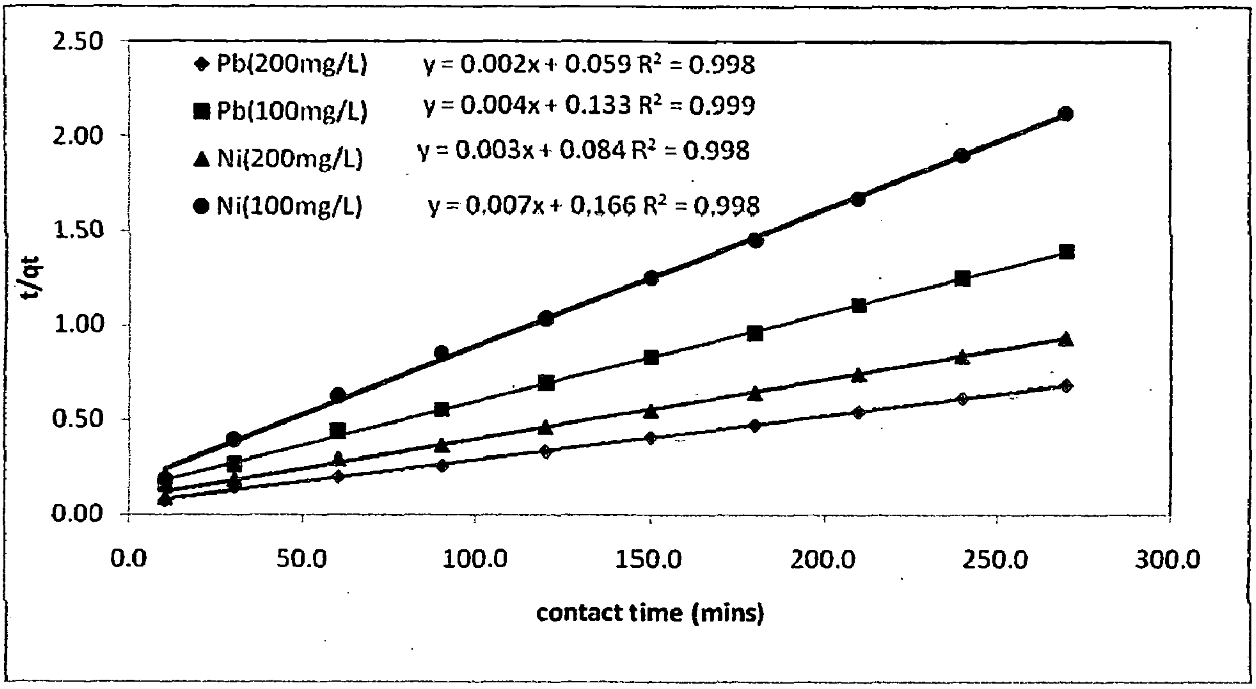


Figure 5.7:
Lagergren's pseudo-second order plot of metal ions-RTAC at C_o=100mg/L and 200mg/L

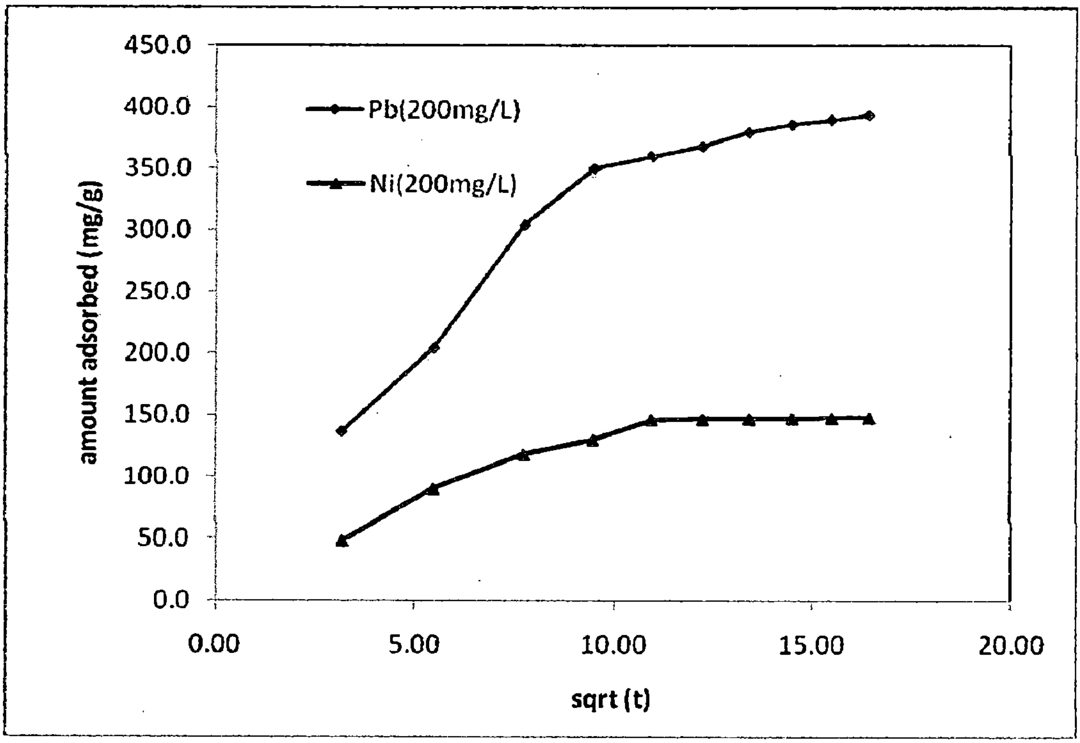


Figure 5.8:
Intraparticle diffusion plot for Pb^{2+} and Ni^{2+} uptakes onto RTAC (Co=200mg/L, temp-45°C, particle size: 200- 250µm, pH: 7.5, adsorbent dose =50mg)

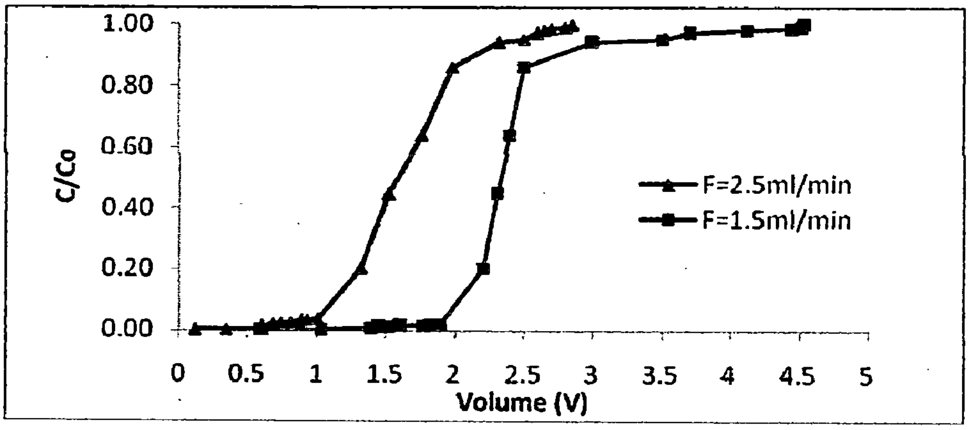


Figure 5.9a:
Effect of flow rate on breakthrough volume in a 15 cm fixed-bed column (C_0 of Ni^{2+}= 200 mg/L)

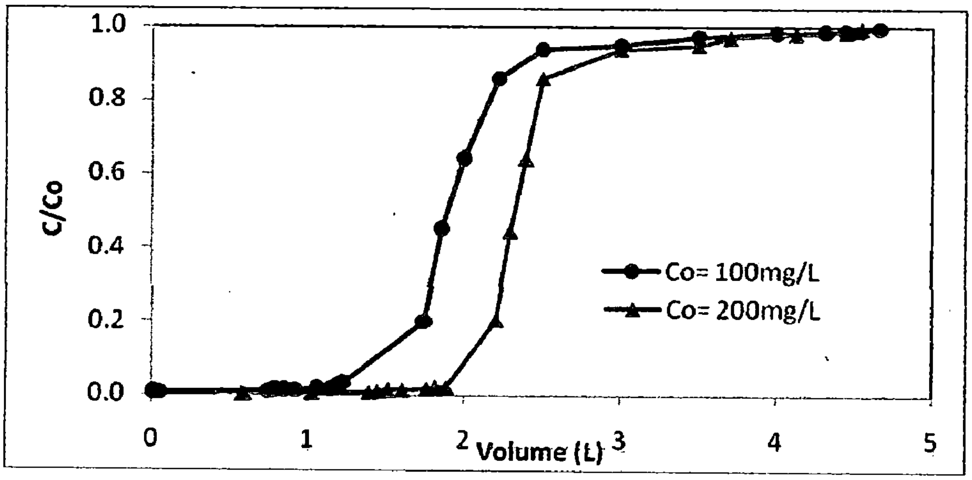


Figure 5.9b:
Effect of inlet Ni^{2+} concentration on breakthrough volume in a 15 cm fixed-bed column (F=1.5mL/min)

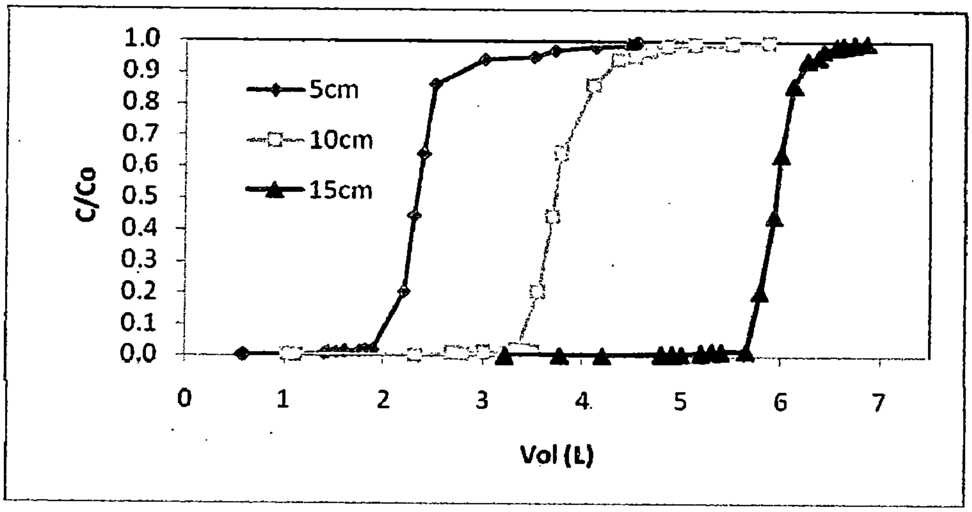


Figure 5.9c:
Effect of bed depth on breakthrough volume at a constant flow rate of 1.5mL/min (C_o of Ni^{2+}= 200mg/L)

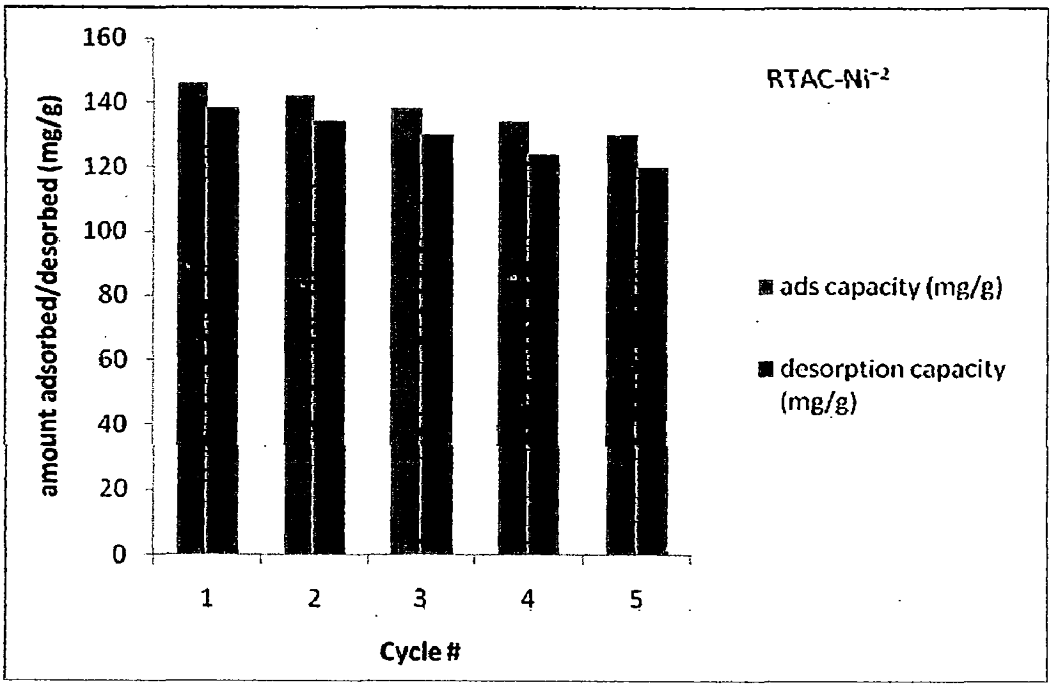


Figure 5.10:
Recycling of RTAC in the removal of Ni^{2+} (C_0= 200mg/L; time 120 mins; temperature 45°C; adsorbent dose 50mg and pH-7.5)

Table-5.1:

Zero point charge and textural properties of the adsorbents and selected properties of the studied metal ions

Adsorbent textural analysis

Adsorbent	pH_{PZC}	S_{BET} (m^2/g)	V_{tot} (cc/g)	V_{micro} (cc/g)	V_{micro} (%)	V_{meso} (cc/g)	V_{meso} (%)
CAC	7.1	1168	0.68	0.48	70.59	0.20	29.41
RTAC	7.0	562	0.97	0.28	28.87	0.69	71.13

Adsorbate analysis

	Pb^{2+}	Ni^{2+}
Molecular weight	207.20	58.69
Electronegativity(Pauling)	2.33	1.91
Ionic Radii (nm)	0.133	0.069
Hydration energy (kJ/mol)	-1,481	-2,067

Table-5.2:
Isotherm model and Thermodynamic parameters for the adsorption of Pb^{2+} and Ni^{2+} onto RTAC

Isotherm parameters	RTAC-Pb^{2+}			RTAC-Ni^{2+}		
	298K	308K	318K	298K	308K	318K
Langmuir isotherm						
Q_o(mg/g)	312.50	322.58	327.87	131.58	135.13	138.89
b(L/mg)	1.07	1.55	2.00	1.04	1.48	1.80
R^2	0.996	0:99	0.997	0.996	0.996	0.997
Thermodynamic Parameters						
ΔG (kJ/mol)	-0.1599	-1.122	-1.876	-0.099	-1.004	-1.554
ΔH (kJ/mol)	25.37			21.50		
ΔS (kJ/mol/K)	0.085			0.072		
Freundlich isotherm						
Kf	49.545	57.544	67.4528	23.9332	30.7610	40.3645
n	1.8315	1.8692	1.9493	2.6247	2.8986	3.3113
R^2	0.952	0.929	0.921	0.928	0.892	0.886
D-R isotherm						
q_D	316.23	331.13	346.74	130.62	139.64	144.88
E_D	4.49	4.53	4.60	4.19	4.27	4.29
R^2	0.966	0.981	0.978	0.959	0.970	0.971

Table-5.3:
Kinetic Parameters for the adsorption of Pb^{2+} and Ni^{2+} onto RTAC

Adsorbate	(exp) qe(mg/g)	Initial conc.(C_o) (mg/L)	**Pseudo First Order**			**Pseudo Second Order**		
			qe(mg/g) (theoretical)	k_1(min^{-1})	R^2	qe(mg/g) (theoretical)	k_2 (g/mg/min)	R^2
Pb^{2+}	393.80	200	284.45	0.018	0.987	400.00	0.0002	0.99
	194.00	100	158.85	0.016	0.988	188.68	0.0001	0.99
Ni^{2+}	288.00	200	236.05	0.0165	0.992	294.12	0.00036	0.99
	127.40	100	100.46	0.0156	0.992	129.87	0.00014	0.99

Table-5.4:
Column adsorption capacities of RTAC for nickel at various operating conditions at break through point (C_b=1mg/L)

Flow rate (mL/min)	C_o (mg/L)	D (cm)	Wt of adsorbent (g)	T_B (hr)	V_B (L)	Ts (hr)	Vs (L)	qb (mg)	qs (mg)	Adsorption column capacity (mg/g)	% metal removal
2.5	200	5	4	3.87	0.58	6.73	1.01	115.42	194.81	48.70	96.44
		10	6	7.00	1.05	12.60	1.89	208.95	366.21	61.03	96.88
		15	8	14.07	2.11	19.13	2.87	419.89	559.19	69.90	97.42
1.5	200	5	4	11.44	1.03	21.00	1.89	204.97	370.01	92.50	97.89
		10	6	25.89	2.33	35.67	3.21	463.67	629.93	104.99	98.12
		15	8	46.78	4.21	62.44	5.62	837.79	1106.30	138.29	98.43
1.5	100	5	4	8.44	0.76	13.67	1.23	75.24	108.06	27.01	87.85
		10	6	13.89	1.25	22.00	1.98	123.75	176.44	29.41	89.11
		15	8	29.33	2.64	33.22	2.99	261.36	272.81	34.10	91.24

Table-5.5:
Adsorption-Desorption data in consecutive cycles

	Adsorption				Desorption		
Cycle #	C_o (mg/L)	C_e (mg/L)	Adsorption (mg/g)	Dec. in ads. (%)	C_f (mg/L)	Desorption (mg/g)	Desorption (%)
1	200	127	146	--	196	138	98.00
2	196	125	142	2.74	192	134	97.96
3	192	123	138	2.82	188	130	97.92
4	188	121	134	2.90	183	124	97.34
5	183	118	130	2.99	178	120	97.27

Table-5.6:

Quality of real waste water simulating a typical electroplating industry effluent

	pH	Ni^{2+} mg/L	Zn^{2+} mg/L	Pb^{2+} mg/L	Cd^{2+} mg/L
Quality of waste water before treatment	10.15	22.23	3.0	12.33	2.0
Quality of waste water after treatment	10.15	8.1(61.8%)	1.6(46.7%)	1.5(87.8%)	1.3(35.0%
Quality of waste water after treatment	7.5	2.82(85%)	0.98(67.3%)	0.40(96.7%)	0.87 (56.5%
Quality of waste water after treatment	2.5	21.18(4.6%)	2.11(29.7%)	10.83(11.9%)	1.92 (4%)

Table-5.7:
Comparisons of RTAC with other low cost adsorbents for Pb^{2+} and Ni^{2+} removal

Adsorbent	Metal ions	Adsorption Capacity	Ref.
Raw dolomite	Lead	13.39mg/g	89
Natural Diatomite	Lead	24.89mg/g	90
Olive Stone	Lead	5.9mg/g	91
Saw dust	Lead	21.05mg/g	92
Calcined phosphate	Nickel	15.53mg/g	93
Red mud	Nickel	13.69mg/g	93
Clarified Sludge	Nickel	14.3mg/g	93
RTAC	Lead	327.87mg/g	this study
RTAC	Nickel	138.89mg/g	this study

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Chapter 6

RUBBER TIRE ACTIVATED CARBON FOR THE REMOVAL OF ANILINE DERIVATIVES

6.1. INTRODUCTION

Recently, aromatic amines have emerged as environmental contaminants due to excessive use of pesticides and herbicides, from chemical manufacturing residues, and from byproducts of energy technologies [1,2]. Whereas microbial and plant metabolism of phenylurea, acylanilide, phenylcarbamate, and nitroaniline herbicides have resulted in the release of aniline derivatives, halogenated anilines such as 2,4,5-trichloroaniline, 4-chloroaniline and 3,4-dichloroaniline are mainly released into the environment as degradation products and intermediates of various phenylurea and phenylcarbamate pesticides [3,4]. Aniline derivatives also occur as intermediates in dyes manufacture and this constitutes another possible source of environmental aniline contamination. A number of substituted anilines are carcinogenic, toxic and can induce various adverse physiological responses [1]. Aromatic amines are polar than their precursors, and thus have a higher solubility in water, which is responsible for the high mobility of aromatic amines in aquifers [2]. Such compounds are listed as high-priority as a result of the study of pollutants from coal-conversion process wastes. The toxicity of aniline and its derivatives, even at a trace level, have attracted scientists to develop suitable technology for their removal from water.

Among the different processes developed for their elimination [5], the last decade has seen adsorption technology evolving as an efficient and universal method as per the guidelines of WHO and EPA [6]. The performance of an adsorptive separation is directly dependent on the quality and cost effectiveness of the adsorbent. Hence, recent research is focused on enhancing the effectiveness of activated carbon from various solid waste products by modifying their specific properties which would enable the carbon to develop affinity for certain contaminants to cater to their removal from varying types of wastewater.

The pioneer works of Coughlin and Ezra [7], Mattson et al.[8] and other published literature [9-11] have proved beyond doubt that the adsorption capacity is significantly affected by the activated carbon surface chemistry. Although, most of the adsorption sites are found on the basal planes, corresponding to about 90% of the carbon surface [12], oxygen surface groups have a higher activity and hence define the chemical characteristics of the carbon surface [13]. The carbon surface chemistry is primarily determined by the acidic (carboxylic acid, lactones and phenols) and basic (Bronsted- pyrones, carbonyls, chromenes, quinones and ethers; oxygen free Lewis- π electron density within the carbon basal planes) properties of their surfaces [14-16]. The less polar or non-polar adsorbate is generally adsorbed on the non-polar graphene layers by dispersive forces that depend on the nature of carbon porous structure. However, for the adsorption of a polar adsorbate, the adsorption takes place preferentially on the hydrophilic site of oxygen functional groups by electrostatic interaction [16]. Fixation of more oxygen functional groups would thus promotes the adsorption of polar adsorbates. In this context, such groups can be additionally introduced by oxidation with air, ozone, hydrogen peroxide and nitric acid, resulting in the formation of higher content of acidic groups [14, 15,17, 18].

Although literature is replete with such studies pertaining to carbon surface modification and their effect on adsorption performance, different conclusions often exist due to the complicated nature of the liquid phase adsorption phenomenon. As a result of the various controlling factors, the result of adsorbate-adsorbent interaction is often different for each system, and this necessitates its own investigation to arrive at the most precise adsorption mechanisms.

In a previous study, it was established that a purely mesoporous carbon prepared by physical activation of waste rubber tire (RTAC) affects the liquid phase adsorption behavior of Acid Blue 113 dye [19]. With a view to evaluate the role of surface oxygen groups, in this study, a oxygen enriched rubber tire carbon ($RTAC_{ox}$) is developed by HNO_3 treatment of RTAC. Batch adsorption capacity of RTAC and $RTAC_{ox}$ was assessed for the removal of anilines. For a better understanding of the interplay of various adsorbate-adsorbent interactions, a comparative batch study for four different aniline derivatives viz aniline, p-chloro-aniline, p-toluidine and p-anisidine is simultaneously conducted. In addition, the study has been extended to a commercial activated carbon with the purpose of evaluating the textural properties too. Finally, for designing and application of the $RTAC_{ox}$ for waste water treatment, isotherms, thermodynamics and reusability studies were assessed.

6.2. RESULTS AND DISCUSSION

6.2.1. Characterization of RTAC and $RTAC_{ox}$

A summary of the textural characteristics of the rubber tire activated carbons and of the CAC is outlined in Table-6.1. The thermal treatment has resulted in the development of high surface area (562 m^2/g) and mesoporous RTAC (71% volume). On the other hand, the surface area and the micropore volume are decreased, with a simultaneous increase in the mesopore volume in $RTAC_{ox}$ as compared to those in RTAC. The HNO_3 treatment has caused the destruction and the widening of the activated carbon micropores, giving rise to an increase in the mesopore volume. The CAC on the other hand has a microporous structure with a micropore volume accounting to 70.6% of total pore volume.

SEM micrographs of CAC, RTAC and $RTAC_{ox}$ present the morphological characteristics favorable for amine adsorption. Figure 6.1a shows a heterogenous, porous surface morphology of CAC having a mean particle diameter of 20 μm. Figure 6.1b shows morphology of a RTAC particle with much bigger pores and Figure 6.1c shows a much smoother and porous morphology of $RTAC_{ox}$ particle. EDAX confirms the carbonaceous nature of the activated carbons which is responsible for imparting porosity to the carbons as observed in the SEM results. The particle surface morphology of $RTAC_{ox}$ after adsorption of p-anisidine is completely changed as revealed in Figure 6.1d. The corresponding EDX further corroborates the adsorption of amine onto $RTAC_{ox}$.

Spectroscopic analysis (Figure 6.2a) shows the successful insertion of carboxylic and phenolic groups as a result of HNO_3 treatment on the $RTAC_{ox}$ surface and which were found to be absent on the RTAC surface. Presence of carboxylic groups is revealed by the characteristic peaks at 1709.99 cm^{-1} (C=O stretch of acid), 1266.29 cm^{-1}(C-O stretch of acid) and 2921.23 cm^{-1} (O-H stretch of acid) on the spectrum of $RTAC_{ox}$ [20]. Additional peaks at 3365.39 cm^{-1} (H bonded OH group) and at 1108.35 cm^{-1} (C-O stretch) corroborates the presence of phenolic group on the $RTAC_{ox}$ surface [20].

Figures 6.2b, 6.2c showing the IR spectrum of the RTAC-amine adduct and $RTAC_{ox}$-amine indicates significant changes in the peak frequencies of OH, C=O and C-O stretch in acids suggesting that such ionizable functional groups on the adsorbent surface are able to bind with the amine groups of adsorbates. Additional peak frequencies of 2929.40 cm^{-1} (NH stretch of amines) 1507.07 cm^{-1} (NH bend of amines) and of 1350.10 cm^{-1} (C-N stretch of amines) on the RTAC-amine and $RTAC_{ox}$-amine adduct have further established the adsorption of amines [20, 21]. Presence of amide functional group as revealed from 1629.97 cm-1 (C=O stretch), 3219.52 cm-1 (NH stretch) on the $RTAC_{ox}$-amine adduct [21] gives a probable acid-base interaction occurring through the carboxylic group of $RTAC_{ox}$ with the amino group of adsorbates. Such amide groups were found to be distinctly absent on the RTAC-amine adduct spectrum.

6.2.2. Preliminary Adsorption Studies

To optimize the effect of various parameters on adsorption of the studied aromatic amines onto CAC, RTAC and $RTAC_{ox}$, batch experiments were run under different conditions. The results of the experiments are discussed below.

6.2.2.1. Comparison of batch adsorbent efficiency and adsorbate performance

Figure 6.3 reveals the following observations:

a. The adsorbents show the following order of efficiency: RTACox > RTAC > CAC although the surface areas show a reverse trend as evident from Table-1. Obviously both surface porosity and the surface chemistry of the adsorbents play an important role in determining the adsorption capacity.
b. Also, the RTAC and CAC show a similar trend for the adsorption of aromatic amines: aniline > p-toluidine > p-anisidine > p-chloro-aniline.
c. Whereas, $RTAC_{ox}$ shows a different adsorption trend: p-anisidine > p-toluidine > aniline > p-chloro-aniline.

Micropores are the major adsorption sites and adsorption on activated carbon usually proceeds through diffusion of adsorbates from the bulk liquid phase through the mesopores and then into the micropores [22]. While diffusing into the micropores, pore blockage may occur due to aggregation of adsorbate molecules or in some cases, the micropore cross sectional area may be too small for the adsorbate to penetrate [23]. So in the absence of mesopores as in the case of CAC, the adsorbates take a longer time to diffuse into the micropores causing greater pore blockage and resulting in lesser adsorption efficiency [24]. In RTAC, the mesopores help in accelerating the diffusion of the adsorbates into the micropores and the probability of pore blockage gets reduced thereby increasing the adsorption efficiency.

A glance at the possible interactions between the adsorbent-adsorbate will help in understanding the adsorptive trend as observed for the RTAC and CAC. Since the adsorption experiments of this work were performed at pH 5.5 well below the pH_{PZC} of RTAC and CAC (see Table 6.1) the surface charge of the adsorbents was predominantly positive. Taking also into account the pK_a values of the solutes (see Table 6.1) it is expected that at this pH, the adsorbates are in molecular form and electrostatic adsorbate/adsorbent interactions are not dominant in the adsorption processes. On the other hand, the adsorption can also be controlled by dispersive interactions between the π electrons of the aromatic ring of the solute and those of the graphene layers of the carbon surface [13, 25]. Then, the presence of electron-donating groups on the ring ($-OCH_3$ of p-anisidine, $-CH_3$ of p-toluidine) would lead to a higher adsorption energy while electron-withdrawing groups (–Cl of p-chloro-aniline) would lead to a lower solute affinity by both adsorbents [26]. Thus the following order would be expected for the affinity and adsorption of the four solutes: p-anisidine > p-toluidine > aniline > p-Cl-aniline. As can be seen from Fig 6.3, this trend is not followed. But a positive correlation found between the adsorbate molecular size/solubility (Table-6.1) and the adsorption efficiency reveals that such factors have played a decisive influence on the adsorption process. Such revelation is confirmed by observations made by Caturla et al. [27]. Therefore, in the case of RTAC and CAC, the main factor that affects the adsorption behavior is the relation between the porous structure of the adsorbent and the molecular size and solubility of the used adsorbate.

When the same organic compounds are adsorbed onto $RTAC_{ox}$, two main facts are observed: a change in the adsorption trend and an increase in the efficiency; thus the influence of adsorbent surface chemistry is revealed. An increase in efficiency is the result of oxygen surface groups and larger mesopore volume. The enhanced efficiency may imply dispersion forces between π electrons in aniline derivatives and those of the graphene layers of the carbon surface [13, 25]. The oxygen surface groups on $RTAC_{ox}$ have resulted in lowering the pH_{PZC} values and at pH of 5.5, interacts with the more basic adsorbates resulting in amide formation as revealed by FTIR studies; the compound uptake order (p-anisidine > p-toluidine > aniline > p-chloro-aniline) follows closely the basicity or

pK_a value trend. Dispersive interactions between π electrons of the ring of the aromatics and those of the carbon basal planes, electrostatic and acid-base interactions are found to be the primary forces responsible for the physical adsorption of the aromatic amines onto $RTAC_{ox}$.

6.2.2.2. Effect of Concentration

Figure 6.4a and 6.4b show the equilibrium adsorption isotherms of the aromatic amines onto $RTAC_{ox}$ and RTAC respectively. Irrespective of the nature of aromatic amines, in case of both adsorbents, the equilibrium adsorption capacity (q_e) increased with the adsorbate concentration (C_e) in the presence of 25 mg absorbent, a probable reason being that concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases [28].

6.2.2.3. Effect of contact time

The uptake of aromatic amines onto $RTAC_{ox}$ and RTAC depicts that the sorption is quite rapid initially, gradually slows down and then reaches the equilibrium. It is very interesting to note that the equilibrium is achieved within 90 minutes indicating that the $RTAC_{ox}$ possess superior adsorption performance with high adsorption kinetics. On the other hand, equilibrium was attained at 210 mins for RTAC-amine system (Figure 6.5).

The decrease in the efficiency of the adsorbents with time may be due to aggregation of amine molecules around the adsorbent particles [28]. This aggregation may hinder the migration of adsorbate, as the adsorption sites become filled up, and also resistance to diffusion of amine molecules in the adsorbents increases. The difference in the equilibrium time between the two adsorbents might be due to differences in the surface properties of the adsorbents.

6.2.2.4. Effect of pH

The adsorption trend of aniline > p-anisidine > p-toluidine > p-Cl-aniline onto RTAC is found to be pH independent as revealed from Figure 6.6.

For $RTAC_{ox}$, the same adsorptive trend as observed for RTAC (aniline > p-anisidine > p-toluidine > p-chloro-aniline) is observed in pH range 1-4. But at pH > 4, increased adsorption efficiency is observed with the trend followed: p-anisidine > p-toluidine > aniline > p-chloro-aniline. The observed trend can be explained by taking into consideration the aromatic amine solution chemistry as well as the overall charge of the adsorbent surface [28]. The selected aromatic amines have a pKa of 4.15-5.34 (Table 6.1). At pH < pKa, the adsorbates exist in protonated form. On the other hand, depending on the solution pH, the various functional groups as revealed by FTIR study contribute to the overall charge of the adsorbent surface.

At $pH < pH_{pzc}$ (pH_{pzc} is 7.0 for RTAC and 4.2 for $RTAC_{ox}$), the protonation of the adsorbent functional groups cause strong electrostatic repulsion from the protonated adsorbates resulting in decreased adsorption in the pH range 1-6 for RTAC and 1-4 for $RTAC_{ox}$.

But at $pH > pH_{pzc}$, in the case of $RTAC_{ox}$, the deprotonated functional groups undergo electrostatic attraction for the molecular form of aromatic amines causing enhanced adsorption. Also, in slightly acidic medium (pH 5-6), the acid functional groups on $RTAC_{ox}$ undergo acid-base reaction with the amino groups of adsorbates. This is corroborated by the presence of amide functional groups on the $RTAC_{ox}$-amine adduct as revealed by the FTIR studies. Since maximum adsorption capacity is achieved at pH 5.5, all batch experiments were conducted at this optimum pH.

6.2.2.5.Effect of Temperature

The experiments were conducted at 25, 35, and 45 °C temperatures, and the results are shown in Figure 6.7a for $RTAC_{ox}$ with similar trend being observed for RTAC (Figure 6.7b). A perusal of these isotherms amply demonstrates the sensitivity of the adsorption process towards temperature and it is observed that in all cases, adsorption decreases with increase in temperature.

6.2.3. Modeling of Adsorption Isotherms

Adsorption isotherms give important information regarding the adsorbate-adsorbent interactions and are important in the design and analysis of sorption systems [28]. Isotherm data were applied to the Langmuir, Freundlich and the D-R adsorption models and the results of their linear regression were used to find out the fit model among them. The parameters and correlation coefficients obtained from the plots of Langmuir ($1/q_e$ vs $1/C_e$), Freundlich ($\log q_e$ versus $\log C_e$) and D-R ($\ln q_e$ vs ε^2) are listed in Table 6.2.

The correlation coefficients at different temperatures were considerably high ($R^2 > 0.99$) for the Langmuir model followed by the D-R and the Freundlich isotherm model; the linearity of plots as shown in Figure 6.8 (a) and 6.8(b) for $RTAC_{ox}$ and RTAC suggests the applicability of the Langmuir model with the aromatic amines getting adsorbed onto the adsorbent surface to form a monolayer [22]. The D-R plots for $RTAC_{ox}$ and RTAC are shown in Figure 6.10. The values b (Table-6.2) is seen to be higher for $RTAC_{ox}$ indicating higher affinity of adsorbates than for RTAC. This can be attributed to the fact that higher mesopore volume and stronger surface chemistry facilitates the adsorption of the adsorbates onto sites having stronger binding energy. Because of the higher values of Q_0 and b, rubber tire carbon having higher mesopore volume and favourable surface chemistry is a better option for use in waste water treatment.

The Freundlich constant, n >1 illustrates that adsorbate is favourably adsorbed on an adsorbent, and the higher the n value the stronger the adsorption intensity. In the present study, the value of n is significantly higher than unity at all the temperatures studied.

The D–R model constant (β) however, gives an idea about the mean free energy of adsorption (E_D) which in turn gives information about the nature of the adsorption process. The value of the constants q_D and E_D were found to be higher for $RTAC_{ox}$ than for RTAC (Table-6.2) at all temperatures irrespective of the adsorbates implying the importance of carbon mesopore and surface chemistry in liquid phase adsorption.

Moreover E_D was found to be < 8 kJ mol^{-1} at all temperatures (Table 6.2) implying that adsorption of aromatic amines onto both the adsorbents is a physisorption process.

6.2.4. Thermodynamic Study

The values of the thermodynamic parameters viz. the free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for adsorption process are summarized in Table 6.2. The enthalpy change, ΔH°, in case of both $RTAC_{ox}$ and RTAC is negative (exothermic) due to the decrease in adsorption with successive increases in temperature. Further, negative ΔG° values for $RTAC_{ox}$ and for RTAC dictate spontaneous process. The negative values of ΔS° for $RTAC_{ox}$ and RTAC reveal the increased randomness at the solid–solution interface during the fixation of the aromatic compounds on the active sites of the adsorbent. Since the adsorption process is exothermic, it follows that under these conditions the process becomes spontaneous because of the negative entropy change.

6.2.5. Kinetic Study

The Lagergren's pseudo-first-order and pseudo-second-order models were used to test adsorption kinetics data in order to investigate the mechanism of adsorption and were analyzed as discussed earlier. The values of the kinetic parameters as well as the regression coefficients (R^2) of the studied aromatic amines are listed in Table 6.3.

Table-6.3 as well as Figure 6.10 shows that a good linear relationship of t/q_t vs. t has a correlation coefficient very close to 1 and the adsorption capacities calculated by the model is also close to those determined by experiments. Therefore, it can be concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of aromatic amines over either $RTAC_{ox}$ or RTAC.

6.2.6. Mechanism of the adsorption process.

In a well-agitated batch adsorption system, there is a possibility of either film diffusion or intraparticle pore diffusion of adsorbate ions, which can be the rate-limiting step. In the present study, in case of both adsorbents, the plots of q_t versus $t^{0.5}$ were found to be linear for all studied amines, but the plots did not pass through the origin (Figure 6.11) implying that although intraparticle diffusion is involved in the adsorption process, it is not the sole rate- controlling step and that some other mechanisms may play an important role.

6.2.7. Column Adsorption Studies

Breakthrough capacity of the prepared column was determined by plotting C/C_o vs V (effluent volume) for the four studied adsorbates as given in Figure 6.12. Table 6.4 summarizes the column adsorption capacity for the studied aniline derivatives onto $RTAC_{ox}$ under fixed bed depth of 15cm, at fixed inlet concentration of $6x10^{-5}$M and flow rate of 1.5mL/min. The terminologies used in the Table viz T_B, V_B, T_s and V_s stand for breakthrough time, breakthrough volume, saturation time and saturation volume respectively. It can be concluded that the column adsorption capacity of $RTAC_{ox}$ follows the same trend as batch adsorption studies for the studied amines: p-anisidine > p-toluidine > aniline > p-Cl-aniline. Also, greater than 92% amines removal demonstrates the practical application of the proposed adsorbent for waste water treatment.

6.2.8. Testing under real waste water simulation condition

We further tested the practical application of $RTAC_{ox}$ by performing the same column experiments with 1L of actual groundwater samples. Groundwater from a nearby village around IIT Roorkee campus was collected and was spiked with the studied adsorbates. The water analysis revealed a pH of 8.2, Zn^{2+} (2.4mg/L), Fe^{2+} (8 mg/L), p-anisidine (7.4mg/L), p-toluidine (6.5mg/L), aniline (6mg/L) and p-chloro-aniline (7.7mg/L). The results show that when the test column was performed at the pH of 5-6, the removal % were 88, 82.5, 80 and 78% for p-anisidine, p-toluidine, aniline and p-chloro-aniline respectively but the same were to the tune of 40-51% at an acidic pH. This is in accordance to the observation of laboratory batch and column studies. Also, this sort of behavior indicated nonspecificity with respect to studied adsorbates, and thus, can be used for the uptake of aniline derivatives individually or in their mixtures.

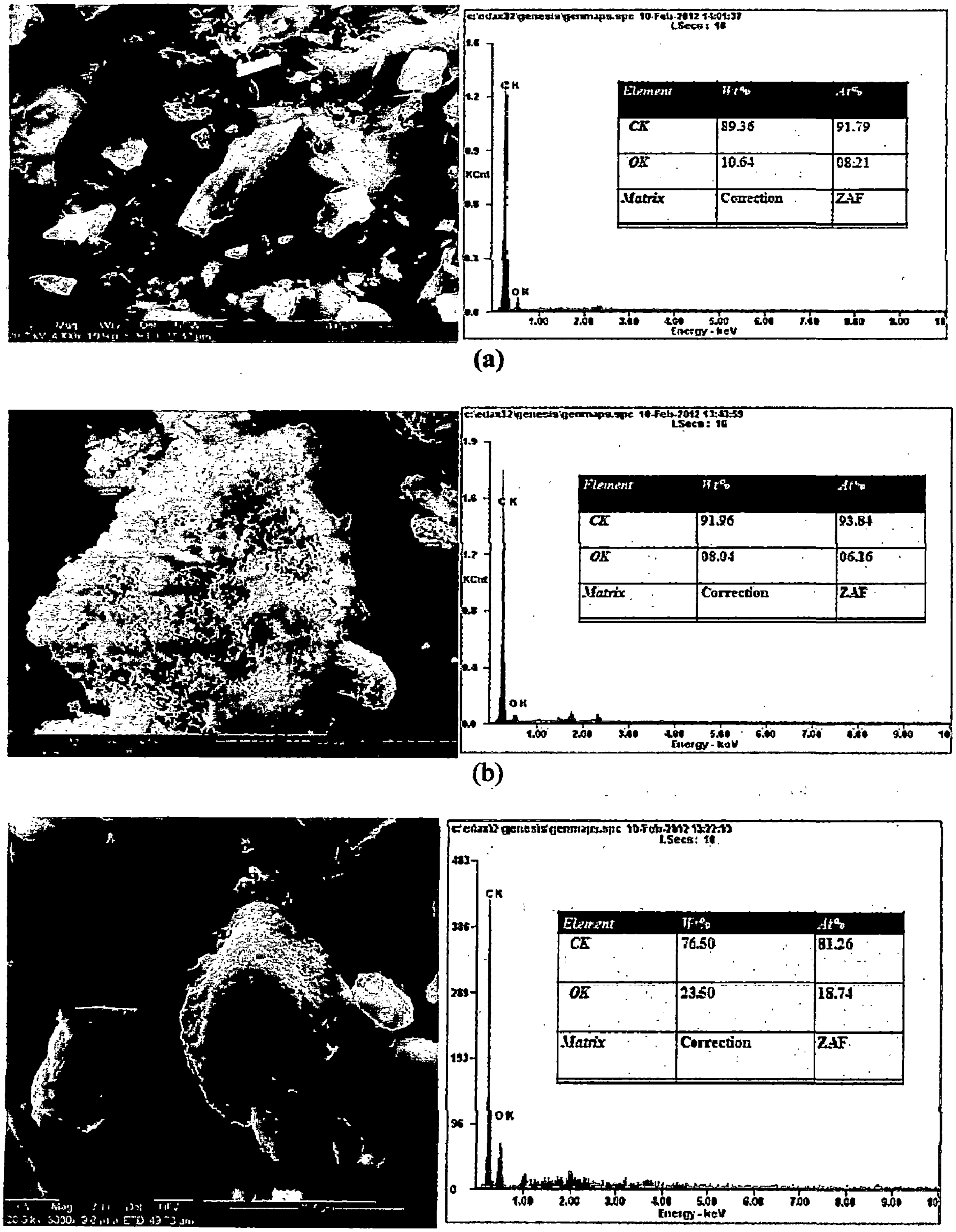
6.2.9. Desorption and reusability studies

Regeneration of the adsorbent for repeated use is of crucial importance in industrial practice for wastewater treatment. Desorption experiments carried out with p-anisidine laden $RTAC_{ox}$ in 0.1M HNO_3 showed that approx 98 % of the adsorbed aniline was desorbed. Results of the adsorption capacity of $RTAC_{ox}$ for five consecutive adsorption-desorption cycles are graphically illustrated in Figure 6.13. In all cycles, desorption was 97.8 - 98.8%. A 12.5% decrease in adsorption efficiency occurred (Table 6.5) after five consecutive cycles of adsorption-desorption that demonstrates good reusability. This fulfils an important criterion for advanced adsorbents.

6.3. CONCLUSION

The objective of this work was to study not only the effect of surface-modification techniques in increasing the efficiency and kinetics of the rubber tire activated carbons for various aromatic amines removal but also in designing and analyzing the specific adsorbent-adsorbate system for waste water treatment. The following conclusions are bulletined:

1. The higher mesoporosity and favourable surface chemistry of a surface modified rubber tire activated carbon has played a significant role in enhancing the adsorption capacity and kinetics of $RTAC_{ox}$ for liquid phase adsorption. This was in agreement with the findings of higher values of equilibrium constant and the mean adsorption energy determined from Langmuir and D-R adsorption models.
2. The porous structure of the adsorbent and the adsorbate size has played an influencing role in determining the adsorption in the case of RTAC and CAC.
3. Batch adsorption studies revealed the optimum levels of various environmental parameters for maximizing efficiency. Langmuir and D-R model helped in indicating the underlying mechanism of the adsorption process. Kinetic modelling revealed the applicability of the pseudo-second-order model and intra particle diffusion to be more suitable to describe the adsorbate-adsorbent system for both RTAC and $RTAC_{ox}$. Thermodynamic studies revealed the feasibility and exothermicity of the developed system.
4. Column studies revealed not only a similar adsorptive trend of studied amines as the batch studies, but demonstrated the practical application of $RTAC_{ox}$ for waste water treatment.
5. The regeneration of $RTAC_{ox}$ and its subsequent use as adsorbent without significant loss in efficiency is of crucial importance in the economic development of adsorbate-adsorbent system for waste water treatment.



(a)

Element	Wt%	At%
CK	89.36	91.79
OK	10.64	08.21
Matrix	Correction	ZAF

(b)

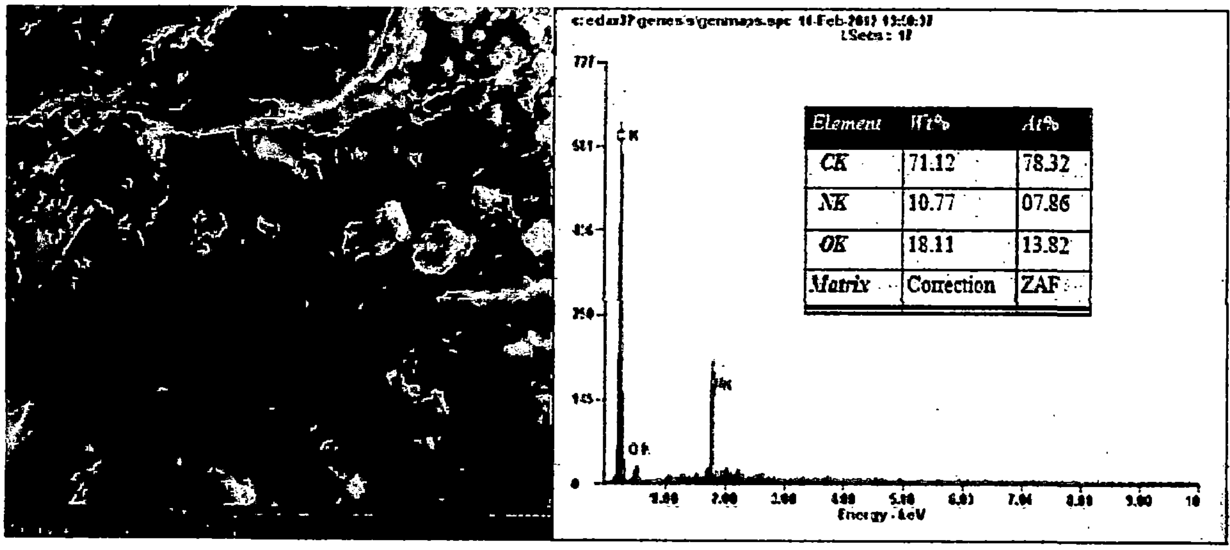
Element	Wt%	At%
CK	91.96	93.84
OK	08.04	06.16
Matrix	Correction	ZAF

(c)

Element	Wt%	At%
CK	76.50	81.26
OK	23.50	18.74
Matrix	Correction	ZAF

Figure 6.1:

SEM micrograph and EDX of (a) CAC (b) RTAC (c) $RTAC_{ox}$ before adsorption



Element	Wt%	At%
CK	71.12	78.32
NK	10.77	07.86
OK	18.11	13.82
Matrix	Correction	ZAF

(d)

Figure 6.1(d):

SEM micrograph and EDX of $RTAC_{ox}$ after adsorption

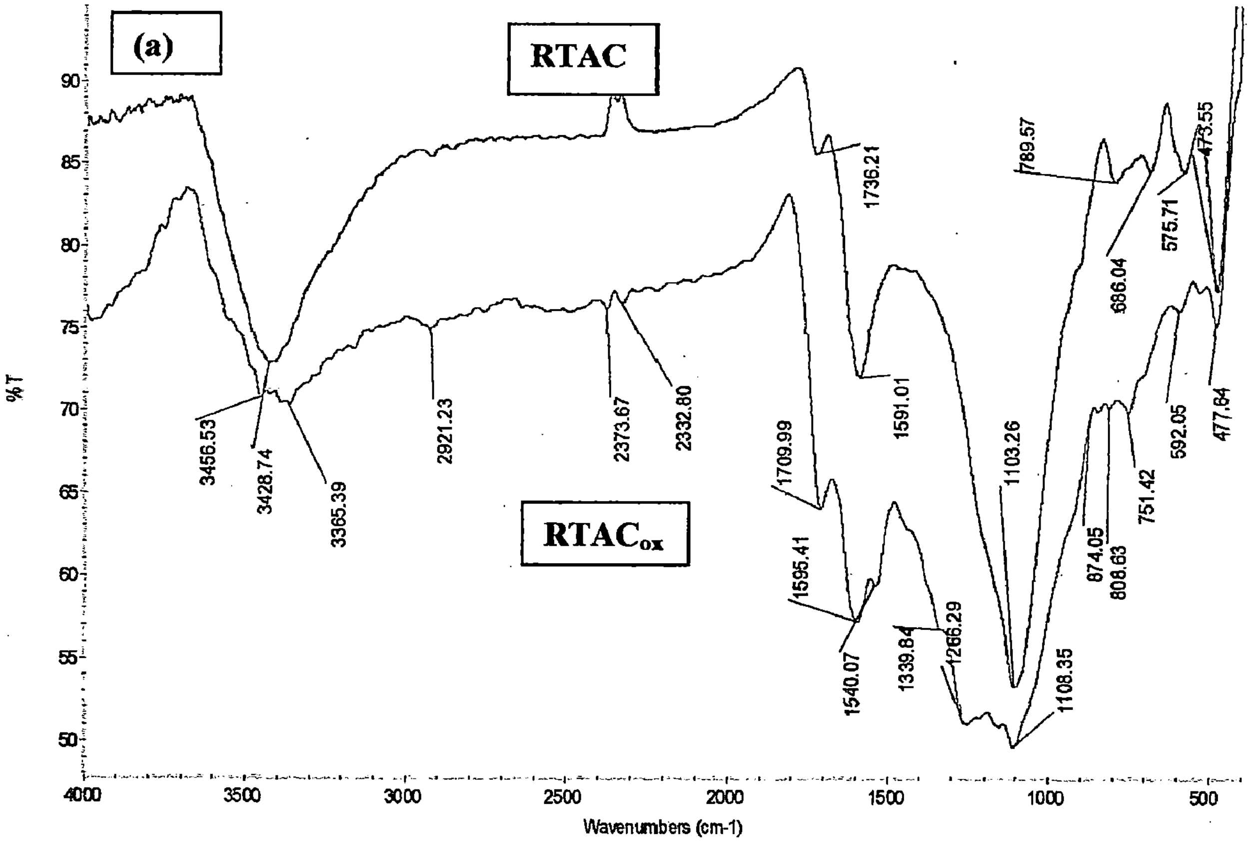


Figure 6.2 (a):

FTIR spectra of the adsorbents before adsorption

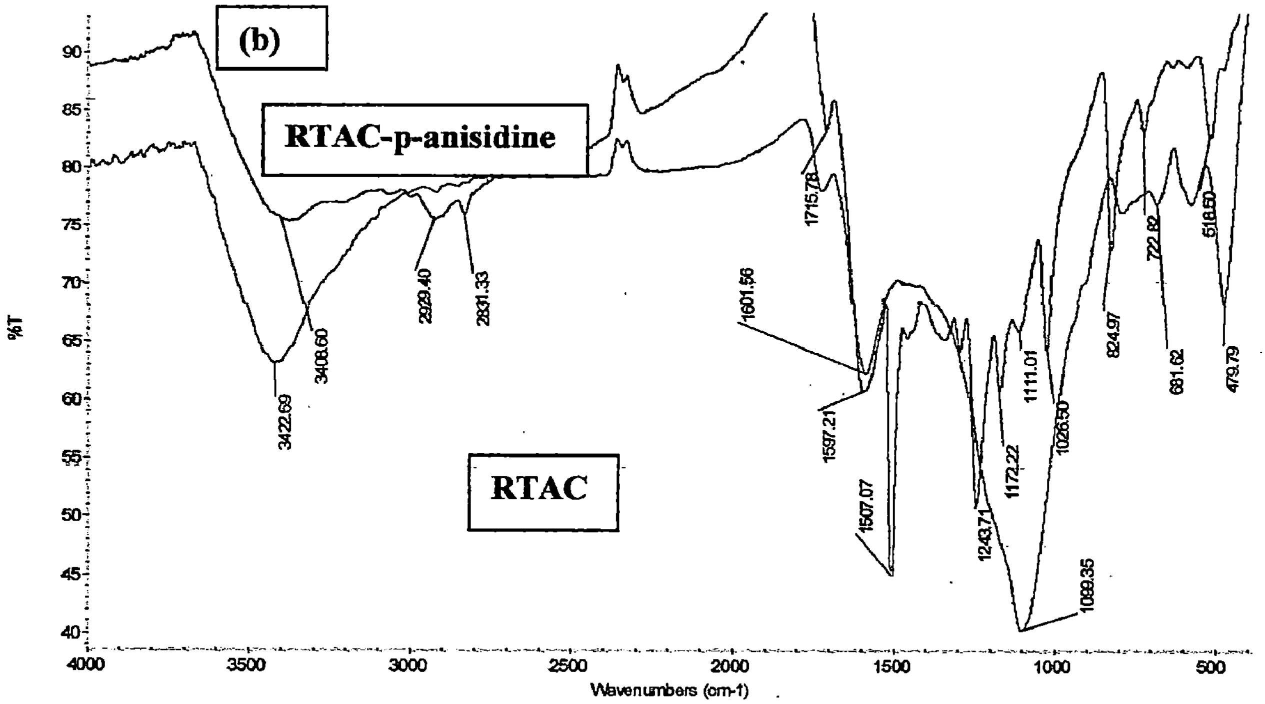


Figure 6.2 (b):

FTIR spectra of RTAC before and after adsorption

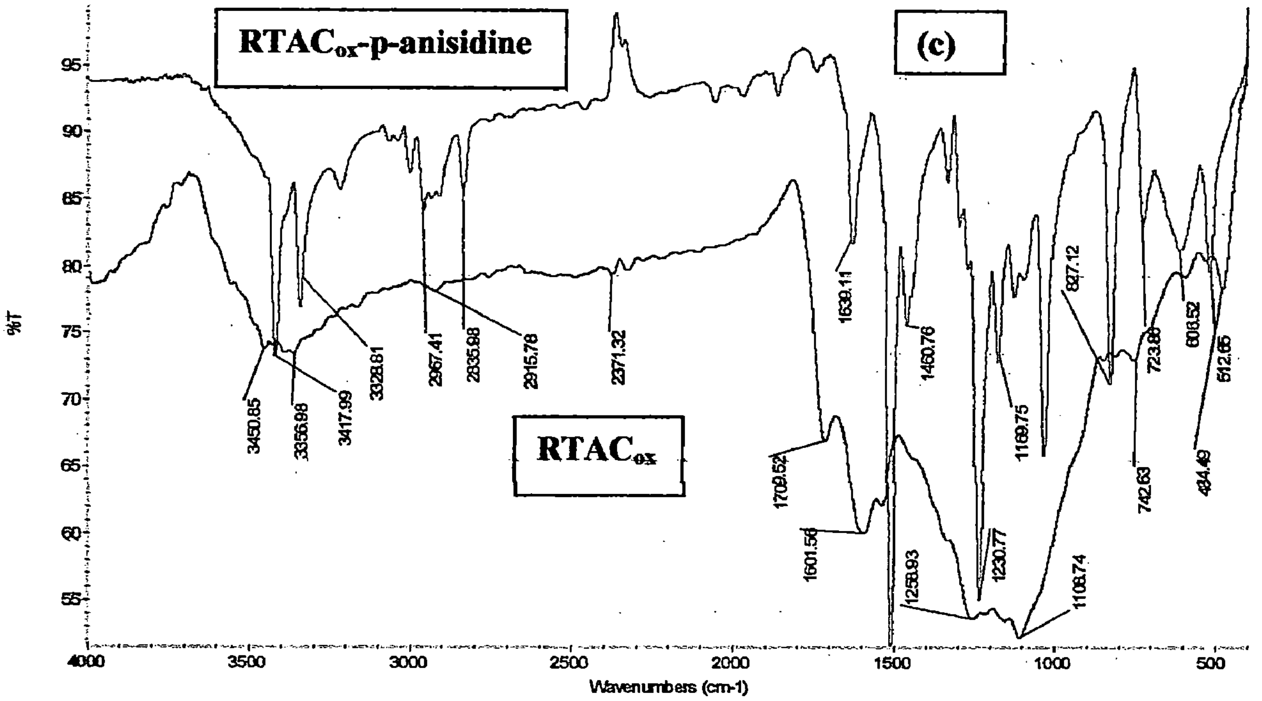


Figure 6.2 (c)

FTIR spectra of RTAC$_{ox}$ before and after adsorption

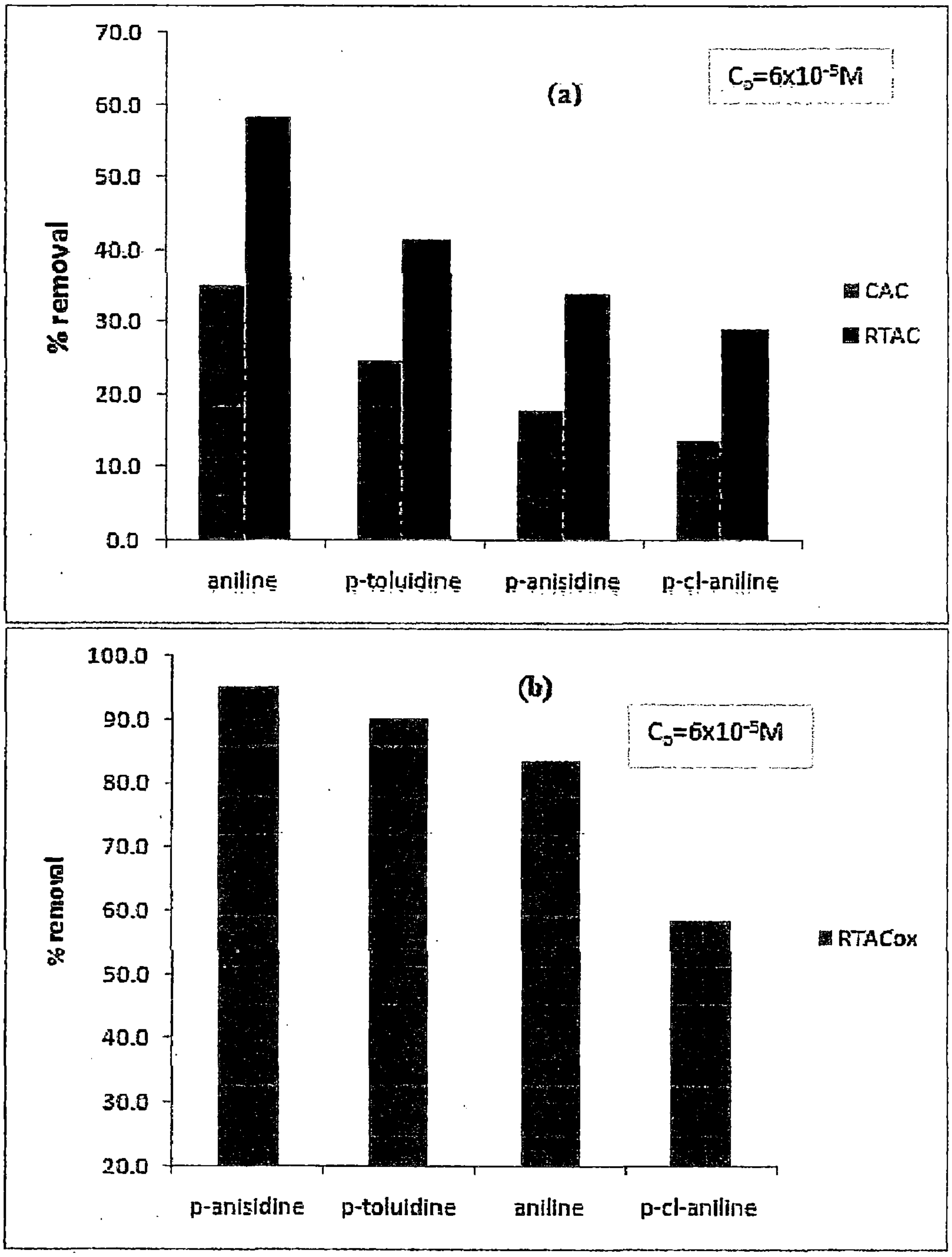
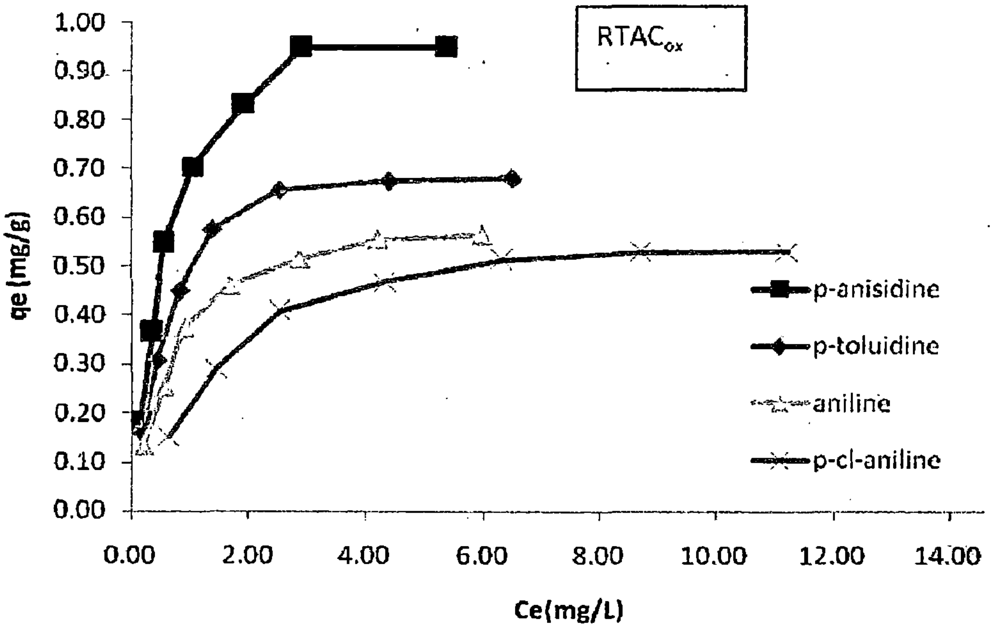
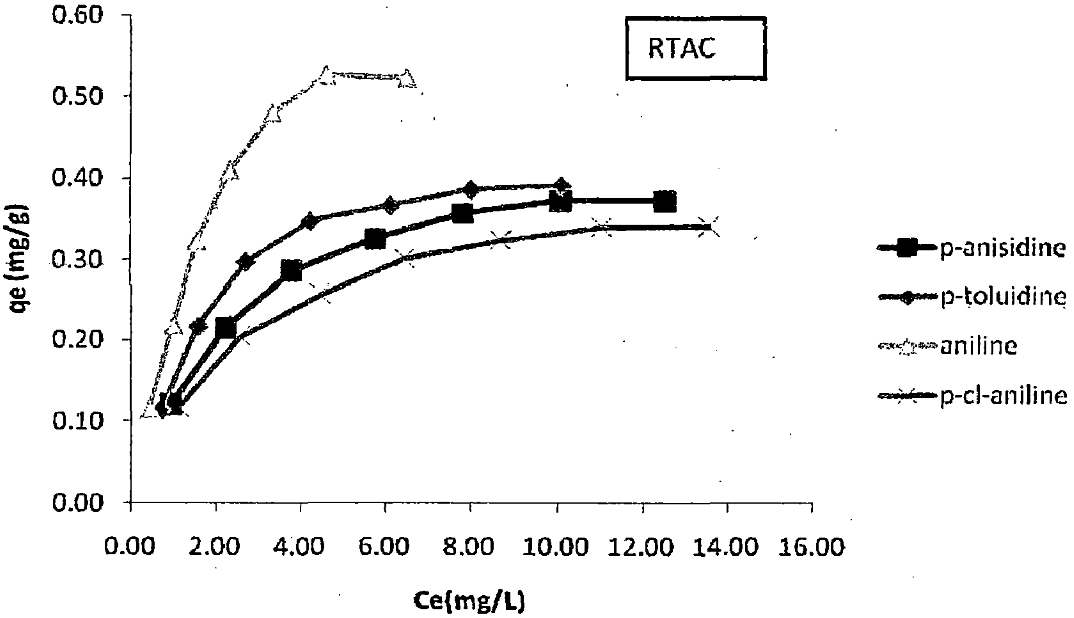


Figure 6.3:

Comparison of adsorbent efficiency and adsorbate performance (pH=5.5, adsorbent dose =25mg, Co=6x10^{-5}M, temp-25°C, contact time- 120mins)



(a)



(b)

Figure 6.4:

Equilibrium adsorption isotherm of studied adsorbates on (a) RTAC$_{ox}$ and (b) RTAC

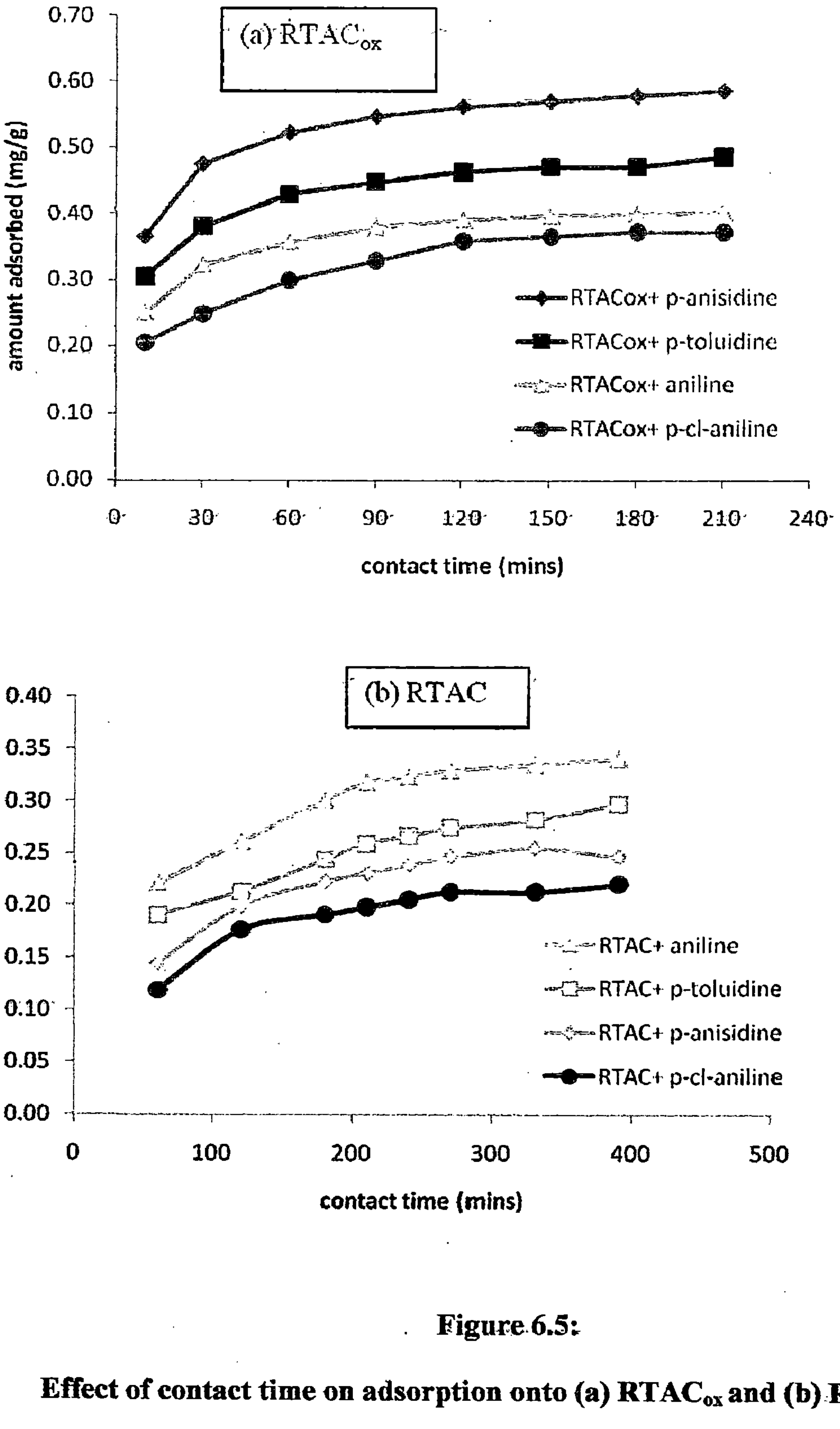


Figure 6.5:

Effect of contact time on adsorption onto (a) RTAC$_{ox}$ and (b) RTAC

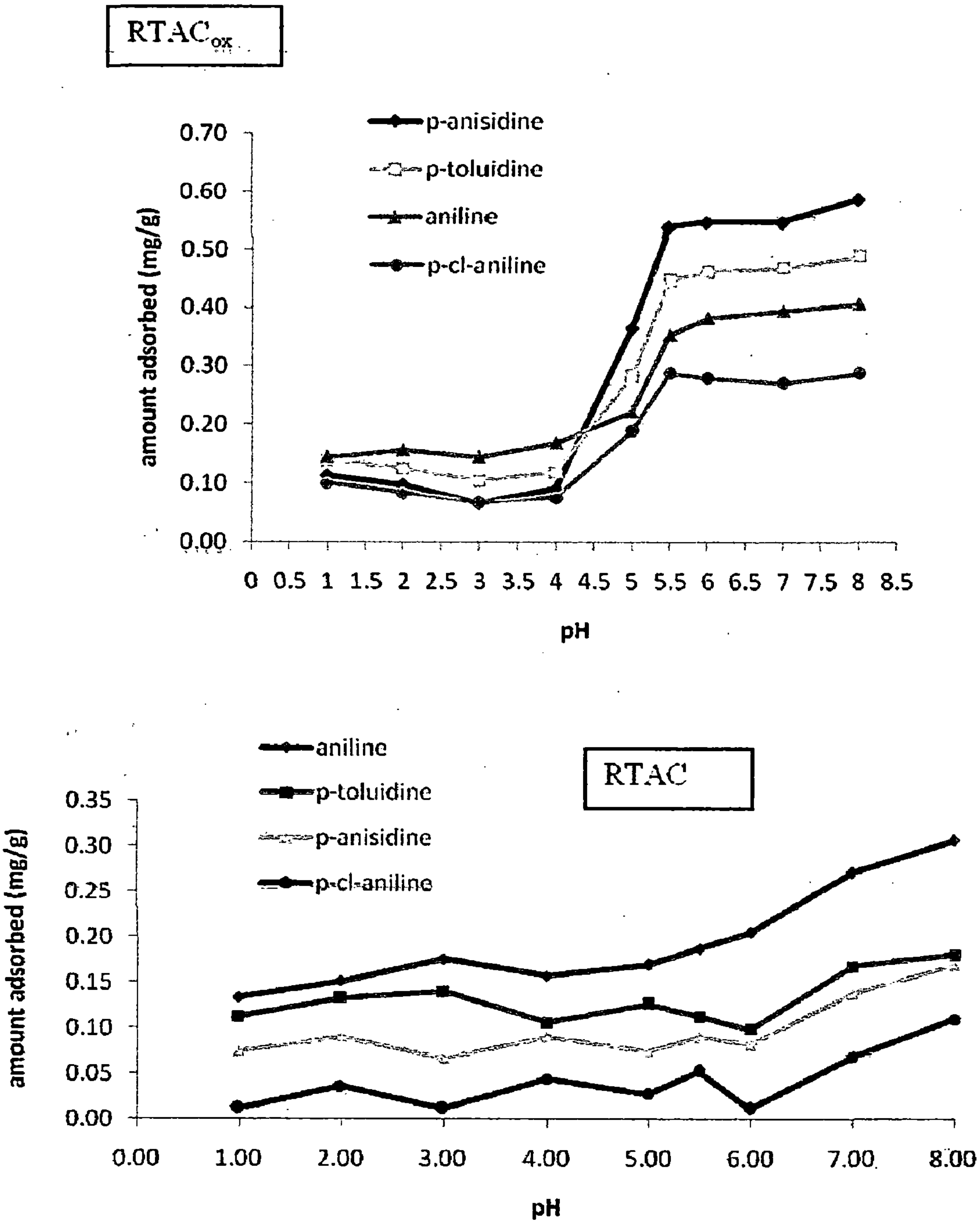


Figure 6.6:

Effect of pH on the adsorption onto RTAC$_{ox}$ and RTAC

(Co= 6x10^{-5}M; temperature 25°C, dosage=25mg)

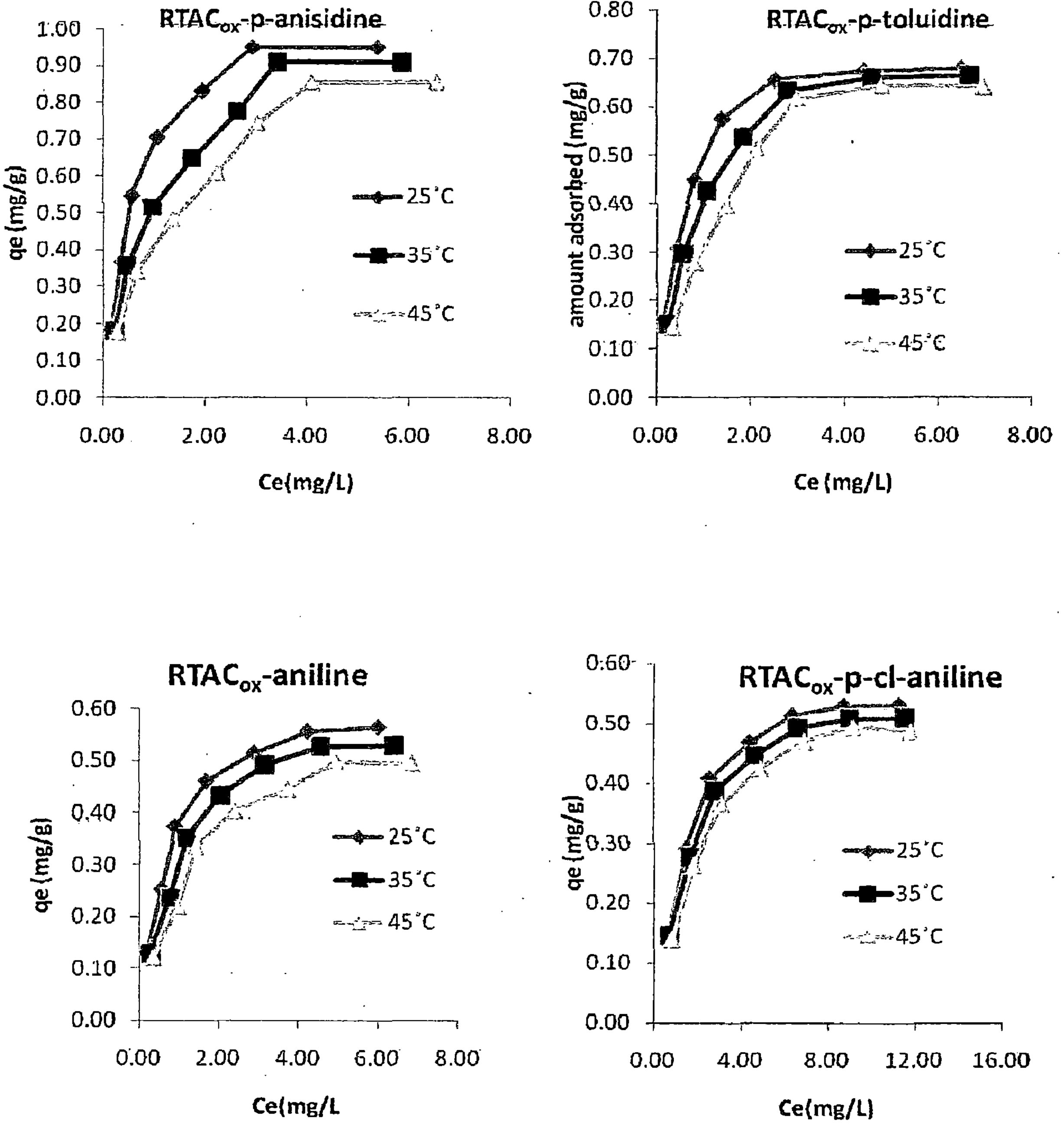


Figure 6.7a:

Effect of temperature on the adsorption onto RTAC$_{ox}$ (C_o= 6x10^{-5}M; dosage=25mg)

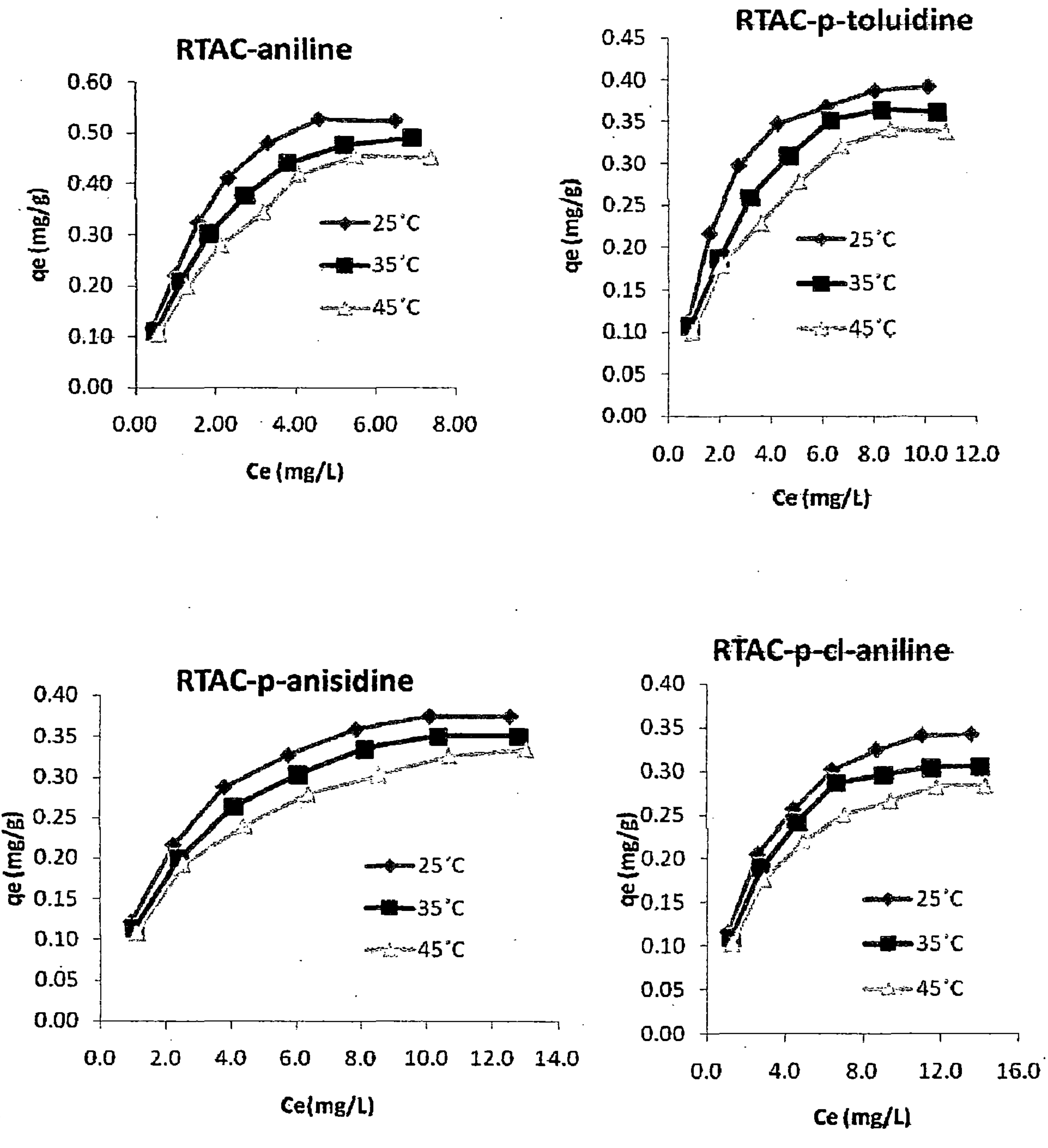


Figure 6.7b:

Effect of temperature on the adsorption onto RTAC

(C_o= 6x10^{-5}M; dosage=25mg)

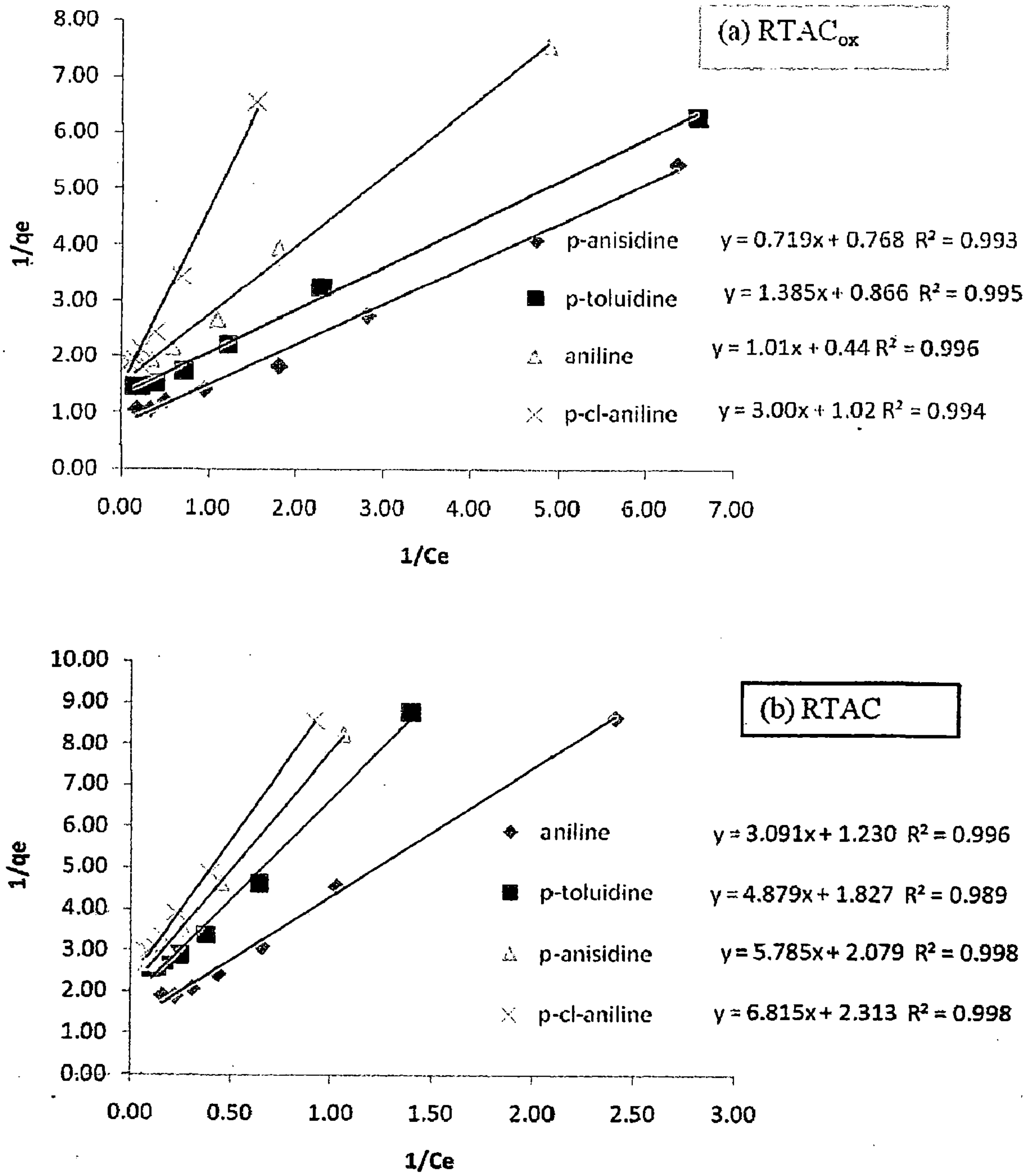


Figure 6.8:

Langmuir adsorption isotherms of the studied adsorbates on (a) RTAC$_{ox}$ (b) RTAC

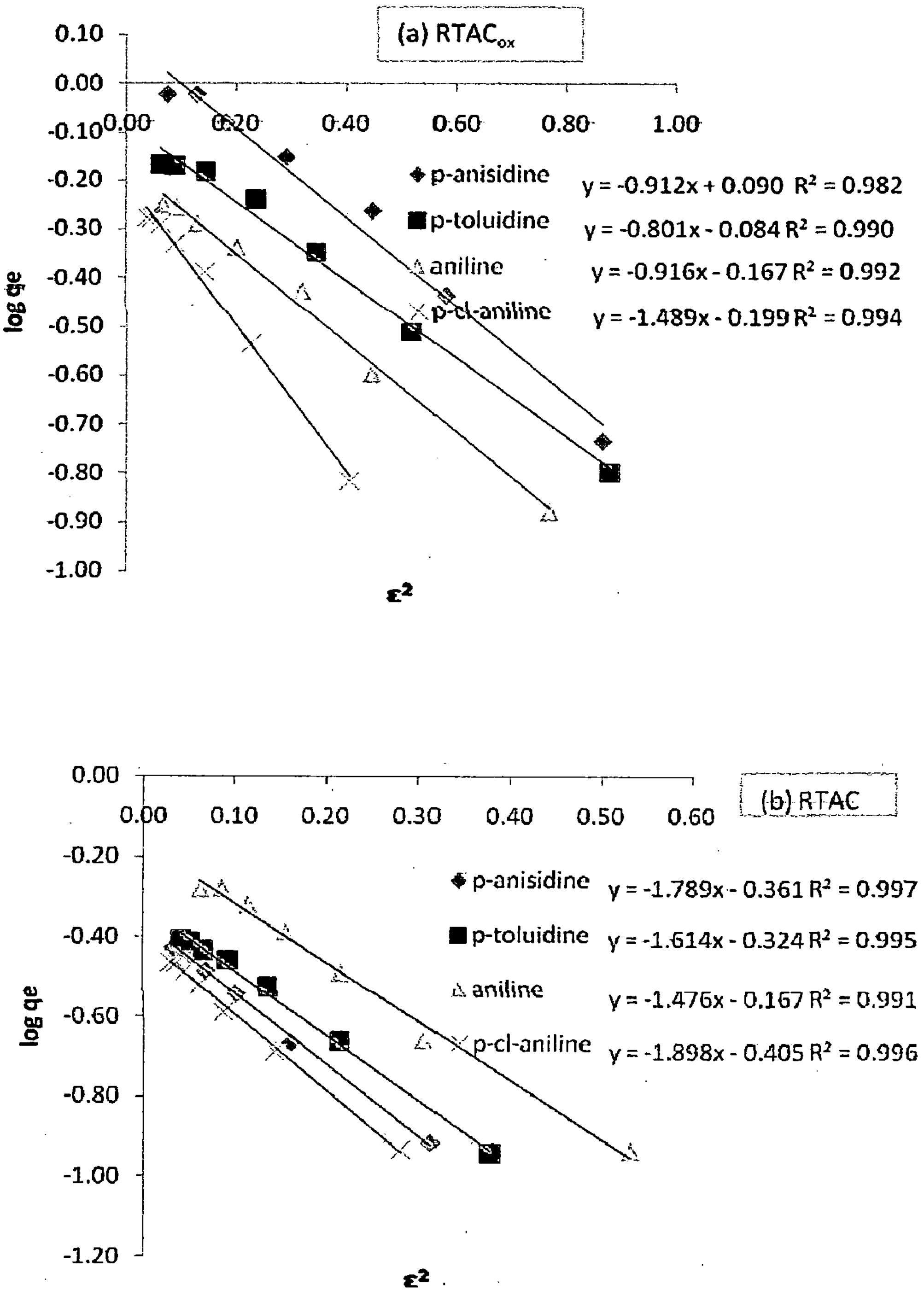
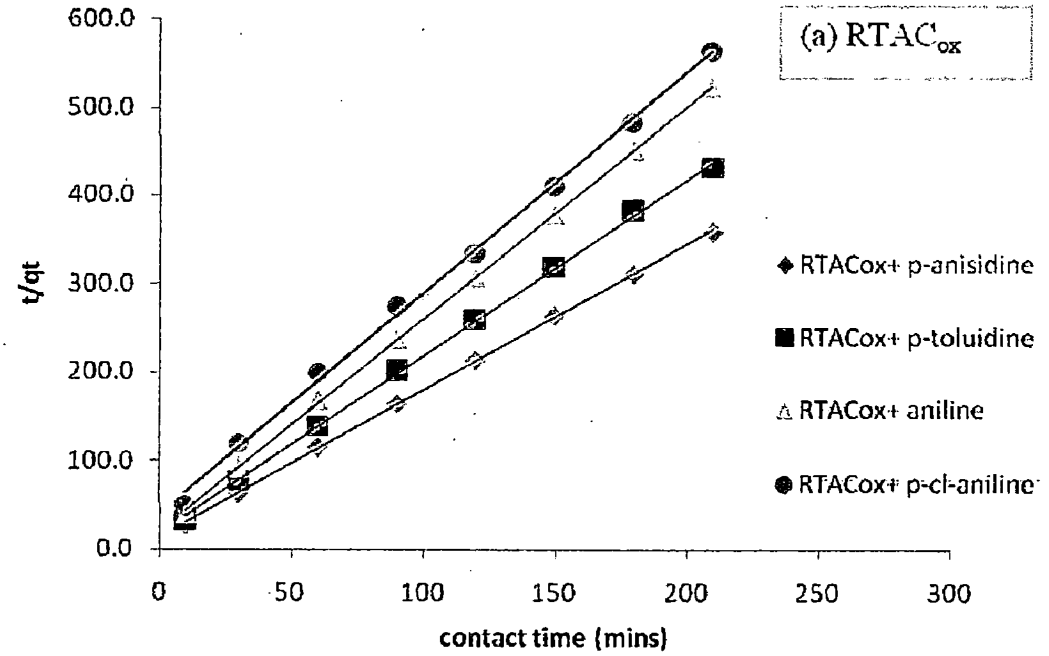


Figure 6.9:

D-R adsorption isotherms of the studied adsorbates on (a) RTAC$_{ox}$ (b) RTAC



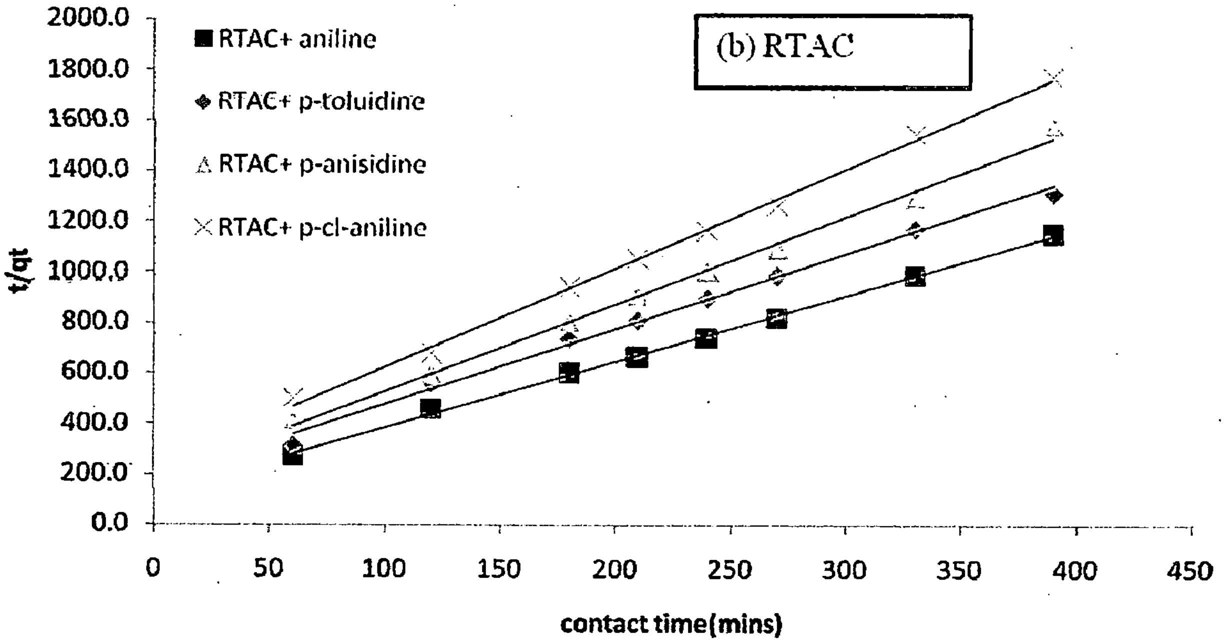
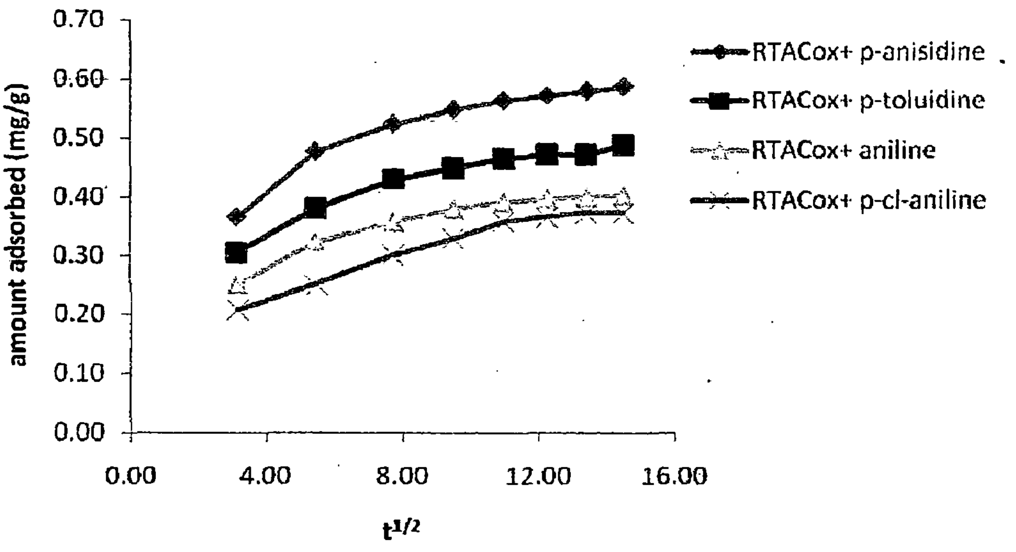
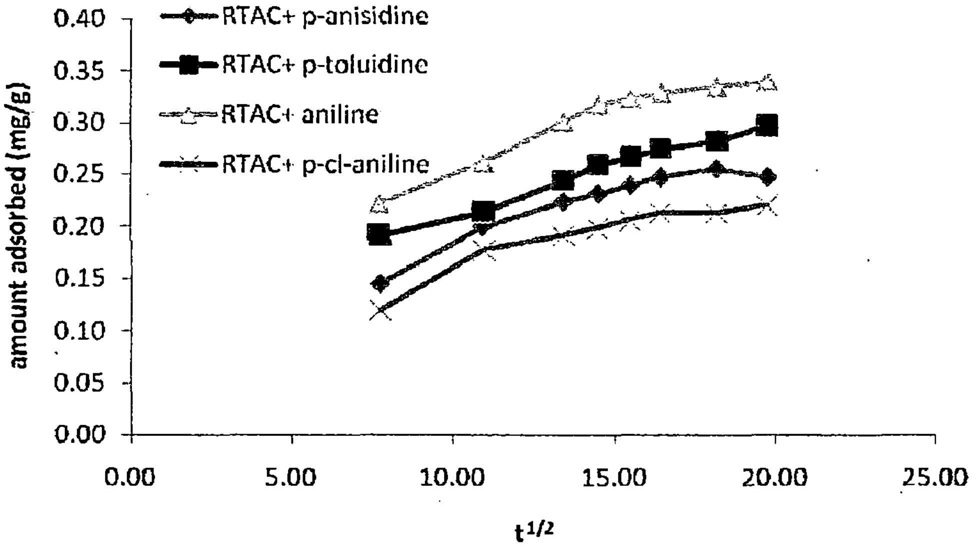


Figure 6.10:

Pseudo 2nd-order kinetic model for (a) RTAC$_{ox}$ (b) RTAC



(a)



(b)

Figure 6.11:

Intra particle diffusion plot of studied adsorbates onto (a) $RTAC_{ox}$ (b) RTAC

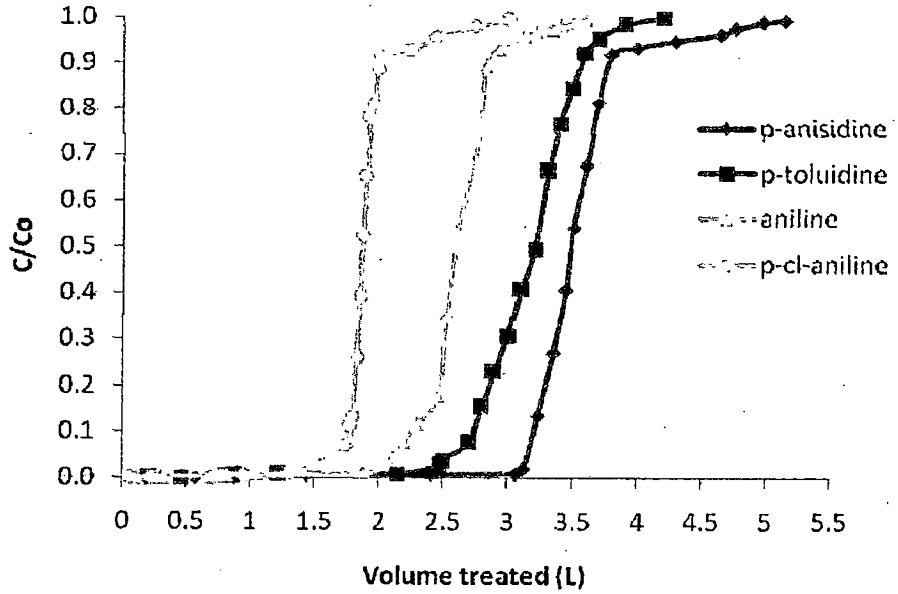


Figure 6.12:

The breakthrough curve for RTAC$_{ox}$-amiline system at a constant flowrate of 1.5 mL/min ($C_o = 6x10^{-5}M$, D=15cm).

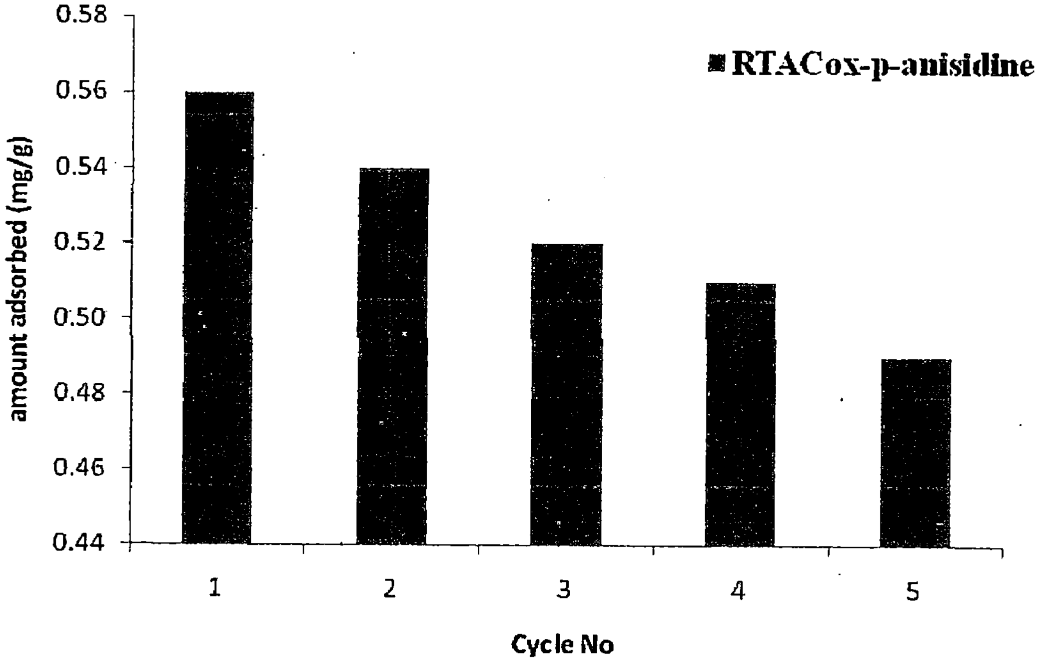


Figure 6.13: Regeneration plot for p-anisidine-RTAC$_{ox}$ column

Table-6.1:
Zero point charge and textural properties of the adsorbents and selected properties of the studied adsorbates

Adsorbent textural analysis

Adsorbent	pH_{PZC}	S_{BET} (m^2/g)	V_{tot} (cc/g)	V_{micro} (cc/g)	V_{micro} (%)	V_{meso} (cc/g)	V_{meso} (%)
CAC	7.1	1168	0.68	0.48	70.59	0.20	29.41
RTAC	7.0	562	0.97	0.28	28.87	0.69	71.13
$RTAC_{ox}$	4.2	397	0.85	0.11	12.94	0.74	87.06

Adsorbate analysis

	p-anisidine	p-toluidine	aniline	p-Cl-aniline
Molecular weight	123.15	107.15	93.13	127.57
Solubility(g/L)	21	11	36	3.9
Log K_{OW}	0.95	1.39	0.94	1.80
pK_a	5.34	5.08	4.63	4.15

Table-6.2a:
Equilibrium Adsorption and Thermodynamic studies of RTAC$_{ox}$-amine system

		D-R model			Freundlich model			Langmuir model			Thermodynamic parameters		
	Temp (°C)	q_D	E_D	R^2	K_F	n	R^2	Q_o (mg/g)	b (L/mg)	R^2	ΔG (kJ/mol/K)	ΔH (kJ/mol/K	ΔS
RTAC$_{ox}$													
p-anisidine	25	1.25	2.59	0.983	0.578	2.10	0.908	1.43	0.96	0.996	-0.104	-15.38	0.05
	35	1.09	2.55	0.993	0.471	2.03	0.952	1.33	0.79	0.995	-0.605		
	45	1.01	2.51	0.986	0.395	1.97	0.971	1.28	0.65	0.999	-1.143		
p-toluidine	25	0.823	2.77	0.990	0.435	2.16	0.967	1.15	0.62	0.995	-1.166	-12.82	0.047
	35	0.819	2.53	0.995	0.363	1.92	0.97	1.12	0.52	0.999	-1.657		
	45	0.811	2.34	0.989	0.300	1.69	0.979	1.09	0.45	0.998	-2.105		
aniline	25	0.680	2.59	0.993	0.318	2.27	0.934	1.01	0.44	0.996	-2.012	-7.765	0.03
	35	0.645	2.47	0.989	0.272	2.01	0.960	0.97	0.40	0.985	-2.331		
	45	0.598	2.41	0.979	0.232	1.94	0.959	0.92	0.36	0.992	-2.668		
p-Cl-aniline	25	0.632	2.03	0.993	0.147	1.67	0.979	0.98	0.34	0.994	-2.673	-5.819	0.03
	35	0.611	1.99	0.989	0.132	1.68	0.975	0.85	0.32	0.995	-2.898		
	45	0.591	1.96	0.979	0.118	1.62	0.973	0.77	0.29	0.995	-3.241		

Table-6.2b:
Equilibrium Adsorption and Thermodynamic studies of RTAC-amine system

		D-R model			Freundlich model			Langmuir model			Thermodynamic parameters		
	Temp (°C)	q_D	E_D	R^2	K_F	n	R^2	Q_o (mg/g)	b (L/mg)	R^2	ΔG (kJ/mol/K)	ΔH (kJ/mol/K	ΔS
RTAC													
aniline	25	0.679	2.04	0.992	0.221	1.74	0.94	0.81	0.40	0.997	-2.28	-8.87	0.04
	35	0.612	2.04	0.994	0.189	1.73	0.956	0.74	0.36	0.999	-2.62		
	45	0.567	2.03	0.988	0.164	1.69	0.963	0.69	0.32	0.998	-3.03		
p-toluidine	25	0.474	1.95	0.996	0.160	2.21	0.904	0.55	0.373	0.989	-2.44	-8.85	0.038
	35	0.435	1.90	0.987	0.131	2.00	0.951	0.49	0.335	0.997	-2.80		
	45	0.402	1.89	0.988	0.115	1.96	0.965	0.46	0.298	0.998	-3.20		
p-anisidine	25	0.435	1.85	0.998	0.152	2.30	0.938	0.48	0.359	0.998	-2.53	-5.40	0.027
	35	0.408	1.84	0.996	0.125	2.21	0.948	0.45	0.319	0.999	-2.93		
	45	0.377	1.82	0.995	0.107	2.08	0.960	0.42	0.300	0.998	-3.067		
p-Cl-aniline	25	0.393	1.80	0.996	0.126	2.34	0.948	0.43	0.339	0.998	-2.682	-3.383	0.020
	35	0.360	1.81	0.995	0.116	2.39	0.922	0.40	0.323	0.996	-2.897		
	45	0.327	1.85	0.998	0.103	2.38	0.945	0.36	0.311	0.998	-3.090		

Table-6.3:
Kinetic model parameters of the studied aromatic amines uptake by RTAC and $RTAC_{ox}$

Adsorbent	adsorbate	qe (mg/g) (exp)	removal (%)	*Pseudo First Order*			*Pseudo Second Order*		
				qe (mg/g) (theoret)	$k_1(min^{-1})$	R^2	qe (mg/g) (theo)	k_2 (g/mg/min)	R^2
$RTAC_{ox}$	p-anisidine	0.59	99.20	0.215	0.0182	0.988	0.625	0.304	0.998
	p-toluidine	0.48	93.22	0.180	0.0196	0.972	0.521	0.204	0.993
	aniline	0.40	90.03	0.154	0.0219	0.998	0.429	0.253	0.991
	p-Cl-aniline	0.38	59.69	0.112	0.0221	0.996	0.385	0.128	0.987
RTAC	aniline	0.34	76.14	0.281	0.0115	0.989	0.394	0.043	0.998
	p-toluidine	0.30	57.82	0.202	0.0069	0.993	0.338	0.046	0.993
	p-anisidine	0.25	41.87	0.244	0.0115	0.989	0.299	0.049	0.991
	p-Cl-aniline	0.22	36.05	0.183	0.0138	0.987	0.256	0.064	0.987

Table-6.4:

Column adsorption capacities of $RTAC_{ox}$ (C_o=6x10^{-5}M, Flow rate= 1.5mL/min, D=15cm, adsorbent weight=18g)

Adsorbate	Co (10^{-5}M)	Co (mg/L)	T_B (hr)	V_B (L)	Ts (hrs)	Vs (L)	Adsorption column capacity (mg/g)	% amines remova
p-anisidine	6	7.39	9.89	0.89	34.00	3.06	2.81	98.92
p-toluidine	6	6.51	9.00	0.81	27.56	2.48	1.94	97.08
aniline	6	5.59	8.33	0.75	26.33	2.37	1.56	95.35
p-Cl-aniline	6	7.65	7.89	0.71	19.00	1.71	1.51	92.81

Table-6.5:

Adsorption-Desorption data of $RTAC_{ox}$-p-anisidine system in consecutive cycles

	Adsorption			Desorption	
Cycle #	C_o (mg/L)	C_a (mg/L)	qe (mg/g)	C_d (mg/L)	% desorption
1	7.39	0.40	0.56	7.30	98.78
2	7.30	0.56	0.54	7.21	98.77
3	7.21	0.68	0.52	7.09	98.34
4	7.09	0.72	0.51	6.95	98.03
5	6.95	0.80	0.49	6.80	97.84

C_a=adsorbate concentration after adsorption; C_d=adsorbate concentration after desorption

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Chapter 7

ORANGE PEEL AND MAGNETIC NANOPARTICLES FOR THE REMOVAL OF METAL IONS

7.1. Introduction

Heavy metals, because of their non-degradable, persistent and accumulative nature are toxic when present in trace amounts and are a source of environmental concern [1]. Toxicity at trace levels leading to adverse health effect is usually associated with exposure to lead, cadmium, mercury and arsenic. A wide range of industries (mining, metal processing, electroplating, electronics, etc.) release such metals into the environment in amounts that can pose a risk to human health [2]. Therefore, metal remediation of waste water prior to discharge, is of great importance. Strict limitations imposed on metal discharge as well as the complexity of effluents makes the waste water treatment process more difficult. Moreover, dissolved and sorbed organic matter like humic acid exists ubiquitously in natural aquatic environment. Such substances, having a variety of components including quinone, phenol, catechol and sugar moieties play a vital role in controlling physicochemical behaviour of metal ions [3] and thereby necessitate metal remediation in the presence of such organic materials.

Adsorption is considered an effective, efficient, and economic method for water purification [4, 5]. Since the performance of a adsorptive separation is directly dependent on the quality and cost effectiveness of the adsorbent, the last decade has seen a continuous improvement in the development of effective noble adsorbents in the form of activated carbon [6], zeolites [7], clay minerals [8], chitosan [9], lignocelluloses [10], natural inorganic minerals [11], functionalized polymers [12] etc. However, most of these adsorbents are either not effective (due to diffusion limitation or the lack of enough active surface sites) or have shown problems like high cost, difficulties of separation from wastewater, or generation of secondary wastes. Considering such drawbacks, recently nano-adsorbents viz. nano-alumina [13], functionalized carbon nanotubes [14] and hydroxyapatite nanoparticles [15] have demonstrated high adsorption efficiency for metal ion removal. One such advanced class of adsorbent- magnetic nano-adsorbent with the help of an external magnetic field has been further successful in circumventing the solid-liquid separation problem usually encountered with nano particles. Such novel adsorbent combining nanotechnology and magnetic separation technique has not only demonstrated high adsorption efficiency due to their large surface to volume ratio, but has shown additional benefits like ease of synthesis, easy recovery and manipulation via subsequent coating and functionalization, absence of secondary pollutants, cost-effectiveness and environmental-friendliness.

Till date, several magnetic nanomaterials, including maghaemite nanoparticles [16], Fe_3O_4 magnetic nanoparticles [17], Fe_3O_4 nanoparticles functionalized and stabilized with compounds, like humic acid [18], amino-functionalized polyacrylic acid (PAA) [19], and various biopolymers like gum arabic [20], chitosan [21] and polysaccharides [22] have been explored for the removal of metal ions.

In this work, a novel magnetic nano-adsorbent (MNP-OPP) was developed by the surface modification of Fe_3O_4 nanoparticles (MNP) with orange peel powder (OPP) with the aim of exploring its feasibility as adsorbent for the removal of cadmium taken as a model toxic metal ion. Orange peel- a low cost, non toxic biosorbent containing active functional groups of hydroxyl and carboxyl present in cellulose, hemi-cellulose and pectin components [23, 24] is selected for its better application and management for waste water remediation.

The objectives of this study are: (1) synthesis of MNP and MNP-OPP by co-precipitation method and their characterization with respect to FE-SEM, TEM, XRD, VSM, pH_{PZC} and FTIR (2) comparative batch adsorption study of the three adsorbents (MNP, OPP and MNP-OPP) for Cd^{2+} with respect to various environmental parameters (3) comparative isotherm, kinetic and thermodynamic study (4) column, desorption and reusability study to investigate the practical utility of the developed adsorbent and lastly (5) to presume the underlying mechanism of metal binding.

7.2. RESULTS AND DISCUSSION

7.2.1. Characterization of MNP-OPP, MNP and OPP

The BET surface area of OPP, MNP and MNP-OPP were found to be 47.03, 76.32 and 65.19 m^2 g^{-1} respectively. Although MNP-OPP had a lower surface area than MNP, its adsorption capacity is higher which indicates that the multiple functional groups on MNP-OPP played an important role in the enhancement of the adsorption capacity.

SEM micrographs of the three adsorbents present the morphological characteristics favourable for metal adsorption. Figure 7.1a shows heterogenous, porous surface morphology of OPP having a mean particle diameter of 60 μm. Figure 7.1b shows a spherical morphology of MNP with particle size of 500nm and Figure 7.1c shows morphology and particle size of MNP-OPP similar to those of MNP but with a much smoother surface.

The particle morphology of MNP and MNP-OPP as shown in the TEM micrographs of Figure 7.2 revealed a smaller size of particles in the nanoscale range. The image of MNP, as shown in Figure 7.2a, showed that the MNP particles were fine, compact, monodisperse and had a mean diameter of 25-29 nm. The TEM image of MNP-OPP in Figure 7.2 b showed that the structure of the nanoparticles was looser; leading to an increase in size, the average diameter of such a structure was 32-35 nm. Modification of MNP with OPP resulted in a slight but not significant agglomeration of its particles. Similar observations were reported [28].

The XRD pattern of the OPP sample did not show any peak, which indicated the amorphous nature of the product (Figure 7.3). The phase structure of Fe_3O_4 is revealed from XRD patterns for the MNP and MNP-OPP samples. Six characteristic peaks for

Fe_3O_4 at 30.1°, 35.5°, 43.1°, 53.4°, 57.0° and 62.6°, corresponding to their indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) were observed for both samples revealing that the composite MNP-OPP nanoparticles were pure Fe_3O_4 with inverse-spinel structure [25]. These peaks are consistent with the database in JCPDS file (PCPDFWIN v.2.02, PDF No. 85-1436) indicating that the OPP binding did not result in the phase change of Fe_3O_4 in the composite. The average particle size'd' of the MNP and MNP-OPP was estimated to be 25 and 32 nm respectively by using the standard Debye Scherrer equation [29].

$$d = (k\lambda/\beta\cos\theta) \qquad (1)$$

Where d is the particles size, k is the Debye–Scherrer constant (0.89), λ is the X-ray wavelength (0.15406 nm) and β is the full width at half maximum, θ is the Bragg angle.

Spectroscopic analysis shows the successful binding of OPP on to the MNP surface. Infrared spectrum of MNP and MNP-OPP (Figure 7.4) showed that the characteristic peak of MNP at 3434.76 cm^{-1} (OH stretch) and 575.15 cm^{-1} (Fe-O) underwent a significant shift in MNP-OPP spectra to 3413.03 cm^{-1} (OH) and 578.34 cm^{-1} (Fe-O) which indicated the interaction of the hydroxyl groups and metal-oxide on MNP during the MNP-OPP formation. Comparison of OPP and MNP-OPP spectra on the other hand revealed the shifting, disappearance and appearance of certain peaks. Significant band shifting from 3423.19 cm^{-1}, 2925 cm^{-1}, 2847 cm^{-1}, 1626.32 cm^{-1} and 1033.02 cm^{-1} on OPP to 3413.03 cm^{-1}, 2929.95 cm^{-1}, 2284.47 cm^{-1}, 1624.23 cm^{-1}, 1019.54 cm^{-1} on MNP-OPP corresponding to the bonded OH stretching, -CH, $-CH_2$ stretching, -C=O stretching in carboxyl and –C-O-C- stretching has revealed the successful binding of OPP onto MNP to form MNP-OPP [30]. The disappearance of the peak at 1731.34cm^{-1} (originally present in OPP) on MNP-OPP revealed the binding of Fe with the OH of carboxyl group [31]. Peaks observed on OPP at 1424.94 cm^{-1} (C-OH of carboxyl), 1312.44 cm^{-1}(C-O stretch in ester), 1262.67 cm^{-1}(C-O in acid) and 1154.54 cm^{-1}(C-O-C stretch in ether) were found to have disappeared on MNP-OPP. The newer peak at 578.34 cm^{-1} assigned to Fe-O group on MNP-OPP indicated the presence of MNP on the composite [32]. This interaction also accounted for the mechanism of surface modification of MNP with OPP.

Figure 7.5 showing the IR spectrum of the MNP-OPP before and after adsorption indicates distinct and significant changes in the absorption peak frequencies of OH, C=O stretch in acids, C-O stretch in phenols and C-O-C stretch in ethers suggesting that such ionizable functional groups on the adsorbent surface are able to bind with the metal ion. Similar observations were made for the IR spectrum of OPP and MNP.

The pH_{pzc} analysis was further conducted to confirm the attachment of OPP surface onto the surface of MNP. From Figure 7.6 it was obvious that the pH_{pzc} shifted from 6.78 (MNP) to 5.21 (MNP-OPP) after binding with OPP. This further revealed that MNP-OPP was positively charged at $pH < 5.21$.

The hysteresis loop of MNP and MNP-OPP at room temperature is shown in Figure 7.7. The absence of remainance and coercivity as observed in the magnetic loop proved that the synthesized MNP was superparamagnetic [25]. Also, the respective saturation magnetizations of MNP-OPP and MNP were 68.1 and 79.6 emu/g, which suggested that the OPP content in MNP-OPP was about 72.64 % (w/w). MNP-OPP can easily be separated from its aqueous dispersions in a few minutes with permanent hand-held magnets. MNP aqueous suspension was easily oxidized to brown suspensions having no magnetization, whereas no significant change in the saturation magnetization and colour was observed after the MNP-OPP was stored in water for 30 days that indicates the chemical and magnetic stability of MNP-OPP. Similar phenomenon was reported by [18].

7.2.2. Preliminary Adsorption Studies

The surface characteristics of the adsorbent surface and its metal binding capacity is mainly controlled by the contact time, metal ion concentration, pH, ionic strength, natural organic matter and other parameters [33, 34]. Therefore, a comparative batch adsorption study was carried out on OPP, MNP and MNP-OPP to study the effect of these environmental parameters.

7.2.2.1. Effect of contact time and concentration

Figure 7.8 shows the time profile of Cd^{+2} removal with 0.2 g L^{-1} of OPP, MNP and MNP-OPP at different initial Cd^{2+} concentrations at 45°C; from which, two important conclusions could be drawn. Firstly, irrespective of initial concentration, the adsorption process for OPP almost finished within 210 min, whereas, a faster process was observed at 90 mins for MNP and at 40 mins for MNP-OPP. A faster adsorption rate for MNP and MNP-OPP could be attributed to the external surface adsorption exhibited by non-porous nano adsorbent [35, 36], which is different from the microporous adsorption process exhibited by the OPP [37]. Since nearly all the adsorption sites of MNP and MNP-OPP existed on their exterior, it was easy for the adsorbate to access these active sites, thus resulting in a rapid approach to equilibrium. This result is promising by virtue of the economic viability as equilibrium time plays a major role in designing a wastewater treatment plant. Secondly, for all three adsorbents, the total amount of Cd^{2+} adsorbed increased with the increasing initial Cd^{2+} concentrations. This is because more Cd^{2+} is available at higher initial concentrations which in turn may have provided higher driving force for the ions from the solution to the adsorbents. The result may be more collisions between Cd^{2+} ions and active sites on the OPP, MNP and MNP-OPP [20]. Similar phenomena were observed in the literature [38, 20].

7.2.2.2. Effect of pH and underlying mechanism

The adsorption of Cd^{2+} on OPP, MNP and MNP-OPP is found to be pH dependent as revealed from Figure 7.9. For OPP, the adsorption capacity was as low as 2.63% at lower pH values but increased with increasing pH from 36.38 % to 48.0 % in the pH range of 4-6, and then appeared to level off at higher pH values. Cd^{2+} adsorption on MNP increased slowly from 35.5% to 70.94% in pH range of 2.0-8.0, and then maintained a high level with increasing pH. The same Cd^{2+} adsorption onto MNP-OPP increased at a much faster rate with increasing pH from about 42.38% to 96.0% in the pH range of 2-7 and then levelled off. The observed trend can be explained by effect of the surface charge of adsorbent and pH_{pzc}. The sole hydroxyl group on MNP, multi hydroxyl groups on OPP and MNP-OPP as revealed by FTIR spectra play a dominant role in the Cd^{2+} adsorption. Depending upon the solution pH, the adsorbent surface undergoes protonation or deprotonation [20]. The protonation/deprotonation reaction undergoes as follows:

$–Fe\text{-}OH + H^+ \rightleftarrows –Fe\text{-}O\text{-}H_2^+$ for MNP (2)

$–HO\text{-}(C{=}O)\text{-}M\text{-}(OH)_n + nH^+ \rightleftarrows –HO\text{-}(C{=}O)\text{-}M\text{-}(OH_2)_n^+$ for OPP (3)

$–Fe\text{-}O\text{-}(C{=}O)\text{-}(OH)_n + H^+ \rightleftarrows –Fe\text{-}O\text{-}(C{=}O)\text{-}(OH_2)_n^+$ for MNP-OPP (4)

At $pH < pH_{pzc}$ (pH_{pzc} of OPP, MNP and MNP-OPP is 3.6, 6.78 and 5.21 respectively), $–Fe\text{-}O\text{-}H_2^+$ and $–Fe\text{-}O\text{-}(C{=}O)\text{-}(OH_2)_n^+$ are the dominant species for MNP and MNP-OPP respectively. These species having high positive charge density make the Cd^{2+} adsorption unfavourable due to electrostatic repulsion. Also, stiff competition between H^+ and Cd^{2+} for the active sites will decrease Cd^{2+} adsorption [39].

But, at $pH > pH_{pzc}$, Fe-OH and $–Fe\text{-}O\text{-}(C{=}O)\text{-}(OH)_n$ are the dominant species in MNP and MNP-OPP respectively. Such deprotonated species undergo electrostatic attraction for Cd^{2+} that result in the formation of metal–ligand magnetic composite complexes. This causes enhanced adsorption [22].

Complexation and ion exchange appear to be the principle mechanism of the adsorption as revealed by equation 6-8.

$–Fe\text{-}OH + Cd^{2+} \rightarrow –Fe\text{-}O\text{-}Cd^+ + H^+$ for MNP (5)

$–HO\text{-}(C{=}O)\text{-}M\text{-}(OH)_n + Cd^{2+} \rightarrow –HO\text{-}(C{=}O)\text{-}M\text{-}(O\text{-}Cd)_n^+ + nH^+$ for OPP (6)

$-\text{Fe-O-(C=O)-(OH)}_n + \text{Cd}^{2+} \rightarrow -\text{Fe-O-(C=O)-(O-Cd)}_n^{+} + n\text{H}^{+}$ for MNP-OPP (7)

7.2.2.3. Effect of ionic strength

The ionic strengths of 0.1M, 0.01M and 0.001M $NaNO_3$ were chosen to investigate their effect on Cd^{2+} adsorptions onto MNP-OPP. Fig. 7.9 reveals that Cd^{2+} adsorption increased with decreasing ionic strength. This phenomenon could be attributed to two reasons: Firstly, a decreasing electrolyte concentration favoured the complexation tendency of Cd^{2+} ions with the hydroxyl functional groups on MNP-OPP; which enhances the adsorption process. This may imply that the nature of interaction between metal and the magnetic composites are mainly ionic in nature. Secondly, an increasing ionic strength of solution influenced the activity coefficient of metal ions that may have limited their transfer to the composite surfaces [40].

7.2.2.4. Effect of presence/absence of HA

Adsorption of Cd^{2+} on MNP-OPP in the presence of humic acid is shown in Figure 7.9. Cd^{2+} adsorption increased steeply at $pH < 7$ in the presence of humic acid but at $pH > 7$, the same shows a slight decrease. In order to understand the mechanism underlying such a phenomenon, individual adsorption of humic acid onto MNP-OPP was carried out at different pH. Figure 7.10 revealed the gradual decrease of humic acid adsorption with increasing pH. At lower pH ($pH<pH_{pzc}$), the positively charged MNP-OPP easily adsorbs the negatively charged humic acid molecules. The surface adsorbed humic acid induces more oxygen functional groups on MNP-OPP, allowing more Cd^{2+} ions to be adsorbed due to the strong complexation of Cd^{2+} with surface adsorbed humic acid [41]. As pH increases ($pH>pH_{pzc}$), more negative charge on hydroxyl groups of humic acid and MNP-OPP causes repulsion so that the adsorption is hindered. At still higher pH, more free humic acid molecules form complexes with Cd^{2+} which diminish adsorption onto MNP-OPP [42, 34].

7.2.3. Modeling of Adsorption and effect of temperature

Figure 7.11 demonstrates the adsorption isotherm of the OPP, MNP, and MNP-OPP for Cd^{2+} ions that were determined at the three studied temperature of 218, 308, 328K. The data of the Cd^{2+} ions adsorbed at equilibrium (qe, mg/g) and the equilibrium metal concentration (Ce, mg/L) were fitted to the Langmuir adsorption model (Figure 7.12). The data fit well to the model as shown in Table-7.1 with correlation coefficients (R^2) in the range 0.994-0.998, and maximum adsorption capacity of OPP, MNP and MNP-OPP being 40.00, 58.82 and 76.92 mg/g respectively. The b values (L/mg) indicated an ascending series of affinity to the OPP, MNP and MNP-OPP as follows: OPP- Cd^{2+} (8.33)> MNP- Cd^{2+} (8.50)> MNP-OPP- Cd^{2+} (8.67).

The high adsorption capacity exhibited by MNP-OPP may be explained by its nano-scale particle size giving access to a larger surface area as well as the incorporation of a large number of hydroxyl functional groups of OPP, which provided effective adsorption sites for the binding of Cd^{2+} ions [20, 21, and 32].

Table 7.1 as well as Figure 7.13 amply demonstrates the sensitivity of the adsorption process towards temperature and it is observed that in all cases, adsorption increases with increase in temperature. Favourable adsorption for Cd^{2+} is revealed further from the values of the dimensionless constant R_L (0.009-0.013) as determined, which is shown in Table 7.1.

7.2.4. Thermodynamic Study

The free energy change (ΔG°) for adsorption process was calculated using the equations:

$$\Delta G^\circ = - RT \ln b, \qquad (8)$$

Where b is the Langmuir constant

The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of ΔG° vs. T (Figure 7.13) using the equations:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (9)$$

Table 7.1 which summarizes the values of these parameters reveal the endothermic nature of the adsorption process (ΔH° values are positive). A possible explanation is that Cd^{2+} ions are well hydrated and will require breaking of the hydration sheath so as to proceed for adsorption; this inturn requires high energy. High temperature hence favours the dehydration process and ultimately the adsorption phenomenon too. Similar observation and explanation have been given [43]

The negative ΔG° value suggests that the adsorption process is a spontaneous process and thermodynamically favourable under the experimental conditions. The decrease of ΔG° with increasing temperature indicates more efficient adsorption at higher temperature. In addition, at higher temperature, the Cd^{2+} ions are readily desolvated, which enhances the sorption process. The positive ΔS° values indicate the affinity of the adsorbents towards Cd^{2+} ions in aqueous solutions and may suggest increasing degree of freedom at the solid–liquid interface during the sorption of metal ions on to the adsorbents [43].

7.2.5. Kinetics Study

The adsorption data was simulated by pseudo-second-order model. The values of q_e and $k_{2,ads}$ determined from the slope and intercept of the plot of t/q versus t (Figure 7.14) are shown in Table 7.2. The calculated qe values are in agreement with the theoretical ones, and the plots show good linearity with R^2 above 0.99. Therefore, the adsorption kinetics follows the pseudo-second-order model.

7.2.6. Desorption and reusability studies

Regeneration of the adsorbent for repeated use is of crucial importance in industrial practice for metal removal from wastewater. Desorption experiments carried out with Cd^{2+}

laden MNP-OPP in 0.1M HNO_3 showed that approx 98 % of the adsorbed cadmium was desorbed.

Results of the adsorption capacity of MNP-OPP for five consecutive adsorption-desorption cycles are graphically illustrated in Figure 7.15. In all cycles, desorption was 98.19-98.66%. A 4.74% decrease in adsorption efficiency occurred (Table 7.3) after five consecutive cycles of adsorption-desorption that demonstrates good reusability. This fulfils an important criterion for advanced adsorbents.

7.2.7. Fixed bed adsorption studies

Breakthrough capacity of the prepared column was determined by plotting C/C_o vs V (effluent volume) as given in Fig 7.16. It is seen that first 2L of influent was adsorbed to the tune of 99%. 74% of Cd^{2+} adsorption took place in the next 2-6 L influent followed by a rapid decrease of adsorption (74-1.7%) for 8 to 20 L. The column was exhausted and no further adsorption of cadmium occurred. A breakthrough capacity of 55.38 mg/g was obtained signifying 55.8% column utilization which is relatively lower than the batch adsorption capacity (76.92 mg/g). This decrease is usually observed and generally attributed to relatively less time of interaction between sorbent and adsorbate surface in column method.

7.2.8. Testing under electroplating industry effluent simulation condition

Urban wastewater from IIT Roorkee campus was collected and was spiked with nickel chloride, zinc nitrate and cadmium nitrate to obtain wastewater which simulated cadmium plating industry effluent. Despite the presence of competitive effect of nickel and zinc metal ions, about 82% reduction in Cd^{2+} concentrations was achieved as a result of treatment with the developed adsorbent. This is revealed in Table-7.4.

7.2.9. Comparison with other reported adsorbents

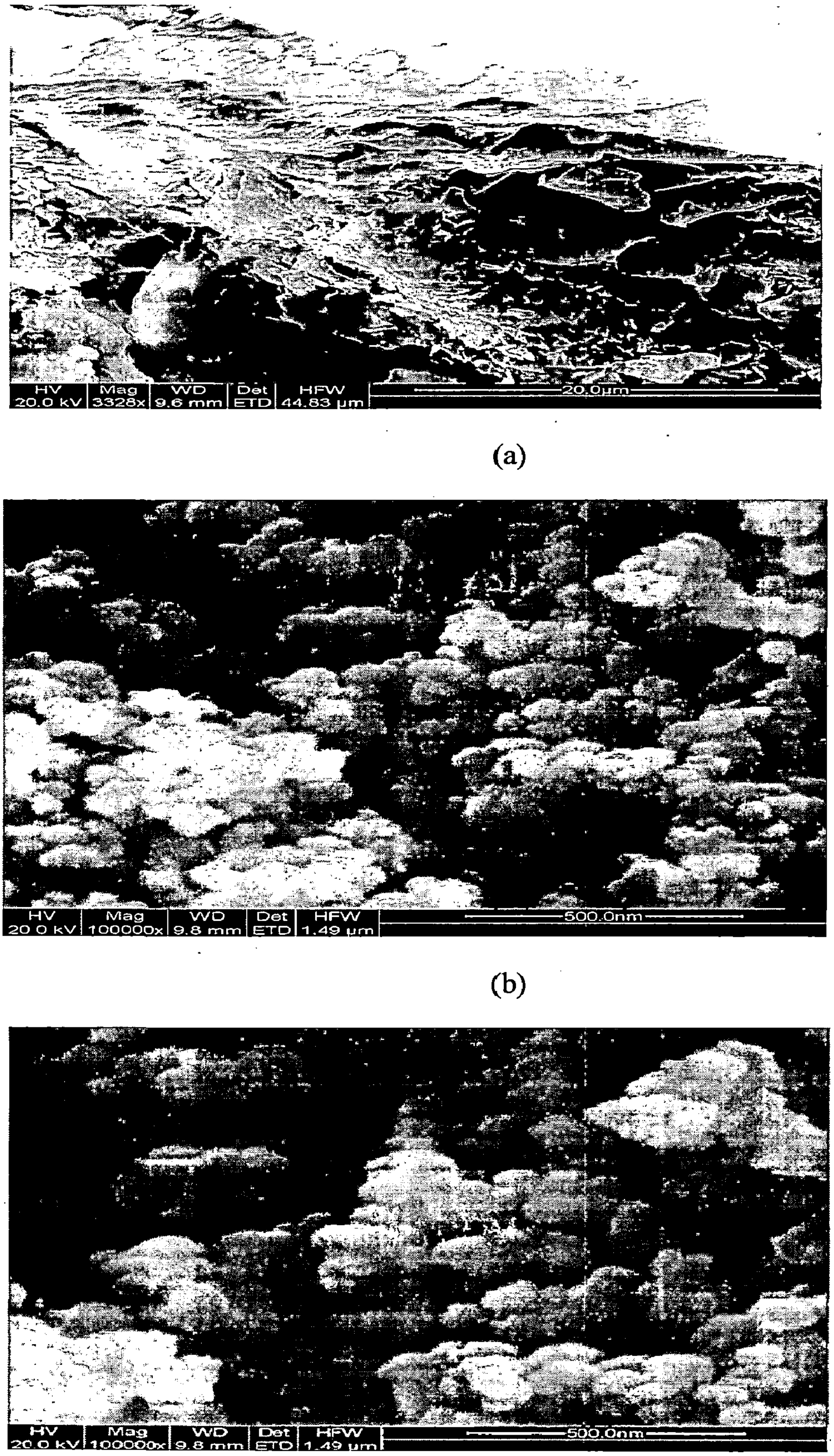
A comparative assessment of MNP-OPP with various other adsorbents reported in literature reveals the efficacy of the developed adsorbent for Cd^{2+} ions removal from waste water as revealed in Table-7.5 [47-50].

7.3. Conclusion

This study focused on assessing the adsorption efficiency of a novel MNP-OPP adsorbent developed from a local agricultural waste-orange peel powder for a toxic cadmium metal ion.

Characterization studies revealed the various physico chemical properties on MNP-OPP which are favourable for metal binding. Comparative preliminary batch studies demonstrated not only the optimal process parameters for maximizing metal sorption but also the principle underlying mechanism. Langmuir adsorption plot showed maximum Cd^{2+} removal by MNP-OPP at 76.92 mg/g at optimal conditions and thermodynamic studies revealed the feasibility of the process. Pseudo-second-order model was determined as the best fit model. Column studies with a breakthrough capacity of 55.38 mg/g as well as 82% Cd^{2+} removals from an electroplating effluent simulated wastewater revealed the practical utility of the developed adsorbent. Finally, desorption and reusability studies indicate a fulfilling of important criteria for advanced adsorbents.

The developed MNP-OPP has demonstrated not only high adsorption efficiency, faster kinetics but also have shown additional benefits like ease of synthesis, easy recovery, absence of secondary pollutants, cost-effectiveness and environmental-friendliness. It can be concluded to be a promising advanced adsorbent in environmental pollution cleanup.



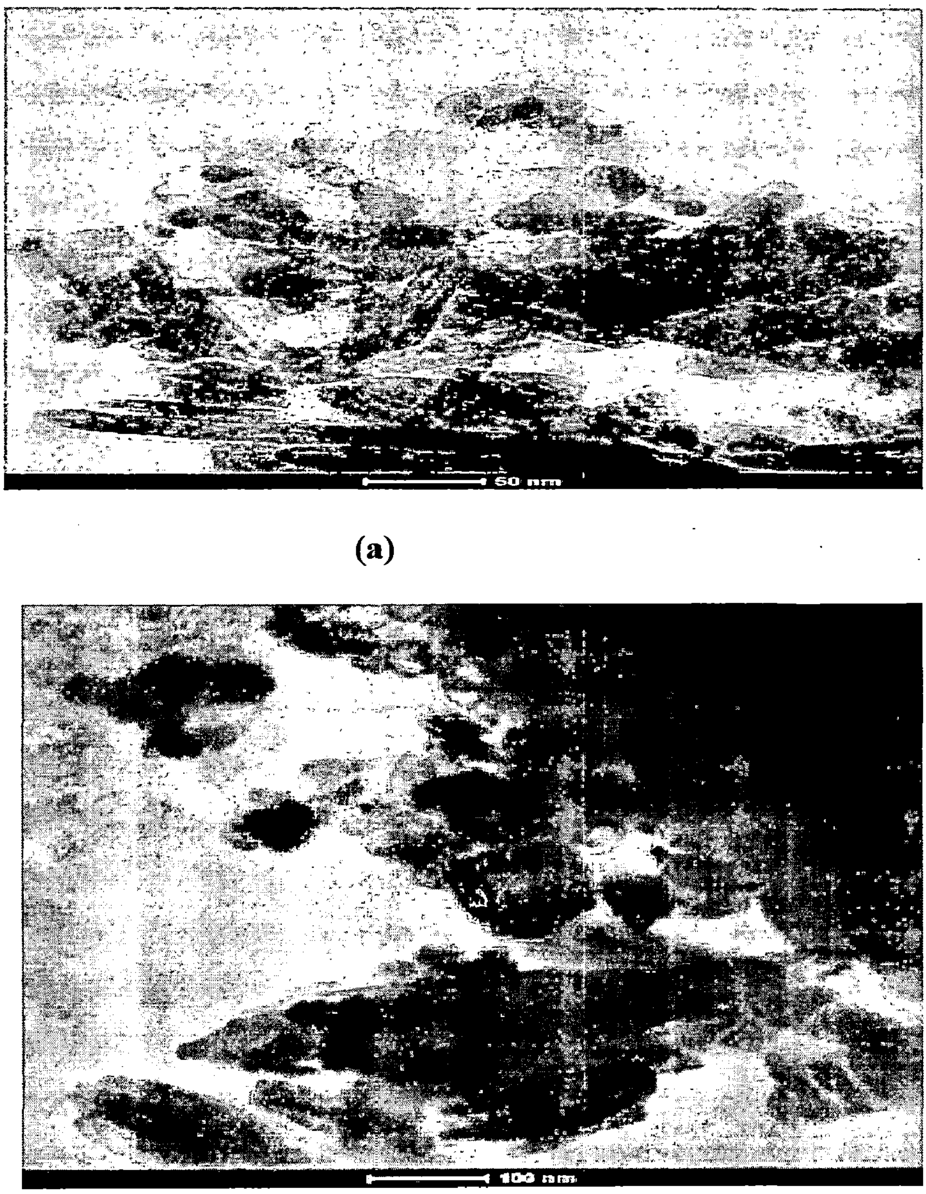
(a)

(b)

(c)

Figure 7.1:

SEM images of (a) OPP (b) MNP and (c) MNP-OPP



(a)

(b)

Figure 7.2:

TEM images of (a) MNP and (b) MNP-OPP

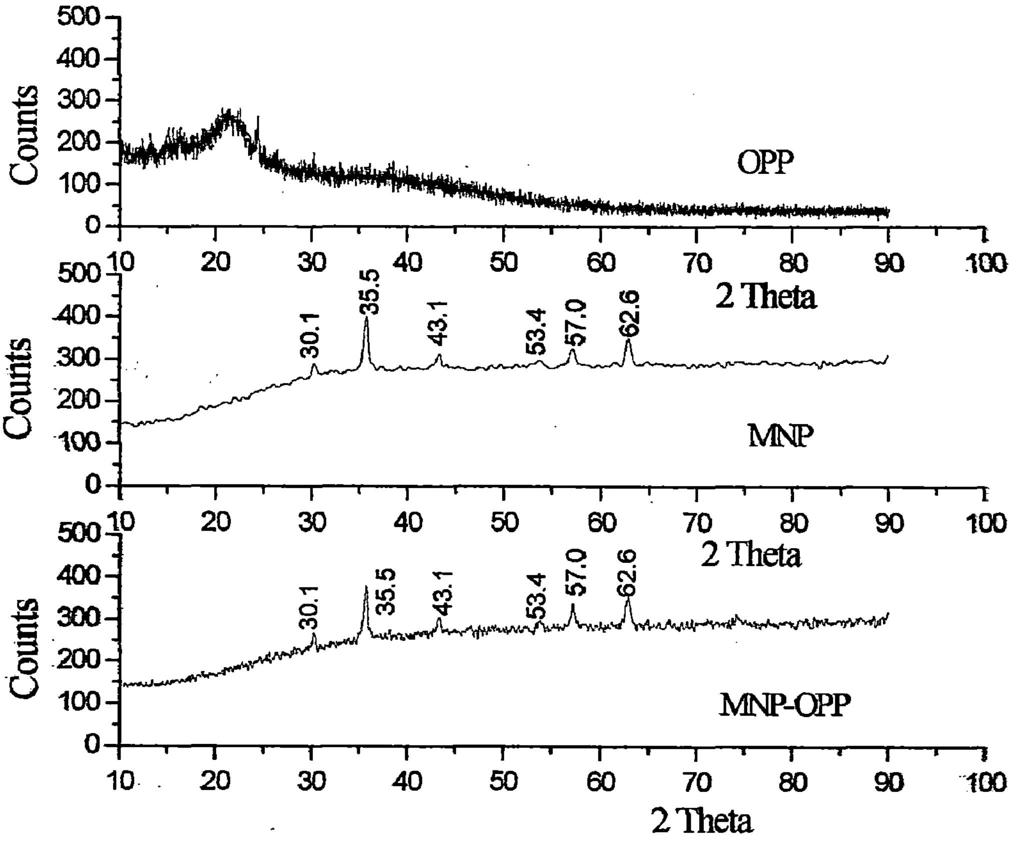


Figure 7.3:

XRD patterns of OPP, MNP and MNP-OPP

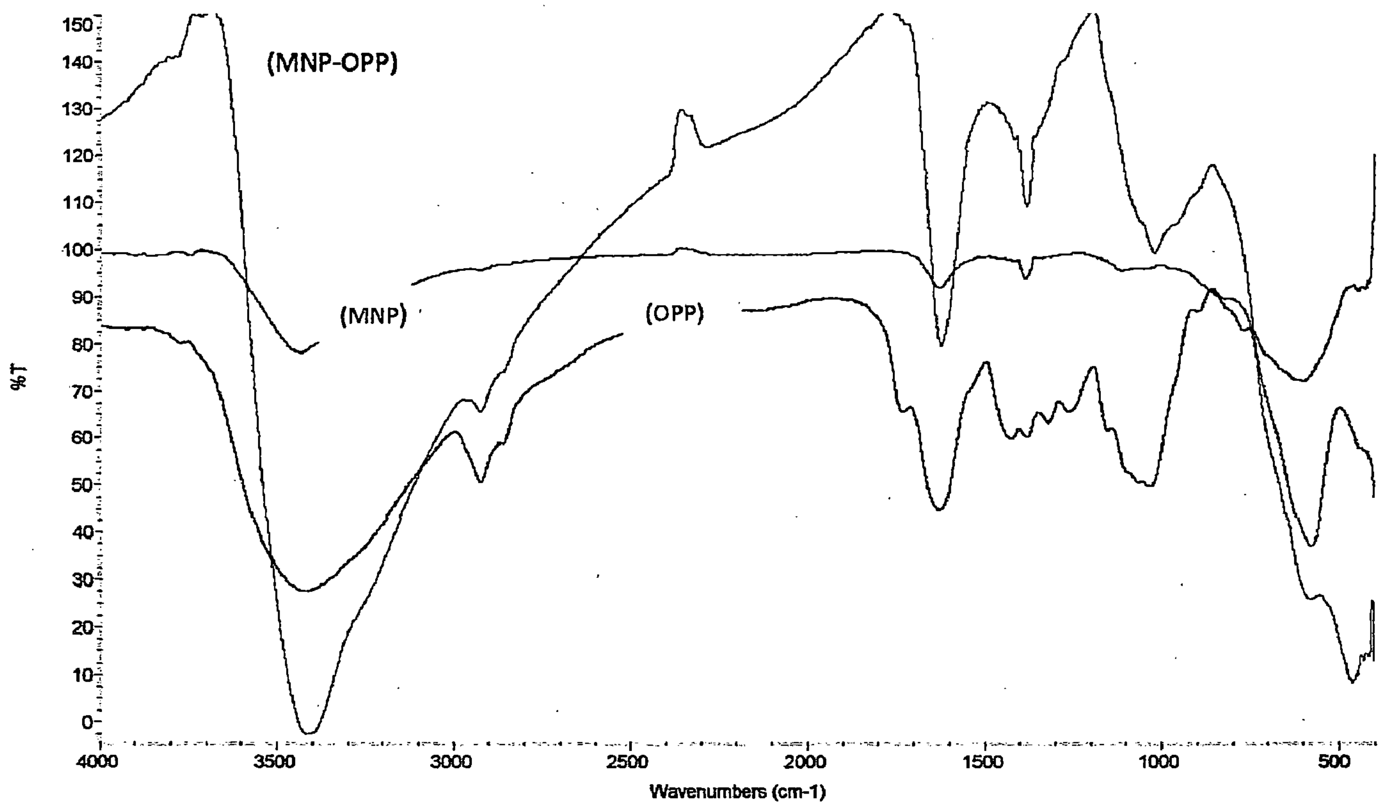


Figure 7.4:

FT-IR spectra of OPP, MNP and MNP-OPP before adsorption

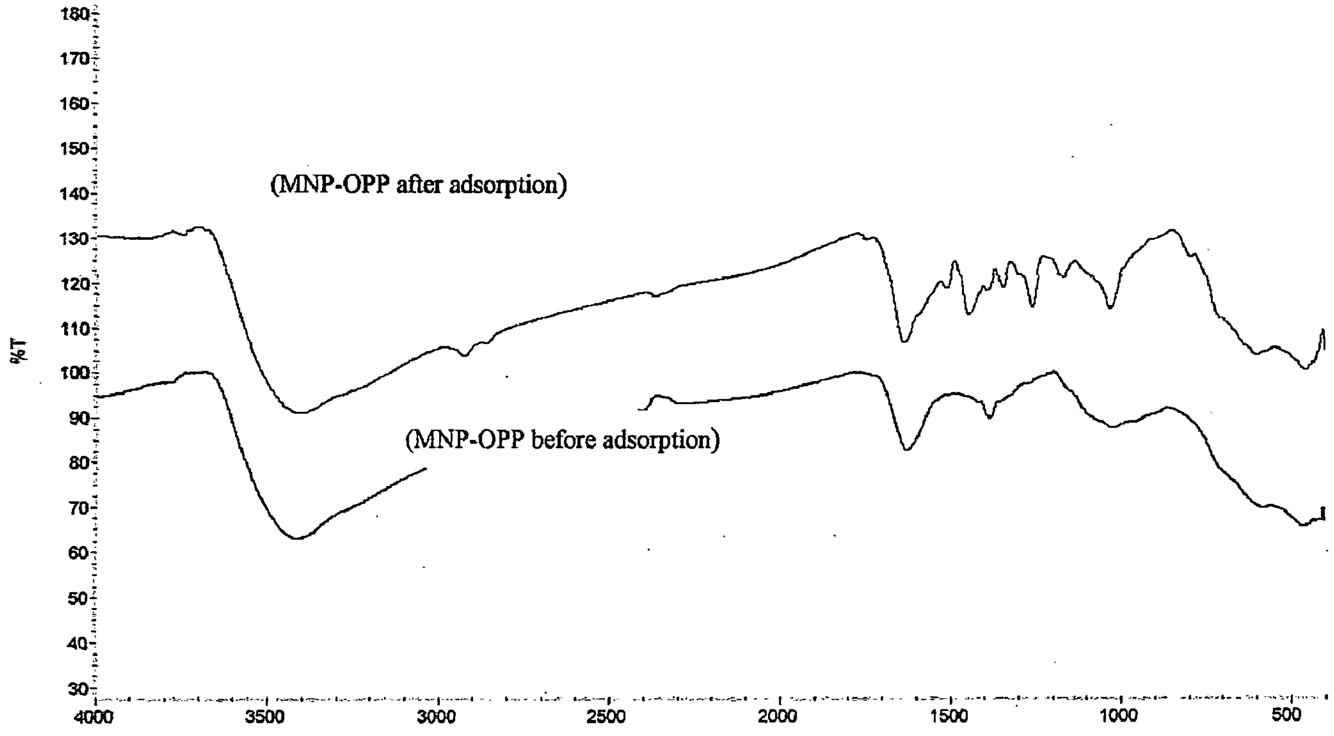


Figure 7.5:

FTIR image of MNP-OPP before and after adsorption

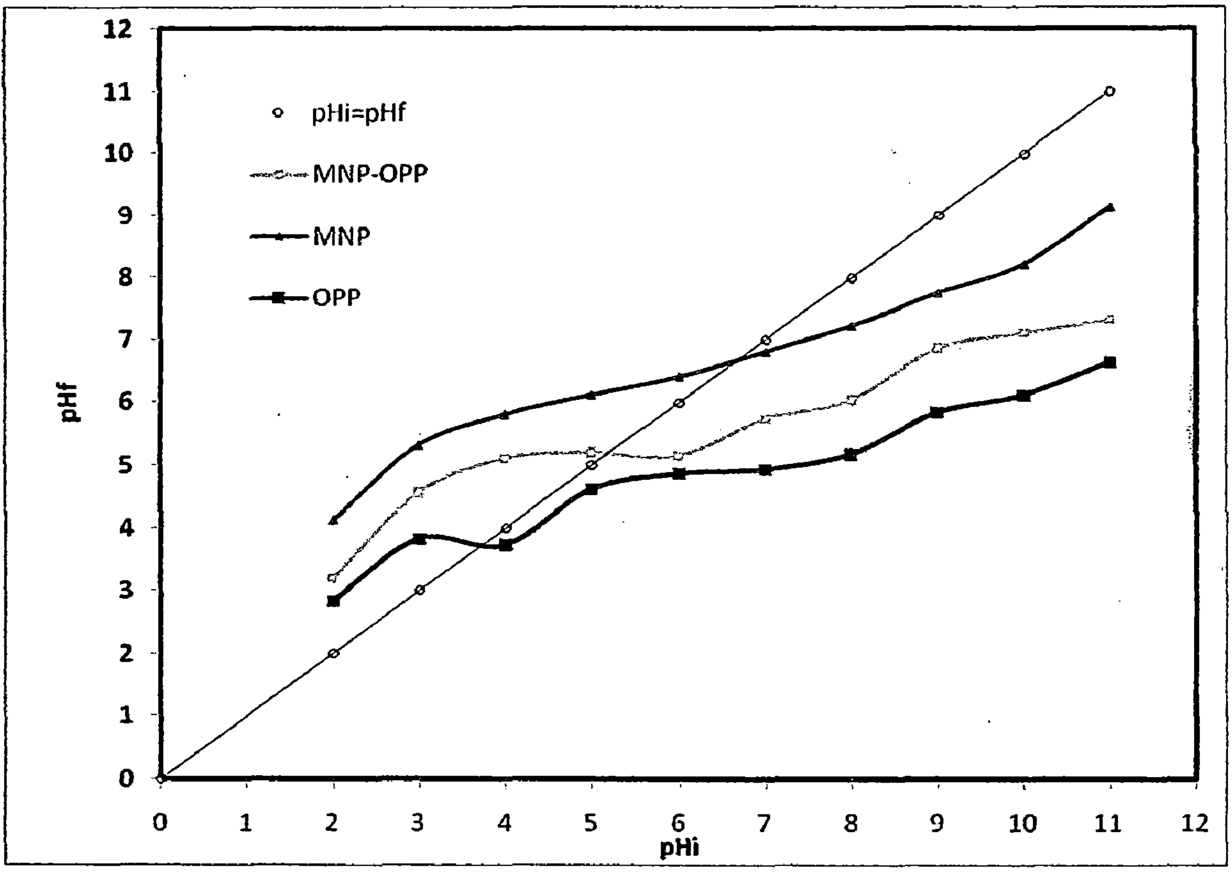


Figure 7.6:

the pH_{pzc} of OPP, MNP and MNP-OPP

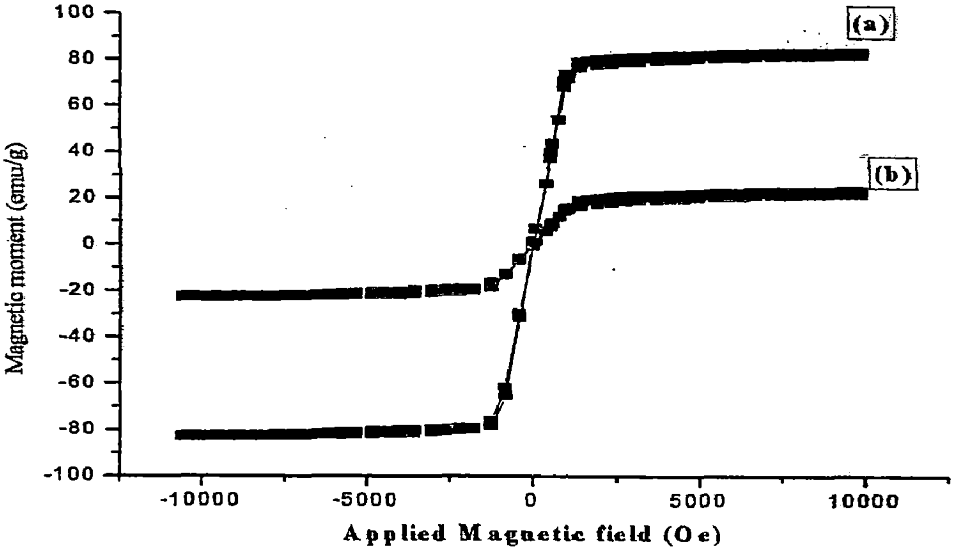


Figure 7.7:

Hysteresis loop from VSM of (a) synthesized MNP and (b) MNP-OPP nanoparticles

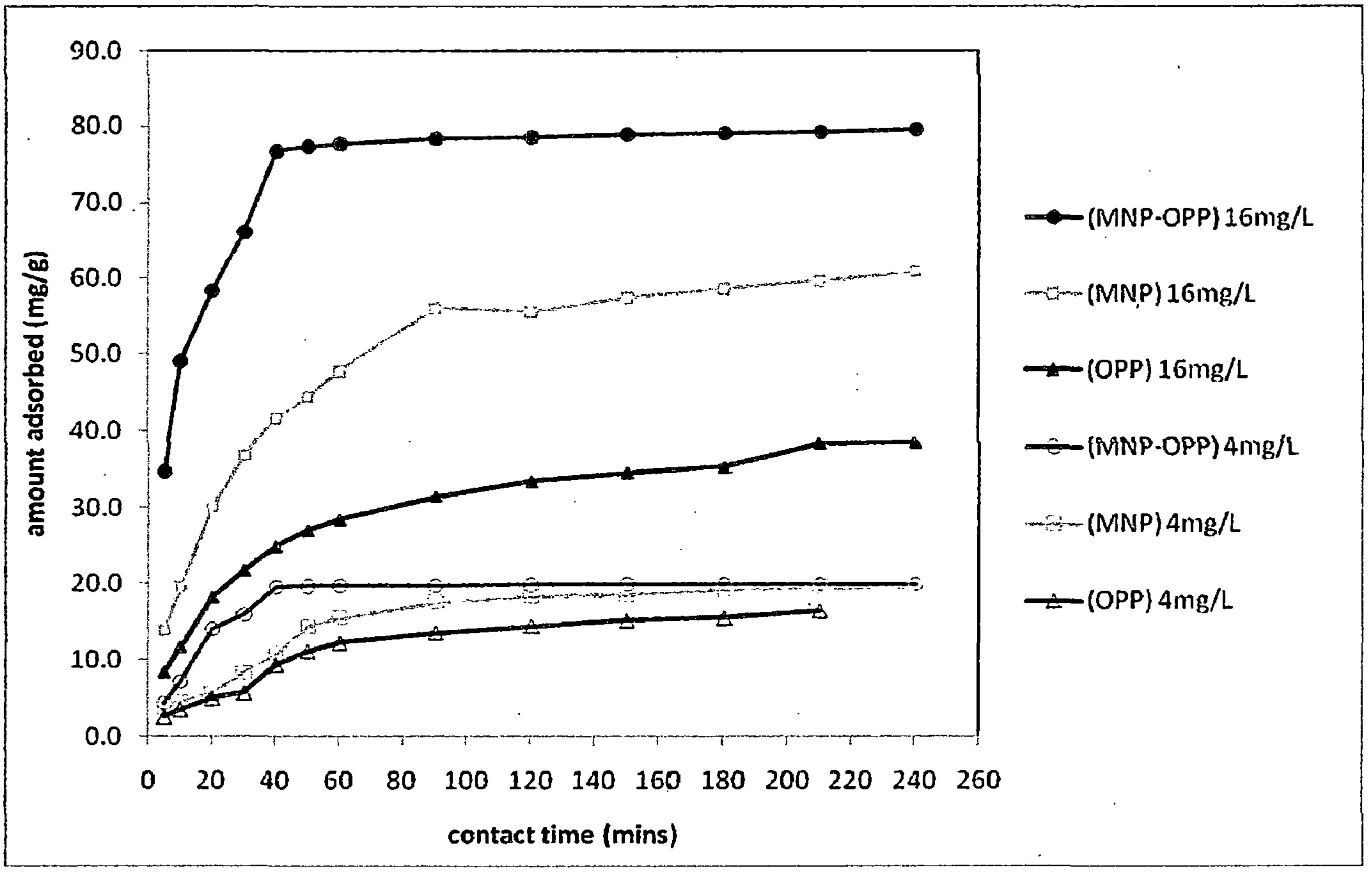


Figure 7.8:

Effect of contact time on the adsorption of Cd^{2+} onto OPP, MNP and MNP-OPP at two different Cd^{2+} concentrations of 4mg/L and 16mg/L [Average value of 3 tests, error < 2.12%]

($NaNO_3$ concentration 0.001M; temperature 318K, adsorbent dose 0.2g/L)

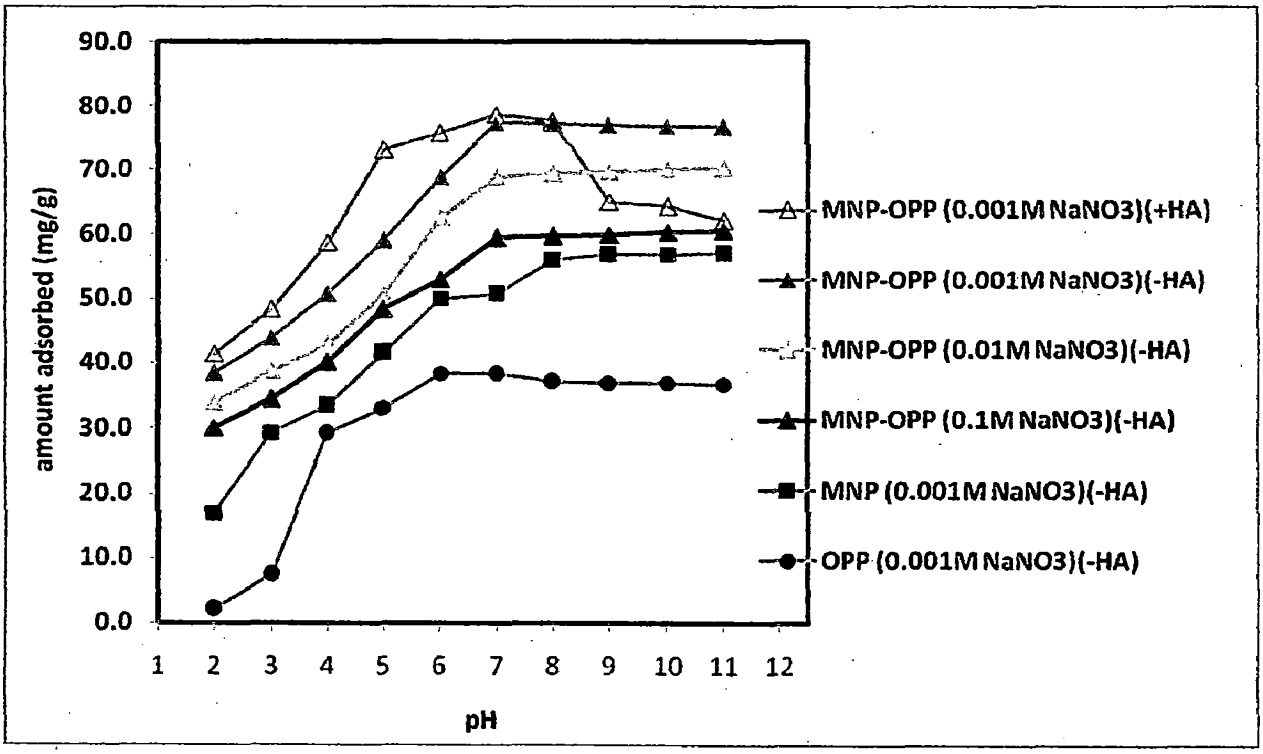


Figure 7.9:

Effect of pH, ionic strength on the adsorption of Cd^{2+} onto OPP, MNP and MNP-OPP in the presence/absence of HA [Average value of 3 tests, error < 2.12%] (Cd^{2+} concentration 16mg/L; HA concentration 10mg/L; time 40 mins for MNP-OPP, 60 mins for MNP and 210 mins for OPP; adsorbent dose 0.2g/L)

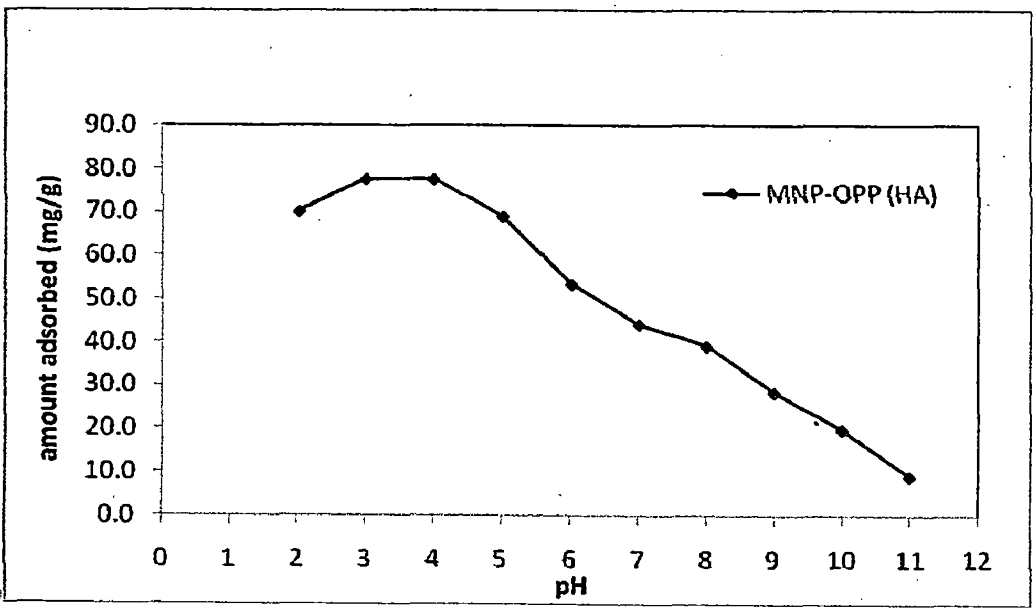


Figure 7.10:

Adsorption of HA onto MNP-OPP as a function of pH [Average value of 3 tests, error < 2.12%] ($NaNO_3$ concentration 0.001M; HA concentration 10mg/L; temperature 318K; adsorbent dose 0.2g/L)

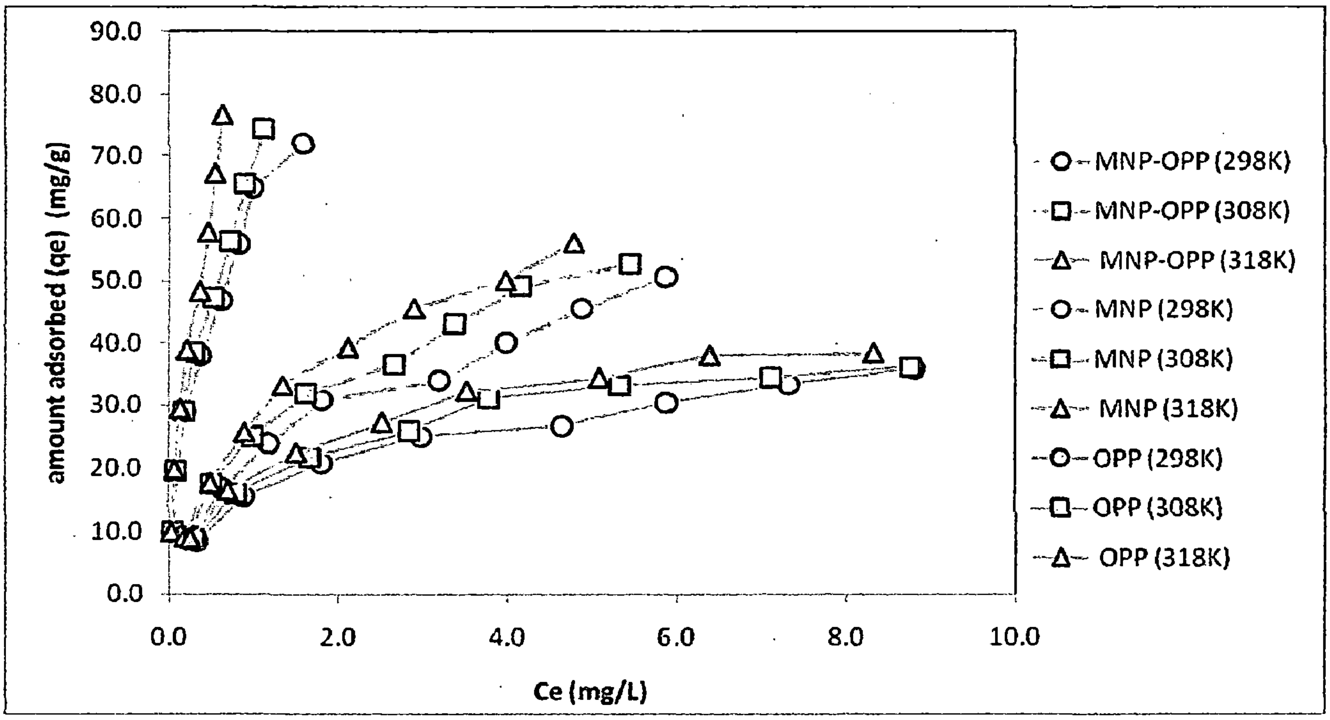


Figure 7.11:

Adsorption isotherm of OPP-Cd^{2+}, MNP-Cd^{2+} and MNP-OPP-Cd^{2+} at 3 different temperatures [Average value of 3 tests, error < 2.12%]

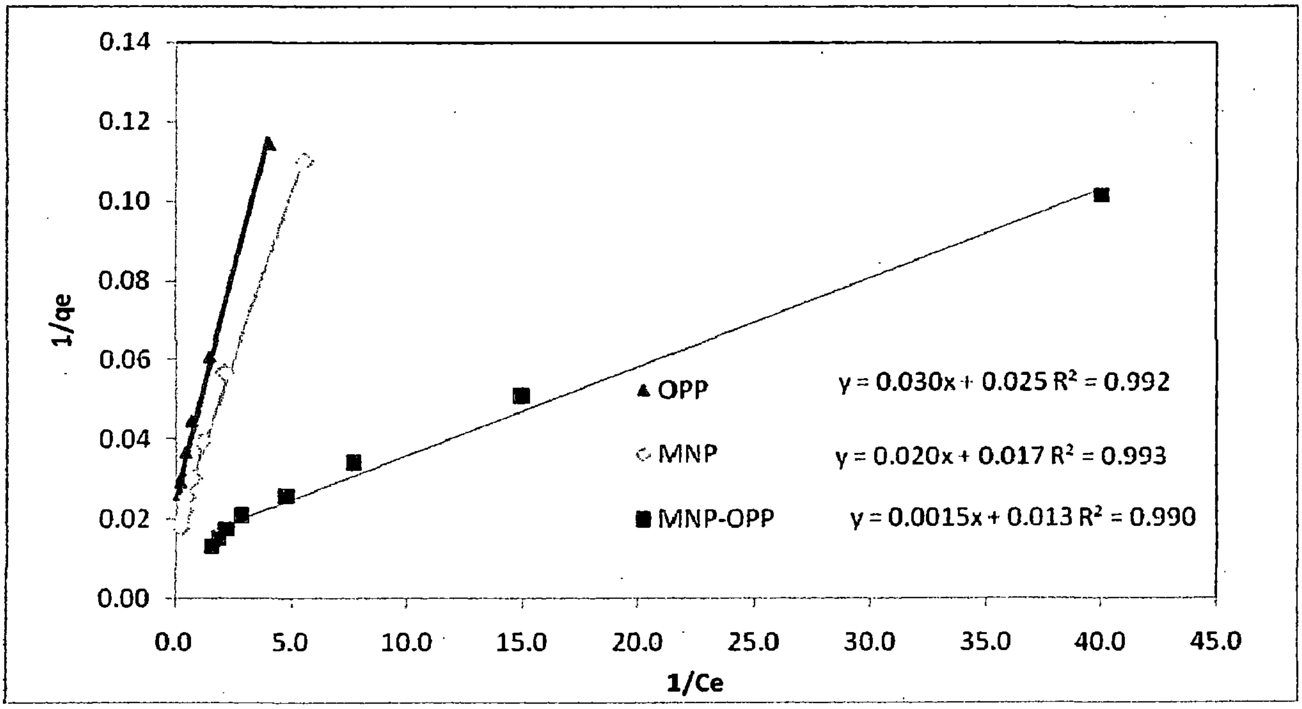


Figure 7.12:

Langmuir plot of OPP-Cd^{2+}, MNP-Cd^{2+}, MNP-OPP-Cd^{2+} [average value of 3 tests, error < 2.12%]

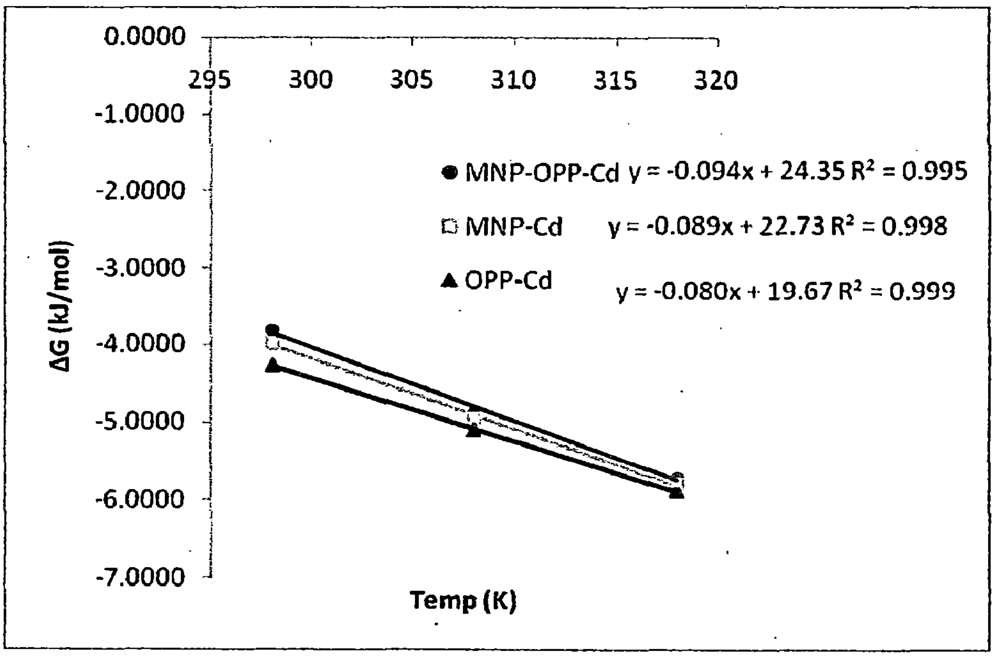


Figure 7.13:

Plot of free energy change vs. temperature for Cd^{2+} adsorption onto MNP-OPP

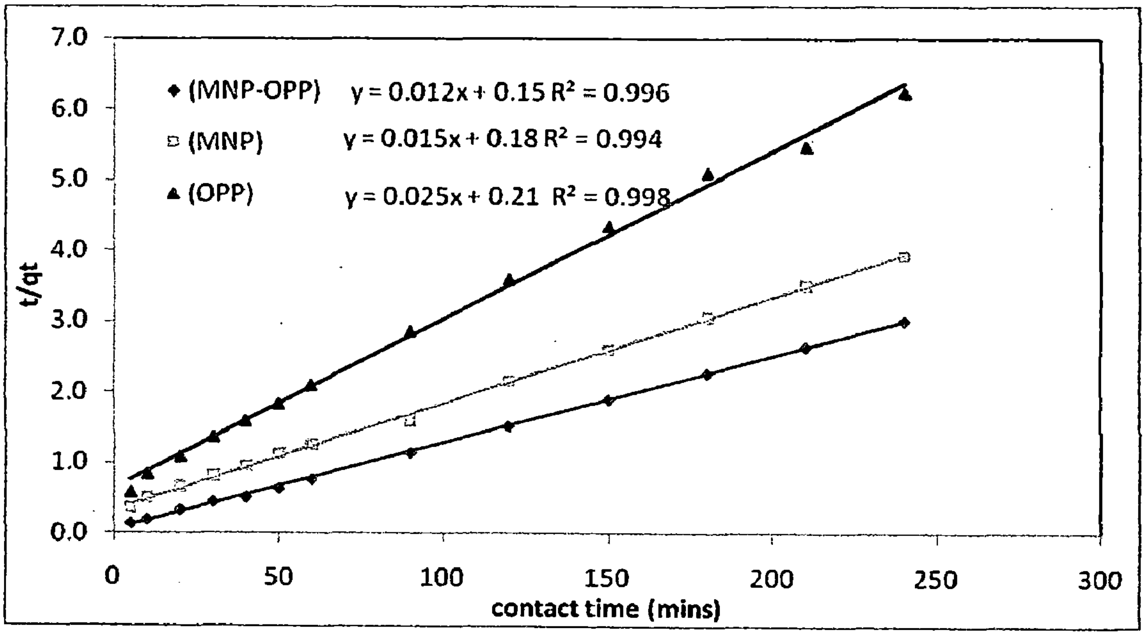


Figure 7.14:

Lagergren's pseudo-second order plot of OPP-Cd^{2+}, MNP-Cd^{2+} and MNP-OPP-Cd^{2+} [average value of 3 tests, error < 2.12%]

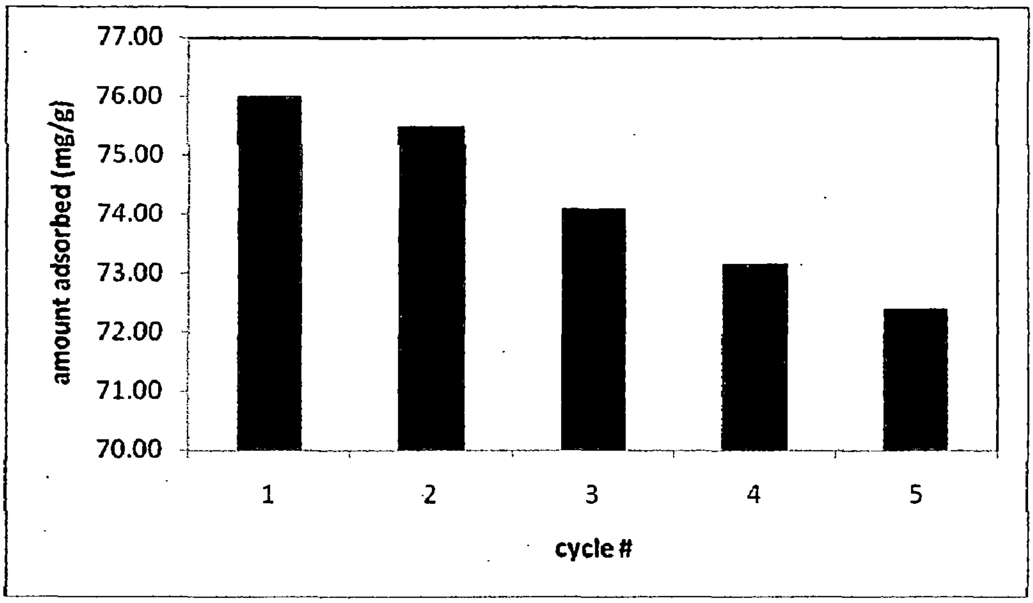


Figure 7.15:

Recycling of MNP-OPP in the removal of Cd^{2+} [average value of 3 tests, error < 2.12%]

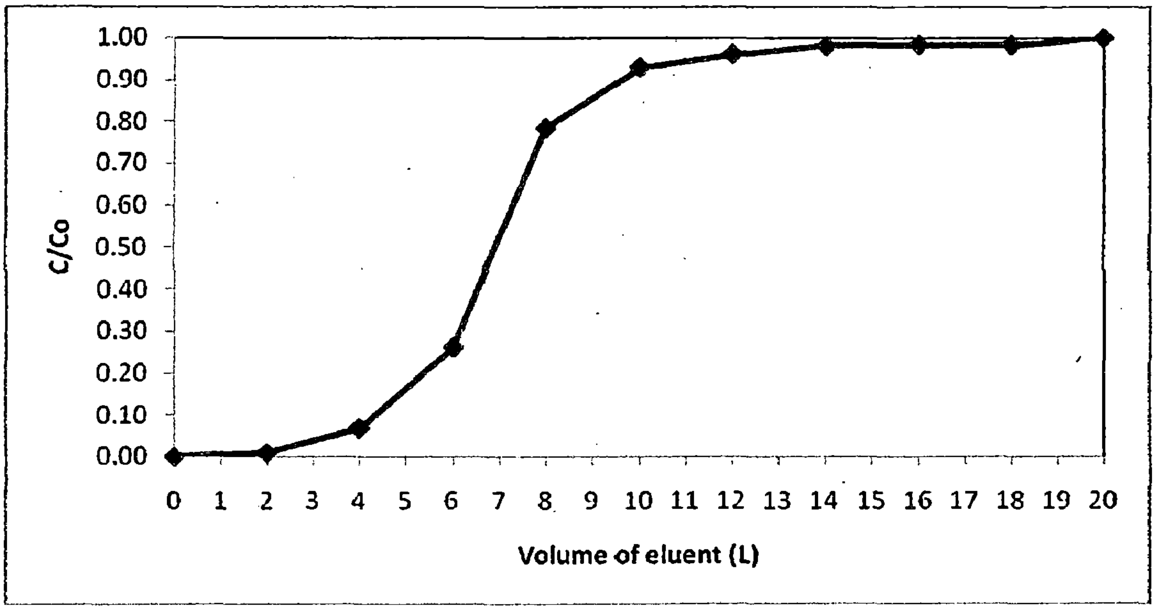


Figure 7.16:

Breakthrough curve of Cd^{2+} adsorption onto MNP-OPP

Table-7.1:

Langmuir Isotherm model and Thermodynamic parameters for the adsorption of Cd^{2+} onto OPP, MNP and MNP-OPP

Adsorbent	C_0 (mg/L)	Temp (K)	Langmuir isotherm parameters				Thermodynamic parameters		
			Q_o (mg/g)	b (L/mg)	R^2	R_L	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol/K)
OPP	16	298	35.71	5.60	0.997	0.011	-4.27	19.67	0.080
		308	37.04	7.32	0.995	0.009	-5.10		
		318	40.00	9.23	0.996	0.007	-5.88		
MNP	16	298	50.00	5.00	0.997	0.013	-3.99	22.73	0.089
		308	52.63	6.91	0.995	0.009	-4.95		
		318	58.82	8.92	0.996	0.007	-5.78		
MNP-OPP	16	298	71.43	4.67	0.997	0.013	-3.82	24.35	0.094
		308	74.63	6.70	0.998	0.009	-4.87		
		318	76.92	8.67	0.994	0.007	-5.71		

Table-7.2:

Kinetic parameters for the adsorption of Cd^{2+} onto OPP, MNP and MNP-OPP

Adsorbent	qe(mg/g) (experimental)	C_0(mg/L)	Pseudo-Second-Order		
			qe (mg/g) (theoretical)	$k_{2,\,ads}$ (g/mg/min)	R^2
MNP-OPP	79.60	16	80.00	0.0010	0.996
MNP	61.00	16	66.67	0.0013	0.994
OPP	38.50	16	40.00	0.0030	0.998

Table-7.3:

Adsorption-Desorption data in consecutive cycles

	Adsorption			**Desorption**	
Cycle #	**C_o (mg/L)**	**C_e (mg/L)**	**qe (mg/g)**	**C_f (mg/L)**	**% desorption**
1	16.00	0.80	76.00	15.71	98.19
2	15.71	0.71	75.05	15.50	98.66
3	15.50	0.68	74.10	15.28	98.58
4	15.28	0.65	73.15	15.10	98.82
5	15.10	0.62	72.40	14.84	98.28

Table-7.4:

Quality of urban waste water simulating a typical Cd-plating industry effluent

	pH	Ni^{2+} mg/L	Zn^{2+} mg/L	Pb^{2+} mg/L	Cd^{2+} mg/L
Quality of waste water before treatment	9.12	9.52	16.28	0.043	35.43
Quality of waste water after treatment	7.23	6.93	9.72	0.040	6.39

Table-7.5:

Adsorption capacities for Cd^{2+} using different adsorbents (at room temperature)

Adsorbent	pH	Adsorption capacity (mg/g)	Reference
Peat	5.0	22.50	[44]
Hazel nut shells	6.0	5.42	[45]
Bamboo charcoal	8.0	12.08	[46]
Sugarcane bagasse	6.0	2.00	[47]
Orange peel (OPP)	7.0	35.71	This study
Orange peel-Fe_2O_3(MNP-OPP)	7.0	71.43	This study

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