Development of low cost adsorbents for the removal of heavy metals from synthetic wastewater

A DISSERTATION

Submitted in partial fulfilment of the

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In

CHEMICAL ENGINEERING

(With specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this report entitled "**Development of low cost adsorbents for the removal of heavy metals from synthetic waste water**", submitted in partial fulfilment of the requirement for the award of the degree of **Master of Technology in Chemical Engineering** with specialization in **Industrial Pollution Abatement**, and submitted to the Department of Chemical Engineering, **Indian Institute of Technology Roorkee** , is an authentic record of the research done by me, under the guidance of Dr. P. Mondal**,** Associate Professor of Chemical Engineering , Indian Institute of Technology Roorkee.

Date: June 16, 2014
Place: IIT Roorkee **SAYAN MITRA**

CERTIFICATE

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

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ABSTRACT

Wastewater generation is a massive problem not only in India but all across the world. Wastewater is generated from industrial and domestic sources. One of the major constituent of the industrial wastewater is heavy metals. Heavy metals are extremely hazardous and pose great threat to the environment. Many of the conventional physico-chemical techniques used for heavy metal removal have their inherent advantages and disadvantages, the cost being a major factor along with the generation and disposal of sludge.

The need of the hour is the viable usage of low cost, eco-friendly techniques for the heavy metal removal from wastewater. Adsorption using Raw Laterite soil, fly ash and bagasse has been studied in the following work.

The adsorbents were chosen for the study due to their low cost and wide availability. In the present study the metal uptake ability of the adsorbents were tested in batch mode. The Raw laterite soil was chosen as the best adsorbent and was further studied. The various process parameters such as contact time, adsorbent dose, pH and the effect of initial concentration were optimized and examined.

The laterite soil showed the best adsorption capabilities at the adsorbent dose 10g/L, at the contact time of 4 hr and at pH 6, the temperature was kept constant at 305K and the rpm at 150. The equilibrium and kinetic studies were performed for the better understanding of the various design parameters. The adsorptive study followed a pseudo-second order model and the Freundlich isotherm was found to fit best to the data generated. Multicomponent adsorption was carried out using raw laterite soil and the data generated fitted well with the Extended Freundlich adsorption isotherm model.

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CHAPTER 1

INTRODUCTION

1.1 General

The growth and progress in industrial sector in the 21st century has taken place not only in India but all over the world. The advancement, however presents several challenges particularly in preservation and protection of the environment. Environmental pollution is caused by the rapid advancements in economic, social and industrial sectors. Generation of waste water is not only a major concern for India, but for the whole world in general.

Heavy metals form major proportion of the industrial waste water. They are extremely hazardous in nature and are of great threat to the environment. Several conventional physico-chemical processes have been utilized for the removal of heavy metals from waste water. They have their own pros and cons; cost being a very important factor along with the generation and disposal of the sludge

For removing heavy metals from waste water, we need to develop low-cost and environment friendly techniques and substances. One such technique has been examined in the present study; adsorption by using laterite soil, flyash and bagasse.

1.2 Heavy Metals

Heavy metals are chemical element which have relatively high densities and are poisonous at low concentrations. Examples of heavy metals include, Arsenic (As), Cadmium (Cd), Chromium (Cr), Mercury (Hg) and Lead (Pb). They are non-biodegradable in nature. To a certain extent they enter our bodies via air water and food. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are hazardous in nature, have long half-lives and are capable of accumulating in various living organisms, thereby hampering with their natural growth and functioning.

Living beings require varying amounts of essential heavy metals such as cobalt, copper, Iron, manganese etc. for endurance; but high levels can be harmful. Other non-essential heavy metals such as chromium, mercury and lead are lethal and their accumulation over time causes various illnesses

Heavy metals pose serious risk to human health and disrupt the human metabolic functions; this is generally done in two ways (Singh et al., 2011; Singh 2007):

a) The heavy metals accumulate in the human body, thereby disturbing the efficiency of the organs and vital glands.

b) They disturb the essential minerals from their original positions and hamper their biological functioning.

1.2.1 Sources of Heavy metals

Pollution occurs due to the presence of toxic elements arising from natural and anthropogenic sources. Natural sources comprise of seepage from rocks into aquatic bodies, volcanic activity, forest fires etc. The man-made sources of pollution consist of smelting, electroplating, production of energy and fuel, excessive use of insecticides and pesticides and industrial manufacturing. (Sekomo et al., 2012; Chen et al., 2011; Ali et al., 2004)

With rapid growth in industrial sectors and rampant consumerism, the effects of anthropogenic sources of pollution have escalated quickly. (Sahni, 2011) The metal specific industrial sources of heavy metals are summarised in Table 1.1 whereas Table 1.2 lists the key Indian sites contaminated with heavy metals.

Table 1.1: Sources of heavy metals (Web 1)

Metal	**Industry**	**Surface water(mg/l)**	**Ground water(mg/l)**
Chromium (Cr)	Mining, industrial coolants, chromium salts manufacturing, leather tanning	2.0	0.1
Lead (Pb)	Lead acid batteries, paints, E-waste, Smelting operations, coal- based thermal power plants, ceramics, bangle industry	0.10	0.015
Mercury (Hg)	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste (damaged thermometers, barometers, sphygmomanometers), electrical appliances etc.	0.01	0.002
Arsenic (As)	Geogenic/natural processes, smelting operations, thermal power plants, fuel burning	0.20	0.01
Copper (Cu)	Mining, electroplating, smelting operations	3.0	0.06
Vanadium (Va)	Spent catalyst, sulphuric acid plant	0.10	0.006
Nickel (Ni)	Smelting operations, thermal power plants, battery industry	3.0	3.0
Molybdenum (Mo)	Spent catalyst	0.05	0.01
Zinc (Zn)	Smelting, electroplating	5.0	0.4
Cadmium (Cd)	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations & fuel combustion	0.20	0.005

Table 1.2 Major heavy metal contaminated sites in India (Sahni, 2011)

Metals				
Chromium	**Lead**	**Mercury**	**Arsenic**	**Copper**
Ranipet, Tamil Nadu	Ratlam, Madhya Pradesh	Kodaikanal, Tamil Nadu	Tuticorin, Tamil Nadu	Tuticorin, Tamil Nadu
Kanpur, Uttar Pradesh	Bandalamotu Mines, Andhra Pradesh	Ganjam,Orissa	West Bengal	Singbhum Mines, Jharkhand

Vadodara, Gujarat	Vadodara, Gujarat	Singrauli, Madhya Pradesh	Ballia and other districts, UP	Malanjkahnd, Madhya Pradesh
Talcher, Orissa	Korba, Chattisgarh			

1.2.2 Toxicity due to Metals

Living organisms are very much affected due to heavy metal poisoning. Symptoms include: amnesia, headaches, Stomach upsets, and allergies, visual and auditory problems etc. Some of the very well documented heavy metals health hazards are summarized in Table 1.3.

Table 1.3 Health impact of heavy metals [Martin and Griswold, 2009; Singh et al., 2011]

Heavy Metals	**Health Impact** (Due to uptake of high quantities)
Arsenic (As)	Skin damage or problems with circulatory systems, bronchitis and increases risk of getting cancer
Cadmium (Cd)	Kidney damage, renal dysfunction, lung disease, lung cancer and bone disease such as Itai-Itai
Chromium (Cr)	Kidney damage, liver damage, nerve tissue damage, causes fatigue and irritability
Copper (Cu)	Stomach upset, kidney damage and anaemia
Lead (Pb)	Deficiency in fine motor functions in children, kidney problems, high blood pressure, congenital paralysis, sensor neural deafness
Mercury (Hg)	Tremors, kidney damage, neurological damage, acrodynia characterized by pink hands and feet, spontaneous abortion
Zinc (Zn)	Stomach cramps, skin irritations, vomiting, nausea and anaemia, fumes of zinc have corrosive effect on skin and cause damage to nervous system
Nickel(Ni)	Cancer, Respiratory failure, Birth defects, Allergies, and Heart failure
Manganese (Mn)	Inhalation and contact causes damage to central nervous system
Barium (Ba)	Contact may cause vomiting, high blood pressure, abdominal cramps, diarrhoea and difficulty in breathing

1.2.2.1 Lead

Lead is a very dangerous element which may cause severe damage even in very minute proportions. Due to several anthropogenic activities, like manufacture and burning of fossil fuel, mining, lead based compounds are scattered all around the globe, even in the atmosphere, hydrosphere and lithosphere. Lead can be utilized in several ways; it is used in the production of bullets and shells, for X-ray shielding devices, lead batteries and metallic products like pipes. Nowadays the major sources of exposure to lead are water pipes in older homes, lead-based paints, household dust, contaminated soil, lead-glazed pottery and lead in certain cosmetics and toys (Salem et al., 2000; Martin and Griswold, 2009).

In adults there are 20-30% chances of lead poisoning and in children the figure stands almost 50%. Lead is absorbed generally through the intestinal tract or it can also be absorbed through lungs. Since lead is chemically similar to calcium due to its size and charge similarities the body treats its uptake like that of calcium.

This is the reason for which lead is present in several organs of the human body. It is present in brain, lungs, teeth and bones, bones being highly affected. When calcium consumption increases, the lead present in the bones is replaced by calcium. Lead freely mobilizes in various parts of the body (Salem et al., 2000). The following are the general indications of lead toxicity

- Seizures
- Tremor
- Encephalopathy
- Coma
- Motor neuropathy
- Cerebral edema
- Renal failure
- Abdominal cramping
- Lethargy
- Myalgias
- Constipation
- Abdominal pain
- Headache
- Vomiting

1.2.2.2 Chromium

Chromium is released in the environment from several industrial sectors like tannery facilities, welding, ferro-chrome pigment production industries and metal treatment

Chromium has the ability to be present in all three states; as a solid, liquid, or gas. Chromium is utilized in metal alloys such as stainless steel, magnetic tapes, as pigments for paints, cement, paper, composition floor covering, and rubber, in wood preservatives and for protective coatings on metal surface by electroplating. Electroplating releases chromic acid spray and chromium trioxide that results in the direct damage of skin and lungs. Also chromium dust may lead to lung cancer. (Martin and Griswold, 2009; Salem et al., 2000).

Several factors determine whether exposure to chromium is harmful or not. These are the dosage of chromium contact, the form of chromium (chromium VI as opposed to chromium III) and the duration,

Chromium can be ingested through breathing of air that contains chromium. Minute quantities of chromium might also enter the body through the gastro-intestinal tract or on exposure to the skin. The following are the symptoms due to chromium toxicity.

- Irritation on the lining of the nose
- Runny nose
- Asthma
- Shortness of breath
- Wheezing
- Irritation and ulcer caused in stomach
- Anaemia
- Tumour
- Damage to intestinal tract
- Lung cancer
- Damage to the reproductive system

1.3 Wastewater

Out of the total percentage of the world’s resources, India accounts for about 2.4% of landmass and for about 4% of water. The total water reserves in the country are predicted to be around 1123 BCM (Kaur et al, 2012). India’s water problem is an artificially created crisis due to human misuse, as India has a favourable climate with enough rainfall and presence of several water sources. One of the principal reasons for water shortages are exceedingly poor management, vague and unclear laws, and corruption of government, industrial and human wastes. (Mehta, 2012)

Multi-sectorial demands for water due to the continuous economic growth of India combined with the amplified energy usage is one of the major reasons for the increased requirement. Another reason for the enhanced water demand is growth in population and agricultural utilization, due to these reasons India’s limited water resources are diminishing at an alarming rate and this may cause the per capita availability of water to reduce under 1000 cubic meters in the coming decade. (Web 5)

An estimated 22900 MLD of residential wastewater is being generated from metropolitan areas on a daily basis while 13500 MLD of wastewater is being introduced from the industrial sector; whereas the treatment capacity available for domestic sewage is around 5900 MLD and it is around 8000 MLD for industrial sewage. There is an enormous gap between the treatment and the generation of wastewater which needs to be rectified immediately to avoid future problems (Web 5; Kaur et al, 2012).

There is a crucial need for effectual water management through recycling and improved usage efficiency (Kaur et al, 2012). The Indian government must strive to achieve a balance between the conflicting requirements of the urban and the rural masses, the economy and the environment, in addition to avoiding a water stress situation by incorporating its state-wide water management programs at a national level. (Mehta, 2012)

Wastewater consists of a mixture of agricultural runoffs, sewage water, industrial waste discharges and hospitals wastes. In order to curtail the environmental and health risks posed by these pollutants, the quantities of the pollutants generated need to be brought down to permitted limits for safe disposal and reuse of wastewater. (Kushwah et al., 2011)

Management of wastewater in India has become a tremendously important sphere of focus due to growing consideration of health norms and also due to the alarming growth in population. Despite the increased recycle of wastewater in the last few years, due to the increased government backing and private partaking, wastewater generation is still a huge problem (Web 5). The current sewage generation and treatment capacity status of various metropolitan cities is listed in Table 1.6; also the total percentage of generated and treated wastewater is listed in Fig. 1.1.

Table 1.4 Wastewater generation and treatment capacity of metropolitan cities (CPCB 2005)

S. No.	**Name of the City**	**Sewage generation(in MLD)**	**Sewage Treatment Capacity (in MLD)**	**Percent of treatment capacity**
1	Hyderabad	426	593	100
2	Vishakhapatnam	135	-	-
3	Vijayawada	128	-	-
4	Patna	279	105	37
5	Delhi	3800	2330	61
6	Ahmadabad	472	488	96
7	Surat	432	202	46
8	Rajkot	108	44.5	40
9	Vadodara	180	206	100
10	Bangalore	772	-	-
11	Indore	204	78	38
12	Bhopal	335	22	6
13	Jabalpur	143	-	-
14	Mumbai	2671	2130	80
15	Pune	474	305	64
16	Nagpur	380	100	26
17	Nasik	227	108	47
18	Ludhiana	235	311	100
19	Amritsar	192	-	-
20	Jaipur	451	54	11
21	Chennai	158	264	100
22	Kanpur	417	171	41
23	Lucknow	364	42	11
24	Agra	260	88	33
25	Kolkata	706	172	24
26	Faridabad	164	65	39
27	Jamshedpur	199	-	-
28	Asansol	147	-	-
29	Coimbatore	120	-	-
30	Madurai	98	-	-
31	Meerut	177	-	-
32	Varanasi	230	102	44
33	Allahabad	176	60	34
34	Kochi	188	-	-
35	Dhanbad	192	-	-
	Total	**15644**	**8040**	**51**

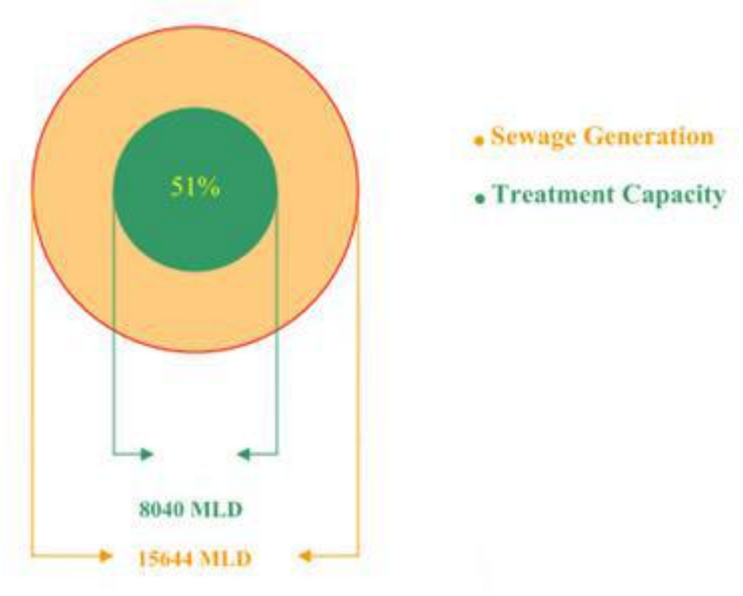


Fig 1.1 Sewage generation and treatment capacity in Metropolitan Cities (CPCB, 2009-10)

1.3.1 Wastewater treatment methods

The treatment of wastewater provides ways and means of removing different toxins and pollutants from industrial and residential wastewater. Several physico-chemical and biological methods have been adopted and employed to remove different kinds of impurities. The objective of various wastewater treatment methods essentially aims to generate an ecologically harmless liquid stream or treated sludge; having the contaminants up to the specified limits which are suitable for recycling or disposal (Web 6).

Wastewater treatment involves three stages, primary, secondary and tertiary. A stage that precedes these three steps is the pre-treatment stage. This step deals with the removal of the readily collectable large sized materials that may otherwise choke the pumps of the primary treatment facilities. The various methods used are screening, sieving, gravel and sand removal, flow equalization (Web 6). Primary treatment step is concerned with the physical treatment, secondary treatment step deals with the biological treatment and the tertiary treatment takes place when the prescribed limits are not met by the secondary treatment. The various types of methods used in each type of treatment are listed in Table 1.7 and the various step of wastewater treatment are shown in Fig 1.2:

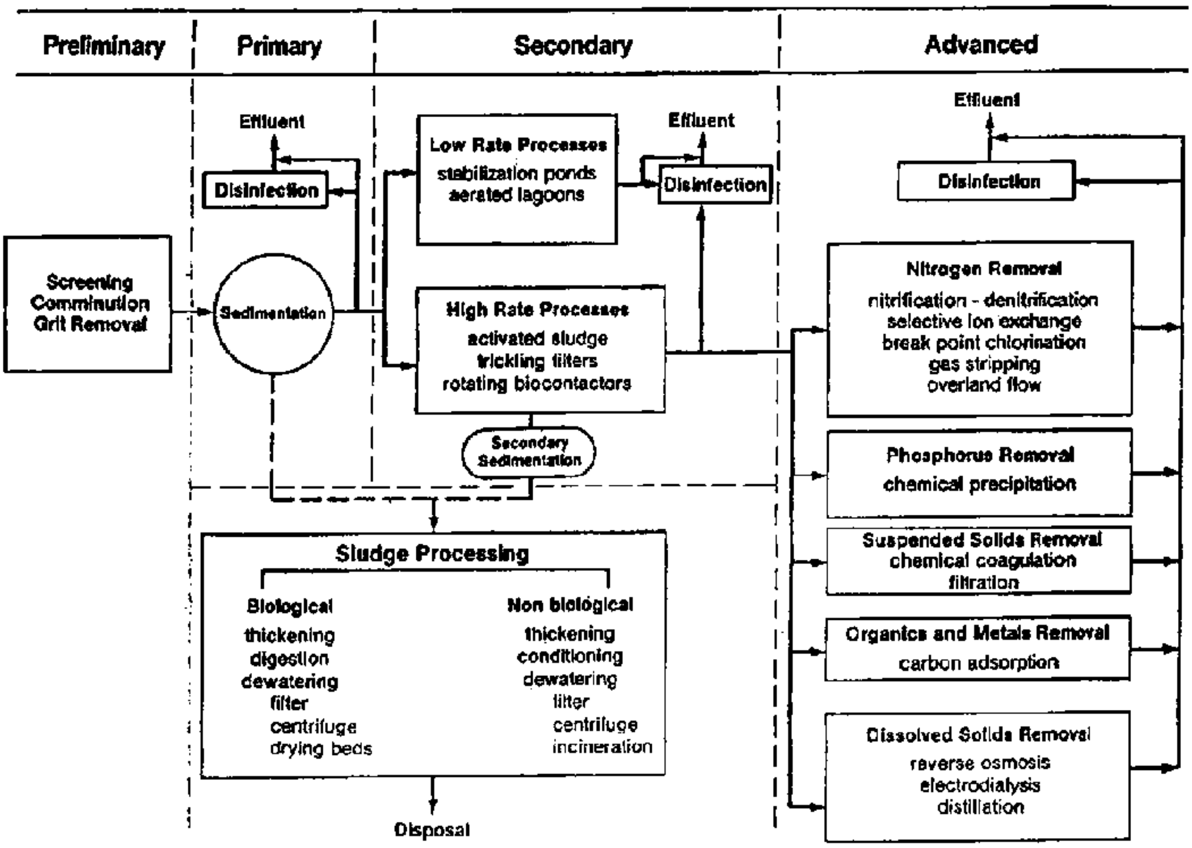


Fig 1.2 Different steps involved in wastewater treatment (Web 6)

Table 1.5 Methods used for waste water treatment (Sekomo et al., 2012)

Primary Methods (Physico-chemical methods	**Secondary Methods (Biological methods**	**Tertiary methods**
• Adsorption • Coagulation-flocculation • Precipitation • Floatation • Chemical oxidation • Membrane separation • Sedimentation • Sand filtration	• Lagoon • Aerated Lagoon • Activated Sludge • Trickling Filter • SBRs and MBRs • Anaerobic treatment	• Electro dialysis • Foam Separation • Ozone oxidation • Ion Exchange

The wastewater treatment procedures mentioned in Table 1.7 are costly and include several intricate operations along with a lot of maintenance. The other drawbacks of the conventional techniques are generation and disposal of the sludge, high requirement of chemicals and fouling of membranes. The cost of different levels of treatments has been summarized in Table 1.6.

Table 1.6 Cost of different levels of treatment of wastewaters (Kaur et al., 2012)

Specifications	**Primary treatment system**	**Simultaneous Primary and Ultra-filtration system**	**Simultaneous Primary, ultra-filtration and reverse osmosis system**
Capital cost (Rs lakhs)	30	91	145
Annualized capital cost (@15% p.a. Interest & depreciation	6	18	30
Operation and maintenance cost (lakhs/annum	6	7	13
Annual burden (Annualized cost +O&M cost) Rs. Lakhs	12	27	43
Treatment cost Rs./kl (Without interest and depreciation	34	52	73

Taking into consideration, the needs of a developing country like India. It is very difficult for the government to come up with the budget to utilize these techniques on nationwide bases. The need of the hour is the usage of techniques which are not costly and are environment friendly at the same time, one such type of technique is adsorption by using low cost and readily available adsorbents.

If adsorbents meet the following criterion, then adsorption can be very advantageous.

I. **Selectivity:** an adsorbent must selectively bind the target component(s). Adsorbents being porous, most of the uptake occurs within an adsorbent particle. Different components are likely to diffuse at different rates giving rise to selectivity for the molecules which diffuse faster than the other. For some adsorbents, selectivity is governed by the difference in the affinity of the target molecules from that of the other molecules. Further the molecular size and the shape of the components vary in a mixture. So, some of the components may not enter the pore of an adsorbent if the molecular size is greater than the pore size. The above three factors affinity, size and intraparticle diffusion rate determine the selectivity individually or collectively.

II. **Adsorption capacity**: an adsorbent must have relatively high capacity of adsorption so that the adsorbent required for separation is not large. It depends primarily on the affinity of adsorption and the specific surface area of the adsorbent (m^2/g). Capacity may slowly decrease upon repeated use and regeneration.

III. **Ease of separation**: if the relative volatility of the components in a mixture is close to unity, both capital and operating costs may be controlled and adsorption may be an attractive option.

IV. **Solute concentration**: low concentration of the target components in the feed favours the balance in case of adsorption

V. **Process conditions**: separation by adsorption is desirable when the process parameters are mild. This is important if the adsorbent is susceptible to thermal damage

Table 1.7: Performance characteristics of various heavy metal removal /recovery Technologies

Technology	pH change	Metal selectivity	Influence of Suspended	Working level For appropriate metal
Adsorption,e.g Granulated Activated carbon	Limited tolerance	Moderate	Fouled	<10
Electro Chemical	Tolerant	Moderate	Can be engineered to tolerate	>10
Ion exchange	Limited Tolerance	Chelate -resins can be selective	Fouled	>10
Membrane	Limited Tolerance	Moderate	Fouled	>10
Precipitation Hydroxide	Tolerant Limited	Nonselective Limited selective	Tolerant	>10
Solvent extraction	Some systems pH tolerant	Metal selective Extractants available	Fouled	>100

1.4 Adsorbents used for the removal of heavy metals

The Lateritic soil structure varies from a loose grainy material to a massive rock type formation. It is generally dusty red in colour due to the occurrence of large quantities of iron. This soil is found in the tropical and sub-tropical regions as it requires extreme temperatures and large quantities of rainfall for its development (Maji, 2007). The term laterite was first introduced into the geological terminology by Francis Buchanan in 1807; he discovered the formations in southern India and coined the name laterite originating from the Latin term “later” meaning brick. (Chowdhury et al., 1965)

Laterite occupies a place of enormous importance in the Indian geology. It has massive economic potential as it is the source of various industrial minerals such as bauxite, manganese ore, iron ore etc. (Chowdhury et al., 1965)

Laterites are the by-products of acute and long lasting tropical rock weathering. To properly appreciate the formation of laterite, emphasis must be put on the chemical reactions happening between the uncovered rocks at the earth’s surface and the penetrated rain water. The factors affecting these reactions are the extent of lateritization, the mineral constitution and porosity of the rocks, properties of the interacting water such as dissolved elements, temperature, pH-Eh which are ultimately regulated by the climate, foliage and the structure of the land.(Web 9; Maiti, 2012)

Heavy rainfall on interacting with rocks, washes out the bases, silicic acid and other soluble components of the soil and in the process enriching it by leaving behind the clay minerals such as kaolinite, gibbsite, iron, silicates, aluminium and goethite leading to the formation of laterite concrete (coarse grained vermicular material) or laterite soil (soft rocks and fine grained soil with lower concentration of Fe and Al). It is due to this iron and aluminium existence that laterite soil can be used as an adsorbent for the uptake of heavy metals. (Maiti, 2012; Maji, 2007)

The extent of lateritization (Tropical weathering) can be described by the silica-sesquioxide (S-S) ratio (Maiti, 2012):

- A ratio of 1.33 or lesser depicts is laterite concretion
- A ratio of 1.33 to 2.00 depicts laterite soil
- A ratio of 2.00 or more depicts the soil to be non-lateritic tropical soil

Laterite soils have generally been used as bricks for buildings, for layering of roads, used for layering in aquifers due to its porous nature, in cement industry for reducing the temperature of clinker and subsequently supplying both aluminium and iron, for wastewater treatment, for recovery of ores such as bauxite, iron, nickel, aluminium.

Laterite is abundantly available not only in India but all around the world. It has been found out that laterites cover about 1/3rd of the entire earth's continental landmass. In the world they are particularly found in Australia, Brazil, Nigeria, Colombia, Central Europe, Burma, Guatemala, Cuba, Indonesia and Philippines (Web 10). In India they are well developed on Eastern Ghats, Rajmahal hills, Sahyadris and Vindhyas.

They also occur at lower levels and in the valleys. Important areas include Kerala, Bangalore, Mysore, Karnataka, Maharashtra, Andhra Pradesh, Orissa, West Bengal, Assam, Meghalaya, Jharkhand and Uttar Pradesh. Due to its abundant availability, low cost, porous nature and other morphological features, laterite soil is a good prospective adsorbent for the removal of contaminants from water.

1.5 Fly Ash

The combustion of pulverized coal at high temperatures and pressures in power stations produces different types of ash. The 'fine' ash fraction is carried upwards with the flue gases and captured before reaching the atmosphere by highly efficient electro static precipitators. This material is known as Pulverized Fuel Ash (PFA) or 'fly ash'.

Fly ash is a fine, glass powder recovered from the gases of burning coal during the production of electricity. These micron-sized earth elements consist primarily of silica, alumina and iron. The difference between fly ash and portland cement becomes apparent under a microscope. Fly ash particles are almost totally spherical in shape, allowing them to flow and blend freely in mixtures. That capability is one of the properties making fly ash a desirable admixture for concrete.

Fly ash is one of the residues generated in the combustion of coal. Fly ash is generally captured from the chimneys of coal-fired power plants, whereas bottom ash is removed from the bottom of the furnace. In the past, fly ash was generally released into the atmosphere, but pollution control equipment mandated in recent decades now requires that it be captured prior to release. Depending upon the source and makeup of the coal being burned, the components of the fly ash produced vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO). Fly ash is commonly used to supplement Portland cement in concrete production, and is increasingly finding use in the synthesis of geopolymers and zeolites.

1.6 Bagasse

Bagasse is a fibrous matter that remains after sugarcane stalks are crushed to extract their juice. (Web 2) It is used as a bio-fuel and in the manufacture of pulp and building materials.
Bagasse is often used as a primary fuel source for sugar mills; when burned in quantity, it produces sufficient heat energy to supply all the needs of a typical sugar mill, with energy to spare. To this end, a secondary use for this waste product is in cogeneration, the use of a fuel source to provide both heat energy, used in the mill, and electricity, which is typically sold on to the consumer electricity grid. The resulting CO_2 emissions are equal to the amount of CO_2 that the sugarcane plant absorbed from the atmosphere during its growing phase, which makes the process of cogeneration greenhouse gas-neutral.

In many countries (such as Australia), sugar factories significantly contribute 'green' power to the electricity supply. For example, Florida Crystals Corporation, one of America's largest sugar companies, owns and operates the largest biomass power plant in North America. The 140 MW facility uses bagasse and urban wood waste as fuel to generate enough energy to power its large milling and refining operations as well as supply enough renewable electricity for nearly 60,000 homes. Ethanol produced from the sugar in sugarcane is a popular fuel in Brazil. The cellulose-rich bagasse is being widely investigated for its potential for producing commercial quantities of cellulosic ethanol. For example, BP is operating a cellulosic ethanol demonstration plant based on cellulosic materials in Jennings, Louisiana

CHAPTER 2

2.1 LITERATURE REVIEW

Maiti et al., 2012 conducted three studies in which the Arsenic adsorption capacity of treated laterite was investigated under different conditions in a batch study, firstly by using a single arsenic species and then in the second study using a mix of both As (III) and As (V) species and then in the third case, study of real arsenic bearing contaminated water was done. The raw laterite was brought from Midnapore. This raw laterite was then treated with acid (0.5 N HCl) followed by treatment with a base (4 N NaOH). In the batch study the concentration of arsenic was kept in range of 0.2 to 20 mg/l and was agitated in a shaker for 24 h at a fixed adsorbent loading of 0.5 g/L at 305 K. The Fixed bed column experiment was done using contaminated groundwater spiked with arsenic collected from Kharagpur and real contaminated groundwater collected from Dhabdhobi.

Maiti et al., 2012 conducted a two part study, in the first part laterite samples collected from four different sites (Kharagpur, Bankura, Manbazar, Purulia) having different compositions were compared and analysed on their arsenic removal ability. In the second part the soil samples were treated with acid followed by base and used as filter medium in a typical household column. In the first case batch study was performed keeping dose as 20g/l, rpm as 150, contact time as 24 hr, temperature as 305K, pH as 7.0 and arsenic concentration was varied from 0.1 to 5 mg/l. after the analysis it was established that the soil from Kharagpur showed the maximum removal percentage. Two household filters using the treated laterite are installed in arsenic affected area of Barasat in West Bengal, and their performance was monitored.

Aminah and Izaat., 2011 investigated the Zn removal potential of laterite soil. The laterite soil used in this experiment was brought from Berseri, Perlis. In this experiment batch study was conducted and various parameters such as the effects of adsorbent dose, initial pH, contact time and initial Zn concentration were studied. Based on the experimental results, zinc removal improved with rise in contact time and concentration, also high acidic pH favoured Zn uptake, but zinc removal decreased with higher dosage of lateritic soil.

Maiti et al., 2010 studied the effect of treated laterite for arsenic removal from water. The raw laterite used was brought from Kharagpur. It was then treated with acid (2N HCl) followed by base treatment (4N NaOH). In this study three types of experiments were done a batch study, a column study and a household filter medium was designed. Arsenic removal from both synthetic water and contaminated groundwater was done. Arsenic adsorption on the treated laterite followed pseudo second order kinetics. Different characterisation tests such as FTIR, XRD, SEM-EDX and HRTEM were done to get a detailed description and classification of the treated laterite.

Maiti et al., 2010 investigated the arsenic removal ability of acid activated laterite soil. The raw laterite was treated with 0.1N HCl to convert it to acid activated soil. The batch experiments for arsenic are performed for both synthetic and natural groundwater. Comparison of the removal ability and characteristics has also been done between the raw laterite and acid activated laterite. As (III) and As (V) adsorption on AAL were inspected under different process parameters such as dose of adsorbent, time of contact, temperature, size of particle, concentration, and competitive ions. The arsenic concentration was altered from 0.5 to 10 mg/l and a fixed adsorbent loading of 5g/l was taken, the temperature was kept at 304K, rpm at 150 rpm and the contact time was kept at 24 hr. AAL showed better removal capability as compared to raw laterite. Column study using AAL as adsorbent bed has been done, it was used to treat arsenic-polluted ground water collected from Dhabdhobi.

Nemade et al., 2009 investigated the As uptake ability of laterite soil. The laterite soil used in the study was brought from Tambati village, for preparation of adsorbent, soil was crushed and washed with tap water and then it was dried at 100oC. Batch experiments were performed to test the effect of various process parameters on the removal of arsenite. The concentration of As (III) was varied from 0.25 to 4 mg/l. After optimisation studies it was found that maximum uptake of As (III) occurred at a dose of 25 g/l (around 95%). The Temperature was maintained at 304 K, pH was 7.1, Contact time was 24 hr and the rpm was maintained at 130. Rapid colorimetric method was used for sample analysis.

Maiti et al., 2008 studied the removal of As (V) ions. Both the equilibrium and kinetic studies were done over a varied range of operating conditions to assess the removal of As (V). The laterite soil used in this study was collected from the Midnapore district. In this study both batch and column study was carried out. The optimum dose was 20g/l, particle size was 0.38mm, the effective pH was maintained in the range of 5.5 to 7.5 and the contact time was 4hr. One of the main reasons for performing the column study was to see how much effluent can be treated before regeneration of bed is required, the Adams-Bohart model was used for estimating the breakthrough curve.

Rahman et al., 2008 investigated the As removal ability of heat treated laterite. The laterite soil used was brought from Ogasawara Island in Japan. Batch experiments were performed and various parameters like dose of laterite soil, arsenic concentration and different rpm speeds were studied. The optimum dose observed was 5g/l, the optimum rpm was 400 and the initial arsenic concentration was varied as 0.3163, 0.5654, 0.8484, 1.0086 mg/L. Adsorption equilibrium data indicated both Langmuir and Freundlich models to be satisfactory.

Yu et al., 2008 studied the Hg (II) removal ability of natural laterite soil. The soil used in this study was collected for the Guizhou Province in China, different soil samples were collected from different weathered zones, in total about 10 samples were collected. The experiments were performed under batch conditions with a dose of 1g/20ml, mercury concentration was 150μg/ml, contact time was 2hr and the pH was maintained in the range of 7 to 9. After the experiment the sample was spun in a centrifuge at 3000 rpm for 5 min and then the samples were analysed for Hg by the Plasma emission spectrograph. Sample 1 showed the best removal capacity of 67.88% because of the elevated presence of illite and non-crystalloids in the laterite soil. The adsorption isotherm that was followed was the Langmuir isotherm.

Maiti et al., 2007 examined the arsenite removal capacity of natural laterite. Batch experiments were carried out to test the various process parameters. The concentration of As (III) was varied from 0.3 to 5 mg/l. After optimisation studies it was found that maximum uptake of As (III) occurred at a dose of 20 g/l. the temperature was maintained at 314K, pH was 7.2, contact time was 16 hr and rpm was maintained at 150. From the kinetic analysis it was perceived that the maximum adsorption occurs within two hours of the process.

Maji et al., 2007 examined the As (III) and As (V) removal capacity of natural laterite soil. The soil crushed, washed and dried. The temperature was maintained at 298K, rpm at 170, concentration of both the arsenic compounds was taken as 0.5 mg/l. the particle size of the laterite was taken as 0.164 mm and the optimum time of contact was 4 hr, the optimum dose was 10g/l for As (III) showing a removal of 98% and 20g/l for As (V) showing a removal of 95%. The adsorption follows Langmuir, Freundlich and D-R isotherms. By the calculation of the E-valued of the D-R isotherm it was found out that As (III) adsorption follows the mechanism of physisorption whereas for As (V) it is both physisorption and ion exchange.

Maji et al., 2007 studied the arsenic removal by laterite soil. In this experimental study batch experiments were performed on both synthetic and real wastewater samples. The experimental conditions for both were kept same, temperature was maintained at 298K, rpm at 170, the pH was kept at 5.7 and the contact time was 4 hr (synthetic samples) and 30 min (real groundwater). Also the effect of various ions (Cl−, NO3- , SO42-, Ca2+,Sio32+,HPO42-,Fe2+ and EDTA) and organic compounds (Humic acid, atrazine and 2,4-dichlorphenoxyacetic acid) on laterite were examined. Laterite showed good removal ability for both synthetic (95% to 98%) and real groundwater samples (85% to 99%).

Rao et al., 2001 studied the removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash. Raw bagasse and fly ash, the waste generated in sugar mills and boilers respectively have been used as low-cost potential adsorbents. Raw bagasse was pre-treated with 0.1(N) NaOH followed by 0.1(N) CH_3COOH before its application. These low-cost adsorbents were used for the removal of chromium and nickel from an aqueous solution. The kinetics of adsorption and extent of adsorption at equilibrium are dependent on the physical and chemical characteristics of the adsorbent, adsorbate and experimental system. The effect of pH, contact time, adsorbent dose, initial concentrations of adsorbate and adsorbent and particle size on the uptake of chromium and nickel were studied in batch experiments. The adsorption data has been correlated with Langmuir, Freundlich and Bhattacharya and Venkobachar adsorption models. The efficiencies of adsorbent materials for the removal of Cr (VI) and Ni (II) were found to be between 56.2 and 96.2% and 83.6 and 100%, respectively. These results were obtained at the optimized conditions of pH, contact time, sorbent dose, sorbate concentration of 100 mg/l and with the variation of adsorbent particles size between 0.075 and 4.75 mm. The order of selectivity is powdered activated carbon>bagasse>fly ash for Cr (VI) removal and powdered activated carbon>fly ash>bagasse for Ni (II) removal.

Gupta et al., 2003 investigated the removal of Lead and Chromium from wastewater using bagasse fly ash, a sugar industry waste. An inexpensive and effective adsorbent was developed from bagasse fly ash, obtained from a sugar industry, for the dynamic uptake of lead and chromium. Lead and chromium are adsorbed by the developed adsorbent up to 96 to

98%. The removal of these two metal ions up to 95–96% was achieved by column experiments at a flow rate of 0.5 ml/min. The adsorption was found to be exothermic in nature.. The developed system for the removal of two ions is very useful, economic, rapid, and reproducible.

Gupta et al., 1999 studied the removal of Cu (II) and Zn (II) from wastewater using bagasse fly ash, a sugar industry waste. The product was characterised by different chemical and physical methods and was used for the removal of copper and zinc from wastewater. Various parameters such as pH, adsorbent dose, initial metal ions concentrations, temperature, particle size, etc. were optimised. Copper and zinc were adsorbed by the developed adsorbent up to 90/95% in batch and column experiments. The adsorption was found to be endothermic in nature. It followed both the Langmuir and Freundlich models. Isotherms were used to evaluate thermodynamic parameters for the adsorption process.

Hala Ahmed Hegazi, 2013 investigated the removal of heavy metals for the treatment of the EL-Ahlia electroplating industry wastewater. Heavy metals like Fe, Pb and Ni were removed efficiently using rice husk and Cd and Cu using fly ash. Results showed that low cost agricultural and industrial wastes like rice husk and fly ash can be used for the removal of the aforementioned heavy metals within the concentration range of 20 to 60 mg/l.

Omar E. Abdel Salam et al., 2011 studied the removal characteristics of Cu (II) and Zn (II) from wastewater by using low cost adsorbents like peanut husk, charcoal, flyash and natural zeolite. The batch method was employed: parameters such as pH, contact time, and initial metal concentration were studied. The influence of the pH of the metal ion solutions on the uptake levels of the metal ions by the different adsorbents used were carried out between pH 4 and pH 11. The optimum pH for copper and zinc removal was found out to be 6 in the case of peanut husk charcoal and natural zeolite, and it was 8 in case of fly ash. An equilibrium time of 2 h was required for the adsorption of Cu (II) and Zn (II) ions onto peanut husk charcoal and fly ash. Equilibrium time 3 h was required for the adsorption of Cu (II) and Zn (II) ions onto natural zeolite. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Langmuir equation than to Freundlich equation. The results showed that peanut husk charcoal, fly ash and natural zeolite all hold potential to remove cationic heavy metal species from industrial wastewater in the order of fly ash < peanut husk charcoal< natural zeolite.

Gupta et al., 2003 investigated the removal of Cd (II) and Ni (II) from wastewater using bagasse fly ash, a sugar industry waste. It was found out that 90% removal of Cd (II) and Ni (II) is achieved in 60 and 80 minutes. Effect of various operating variables, viz., solution pH, adsorbent dose, adsorbate concentration, temperature, particle size, etc., on the removal of cadmium and nickel has been studied. Maximum adsorption of cadmium and nickel occurred at a concentration of 14 and 12 mg/l and at a pH value of 6.0 and 6.5, respectively. A dose of 10 g/1 of adsorbent was sufficient for the optimum removal of both the metal ions. The material exhibits good adsorption capacity and the adsorption data follow the Langmuir model better then the Freundlich model. The adsorption of both the metal ions increased with increasing temperature indicating endothermic nature of the adsorption process. Isotherms have been used to determine thermodynamic parameters of the process, viz., free energy change, enthalpy change and entropy change.

Table 2.1 Summary of work done on adsorptive removal of heavy metals using laterite soil, fly ash and bagasse.

Reference	**Type of water**	**Metal Removed**	**Type of Adsorbent Used**	**Type of Study**	**Process Parameters**
Maiti et al., 2012	Synthetic and Contamined water	As(III);As(V)	Treated laterite (Acid followed by base treatment	Batch and column	Concentration: 0.2 to 20mg/l, dose:5g/l, contact time:24hr, temperature:305K
Maiti et al., 2012	Synthetic wastewater	As(III);As(V)	Raw laterite and treated laterite	Batch and column	Concentration: 0.1 - 5mg/l,dose:20g/l, contact time:24hr, temperature:305K, pH:7
Aminah and Izaat., 2011	Synthetic wastewater	Zn(II)	Raw laterite	Batch	Concentration: 50 to 250ppm,dose: 5g/l ;Contact time: 10 min, pH: 8
Jahan et al., 2011	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:50mg/l Dose:1000g/l,200g/l Contact time:24 hr Temperature:298K pH: 4.7 to 10

Maiti et al., 2010	Synthetic and Contamined water	As(III);As (V)	Treated laterite	Batch and column	Concentration:0.5 to 10mg/l,Dose:5g/l Contact time:24 hr Temperature: 304K
Nemade et al., 2009	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:0.24-4mg/l Dose: 25g/l Contact time:24hr Temperature:304K pH: 7.1
Maiti et al., 2008	Synthetic wastewater	As(V)	Raw laterite	Batch and column	Concentration:0.2-20 mg/l Dose: 20g/l Contact time:4 hr Temperature: 302K pH: 5.0 to 7.5
Rahman et al., 2008	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:0.31 to1.0086mg/l Dose:5g/l, Contact time:24hr Rpm:400
Yu et al., 2008	Synthetic wastewater	Hg(II)	Raw laterite	Batch	Concentration:150μg/l,; Dose: 1g/20ml Contact time:2hr Temperature: 304K pH:7 to 9
Maiti et al., 2007	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:0.35mg/l Dose:20g/l; Contact time:16hr Temperature:314K pH:7.2
Maji et al., 2007	Synthetic wastewater	As(III) and As(V)	Raw laterite	Batch	Concentration:0.5mg/l Dose:10g/l,20g/l ;Contact time:4hr Temperature:298K
Maji et al., 2007	Synthetic wastewater and Contamined water	As(III) and As(V)	Raw laterite	Batch	Concentration:0.5mg/l Dose:10g/l,20g/l Contact time:4hr Temperature:298 K pH:5to7
Rao et al., 2001	Synthetic wastewater	Cr(VI); Ni(II)	Bagasse; Fly ash	Batch	Concentration:5-20mg/l; Dose:10 g/l Contact time:60-80 mins Temperature-298 K pH:6-7
Gupta et al., 2003	Synthetic wastewater	Pb(II); Cr(VI)	Bagasse fly ash	Batch and	Concentration:5-70 mg/l(Pb) Concentration:5-50 mg/l(Cr)

				column	Dose:10 g/l Contact time:60 min(Pb);40 min(Cr) Temp: 303 K pH: 6 (Pb); 5 (Cr)
Gupta et al., 1999	Synthetic wastewater	Cu(II); Zn(II)	Bagasse fly ash	Batch and column	Concentration:5-50 mg/l Dose:10 g/l Contact time:60 min(Cu),75 min(Zn) Temp: 303 K pH: 4(Cu);5(Zn)
Hala Ahmed Hegazi, 2013	Synthetic and industrial wastewater	Cu(II);Ni (II);Fe(III)	Rice husk, Fly ash	Batch	Concentration:10 mg/l Dose: 5-30 mg/l Contact time:2 hr Temp: 298 K pH:3.75-6(RH) pH:6-7(FA) Mixing speed: 150-200 rpm

2.2 Objective of the present study:

The present work aims at developing a technique for the effective removal of Pb and Cr from synthetic wastewater by low cost adsorbents like laterite soil, fly ash and bagasse. Following objectives have been formulated:

- To examine the feasibility of using raw laterite soil, fly-ash and bagasse as adsorbents.
- To study the effect of initial pH of solutions and selection of the best adsorbent.
- To assess the heavy metal removal capacity of the adsorbents.
- To study the kinetics mechanism of the adsorption process.
- To gather experimental data on adsorption equilibrium for the binary systems.
- To examine the feasibility of adsorption isotherm models (i.e., Freundlich, Langmuir) based on the regression analysis coefficient for single-component solutions,
- To determine the feasibility of the multi-component adsorption isotherm equations for multi-component adsorption equilibrium in binary systems containing Pb (II) and Cr (VI).

CHAPTER 3

EXPERIMENTAL SETUP AND INSTRUMENTATION

3.1 Instruments and Chemicals

All the chemicals used for experimental work were of analytical grade (A.R.). Stock solutions were prepared by using distilled water. The instruments used in present study were, Fourier transform infrared spectroscopy (FTIR), Flame atomic absorption spectrometry (FAAS), Brunauer-Emmett-Teller isotherm (BET), X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).

- To find out the type of functional groups present in the soil, FTIR (FTIR, Nicolet 6700 USA) spectrometer was used.

- To find out the concentration of metals in the water samples, AAS (GBC Avanta M) study was done.

- To find out the surface area, pore size and pore volume of the sample ,BET (ASAP 2020 V3.05 H Micromeritics system) analysis of the soil samples was done

- To find out about the crystal structure, chemical configuration and physical properties of the soil , XRD (BRUKER D8 ADVANCE) study was done

- To observe the surface before and after the metal uptake in case of soil, fly ash and bagasse , Scanning Electron Microscope (LEO 435 VP) study was conducted

- The supplementary instruments used in the present study were pH meter (CL 54+ pH meter), muffle furnace, centrifuge, water bath, sand bath, weighing balance, orbital shaker(Metrex Scientific Instruments, New Delhi), distilled water plant and hot air oven.

3.2 Preparation of stock solution

All reagents used in experiments were of analytical grade (AR). Distilled water was used for dilution

- Stock Pb (II) solution: 1.598 g of lead nitrate were dissolved and diluted to 1000 ml with distilled water producing a 1000 ppm solution, and then dilutions were made subsequently to the different concentrations of Pb (II)

- Stock Cr (VI) solution: 2.829 g of potassium dichromate was dissolved and diluted to 1000 ml with distilled water to make a solution of 1000 ppm water and dilutions were made by the following different concentrations Cr (VI)

3.3 Analytical methods

The samples collected were analyzed by Flame atomic absorption spectroscopy (Instrument: GBC Avanta M, Flame: air-acetylene, Wavelength: for Cr: 425.4 nm; for Pb: 283.3 nm, Slit Width for Cr: 0.2 nm; for Pb: 0.5 nm) in order to check the concentration of Pb and Cr ions present in the test samples. AAS was calibrated before analysis using standard solutions of chromium and lead. The calibration curves obtained are represented in Fig 3.4 and 3.5 respectively. The pH of the solutions was checked with CL 54+ pH meter.

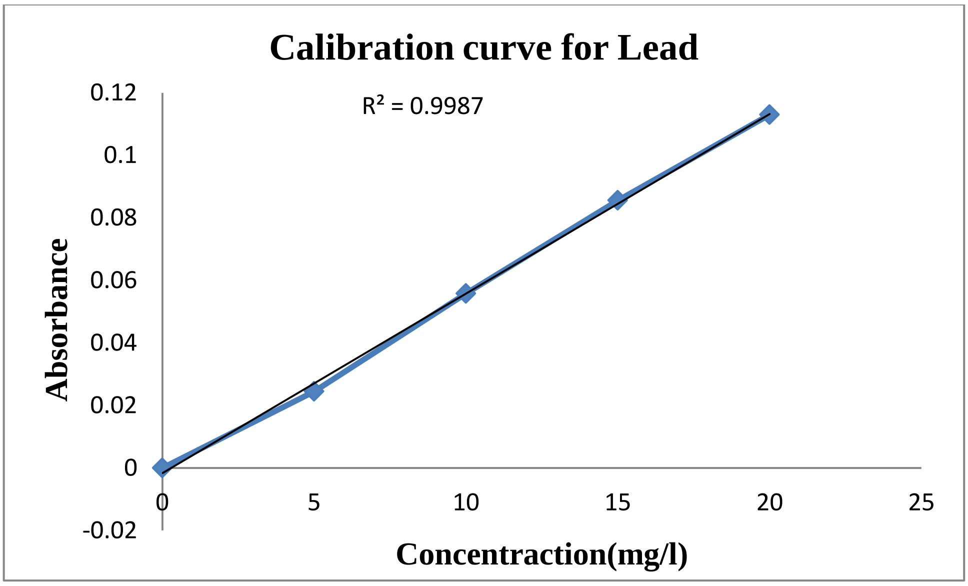


Fig 3.1 Calibration Curve for Lead

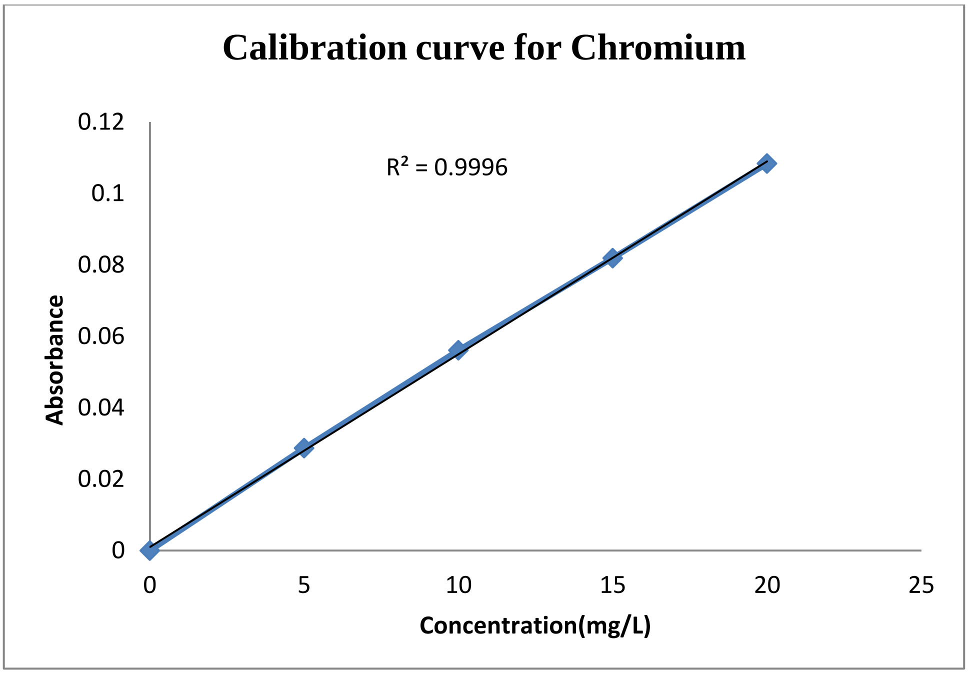


Fig 3.2 Calibration Curve for Chromium

CHAPTER 4

Experimental procedure

4.1 Preparation of adsorbents

4.1.1 Preparation of raw laterite (RL): Raw laterite soil was procured from Burdwan district of West Bengal. Generally most of the studies relating to the laterite soils that have been carried out for the removal of As (III) and As (V) and the soil was procured from West Midnapore district. The present study is a unique study in which multi-component removal is attempted. The pictorial representation of the laterite soil used in the present study is shown in Fig. 3.1

Fig 4.1 Laterite soil

Raw laterite soil was dried for a period of two days to remove the moisture. It was then rinsed well with distilled water until the dirt particles were removed and the wash water became colourless. It was then dried in the oven at 110º C and put through various mesh sizes for sieving purposes. Based on literature review, particle sizes were taken in the range of 0.65-0.8 mm.

4.1.2 Preparation of Fly-Ash (FA): Fly-Ash was washed repeatedly with distilled water until the wash water becomes colourless and dirt or foreign matter is removed completely. It was then oven dried at 100º C for a period of 6-7 hours. The adsorbent was then stored in a covered beaker.

Fig 4.2 Fly Ash

4.1.3 Preparation of bagasse: Bagasse was washed well with distilled water to remove the dust and dried at 40º C for a period of 4-5 hrs. Dried bagasse was then soaked overnight in 0.1(N) NaOH in order to remove the lignin content. It was then washed again with distilled water and soaked with 0.1(N) acetic acid for a period of 2-3 hrs to remove any traces of NaOH. The adsorbent was then kept in a closed beaker until further use.

Fig 4.3 Bagasse

4.2 Experimental procedure

Initially a preliminary adsorption run was carried out for all the three adsorbents prepared; in a batch process under equilibrium conditions taken from literature to test which showed maximum removal capacity. The adsorption was carried out using an adsorbent dose of 10 g/l; an rpm of 150 and the temperature was set at 305 K.

The contact time was set at 4 hr and the metals to be adsorbed were Chromium and Lead whose concentration was taken as 20 ppm. The adsorbent that was good at adsorbing both Cr and Pb was raw laterite. Various optimization studies were carried out to study parameters such as dose of adsorbent, time of contact, effect of pH and initial concentration of chromium and lead

The experiments were carried out in batch mode in 100 ml conical flasks; at a temperature of 305 K, the particle size was taken in the range of 0.6 to 0.85 mm and an rpm of 150 was maintained on the orbital shaker.

Firstly the pH optimization study was carried out was carried out using a fixed adsorbent dose from literature in order to select the best adsorbent, then the dose was optimized by varying in the range of 5g/l to 40g/l and then the time optimization study was carried out.

After all the parameters were optimized then the uptake ability of laterite soil for different concentrations of heavy metals was analyzed.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Adsorbent Characterization

The characterization of the adsorbents has been done by subjecting them to X-ray diffraction analysis, BET surface area analysis, FTIR and SEM analysis.

5.1.1 XRD

5.1.1.1 Raw Laterite (RL)

The XRD patterns of RL in Fig. 5.1, when compared with literature (Maiti et al., 2007; Nemade et al., 2009) indicate the presence of hematite, magnetite, goethite, silicon quartz, iron oxide, and aluminium oxide. The XRD pattern suggests a crystalline structure of the laterite soil.

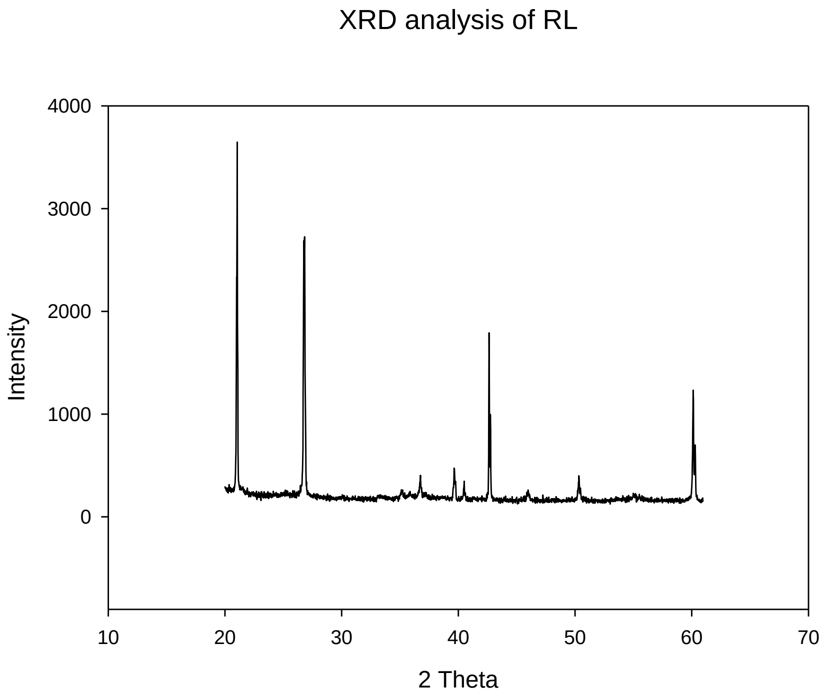


Fig 5.1 XRD Data for Raw Laterite

5.1.1.2 Fly Ash (FA)

XRD analysis of fly ash revels peaks of silicon dioxide and calcium oxides

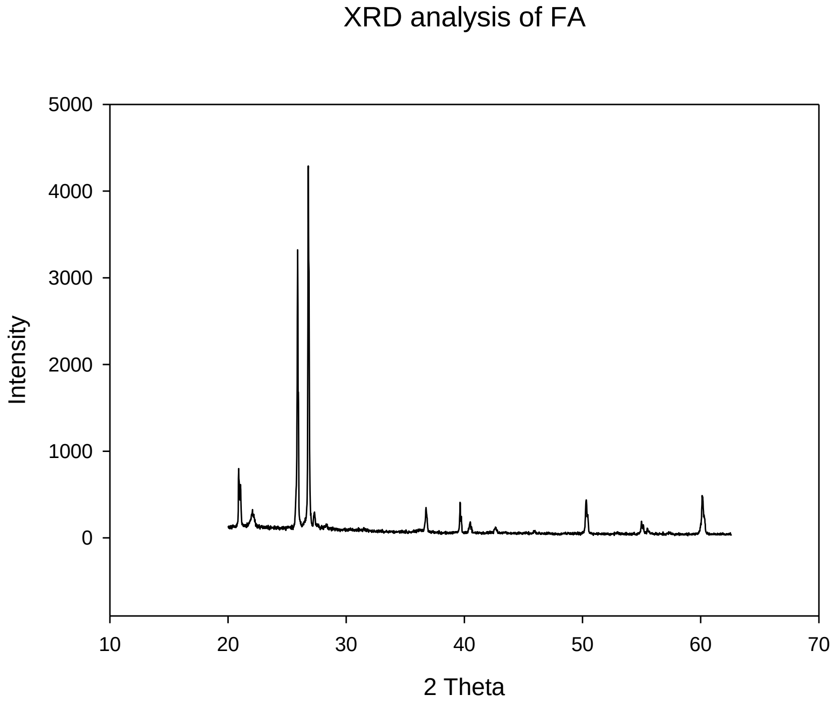


Fig 5.2 XRD Data for Fly Ash

5.1.2 FTIR Characterization

5.1.2.1 Raw Laterite (RL)

The FTIR spectra patterns for the raw laterite are shown in Fig. The presence of iron, aluminium and silica oxides or hydroxides gets confirmed by studying these patterns. The bands at 3624.22 and 3428.9 signify the presence of OH group of Si, Al and Fe. The band at 1627.16 represents the presence of inner layer water molecules. The bands at 1034.49, 913.38 and 788.32 are due to the presence of Si-O-Fe, Al-OH, Fe-OH and Si-O vibrations. The bands at 534.21, 467.25 and 441.61 signify the presence of Hematite (Fe-O bond stretching). These bands have also been reported with slight variation by Maiti et al., 2012.

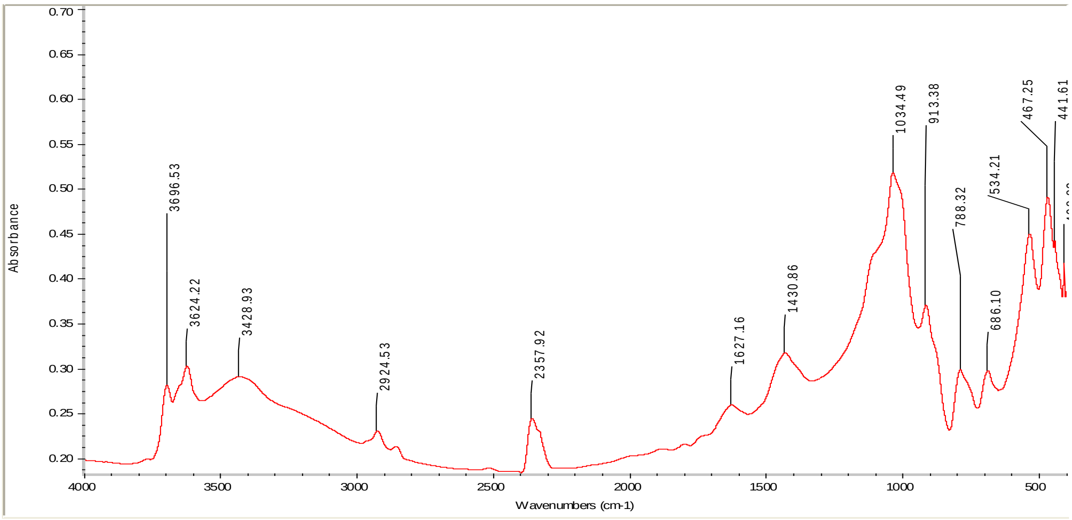


Fig 5.3 FTIR of RL

5.1.2.2 Fly Ash (FA)

The FTIR spectra patterns for the FA are shown in Fig. Bands in between 686.10 and 1034.49 are indicative of the presence of Si-O-Si bonding. Bands at around 875.31 and 1080.46 indicate the presence of $S0_4^{2-}$ groups.

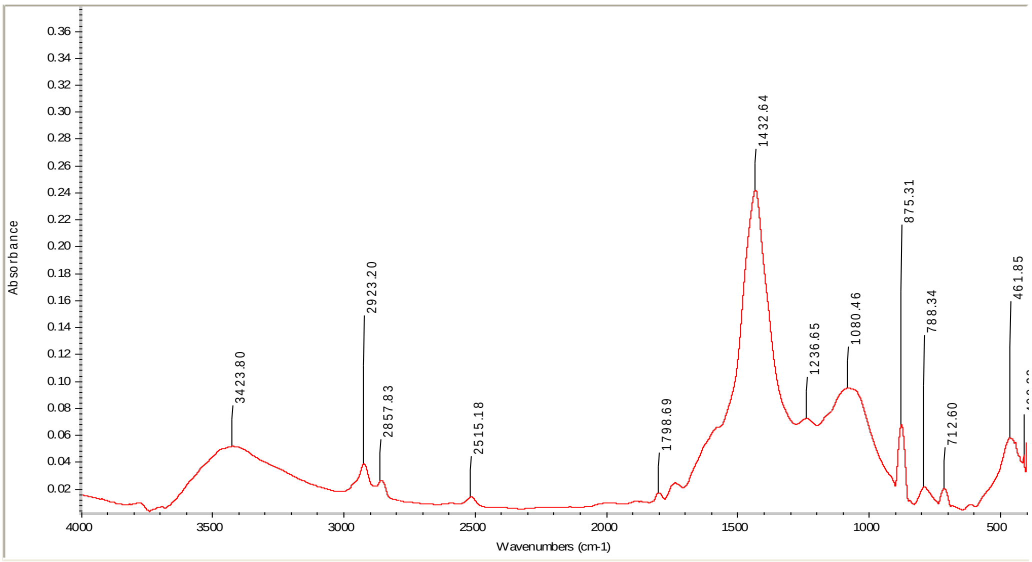


Fig 5.4 FTIR of FA

5.1.2.3 Bagasse

The FTIR spectra patterns for sugarcane bagasse is shown in Fig. the presence of a large number of peaks between 1037.59 and 1737.58 may be due to the presence of several compounds of ketones, phenols and aldehydes.

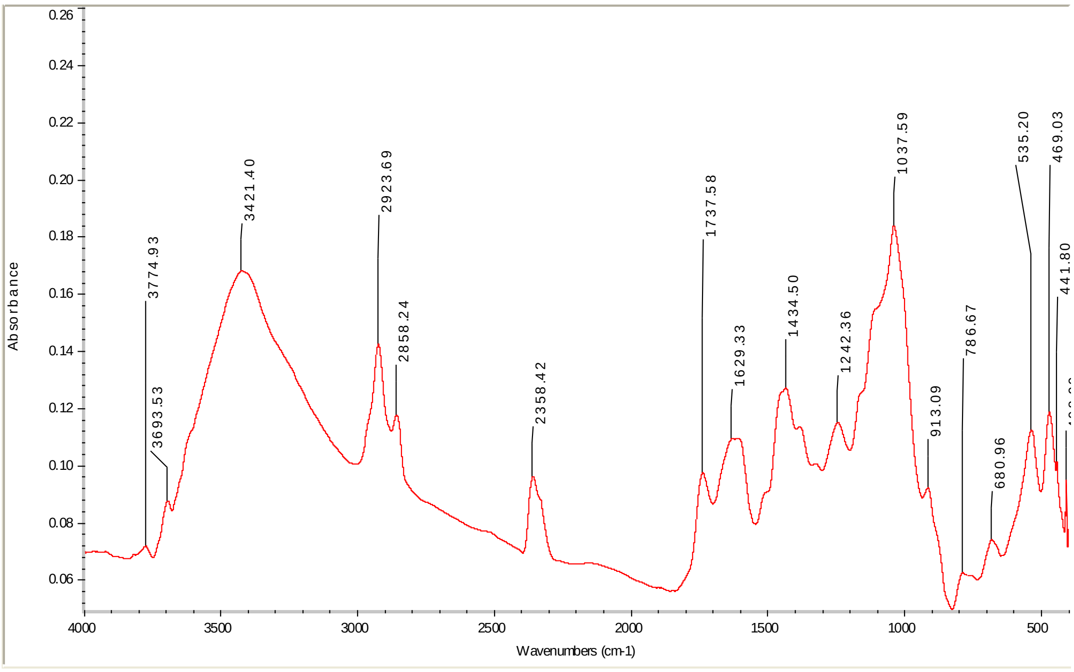


Fig 5.5 FTIR of Bagasse

5.1.3 BET Characterization

The BET surface area analysis results of the adsorbents used are shown in the following tables

Table 5.1 Characteristics of Raw laterite (RL)

Properties	**Raw Laterite**
Particle size (spherical) (mm)	0.6-0.85
BET Surface area (m^2/g)	23.0150
Monolayer Volume(cm^3/g)	5.287
Total Pore volume (m^3/g)	0.0116

Table 5.2 Characteristics of Fly Ash (FA)

Properties	**Fly Ash**
Particle size (spherical) (mm)	0.6-0.85
BET Surface area (m^2/g)	3.9181
Monolayer Volume(cm^3/g)	0.900
Total Pore volume (m^3/g)	0.0020

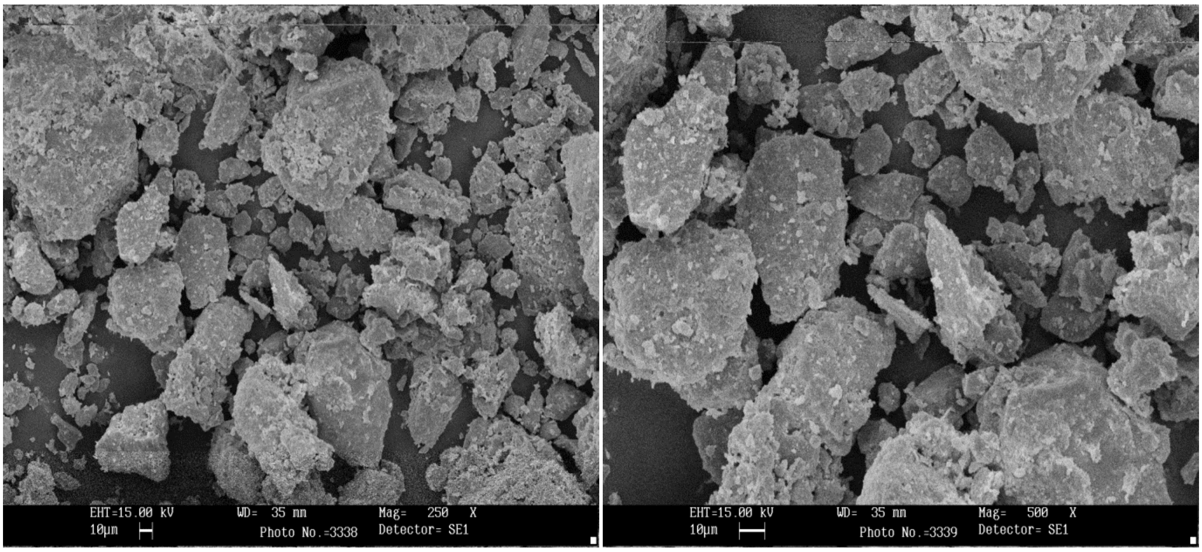
Table 5.3 Characteristics of Bagasse

Properties	**Bagasse**
Particle size (mm)	< 1
BET Surface area (m^2/g)	33.1447
Monolayer Volume(cm^3/g)	7.614
Total Pore volume (m^3/g)	0.0167

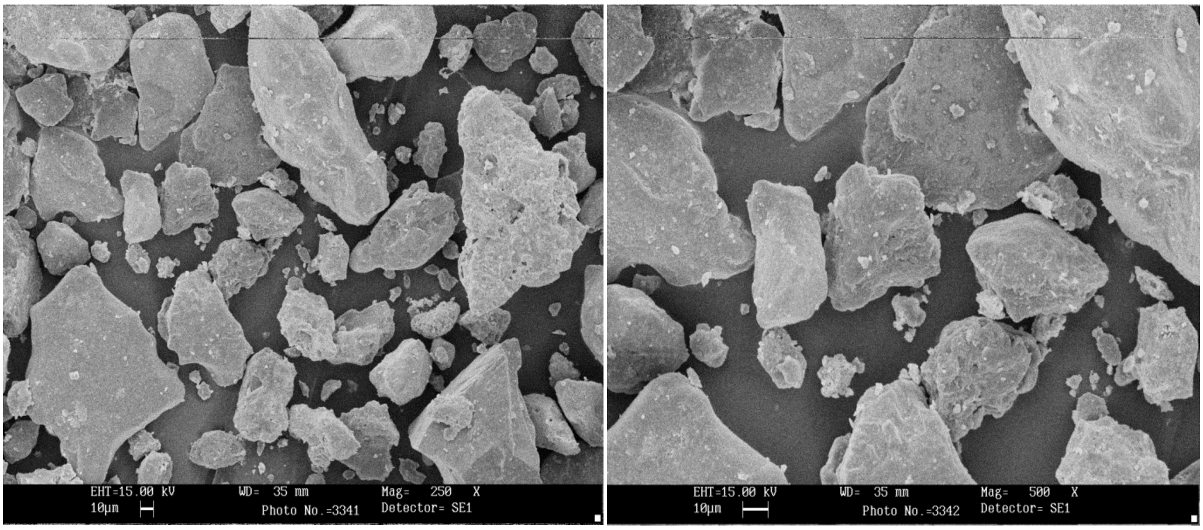
5.1.4 SEM

5.1.4.1 RL

The scanning electron microscopy is generally used to characterize the differences observed on the surface of the adsorbents before and after the adsorption has taken place. The SEM pictures have been shown in Fig. From these pictures a marked difference is noticed between the before and after pictures. The pictures are depicted in a magnification of 250 x and 500 x. In the after adsorption picture there is presence of small light coloured particles on the surface of the adsorbent, this may indicate the presence of chromium and lead.



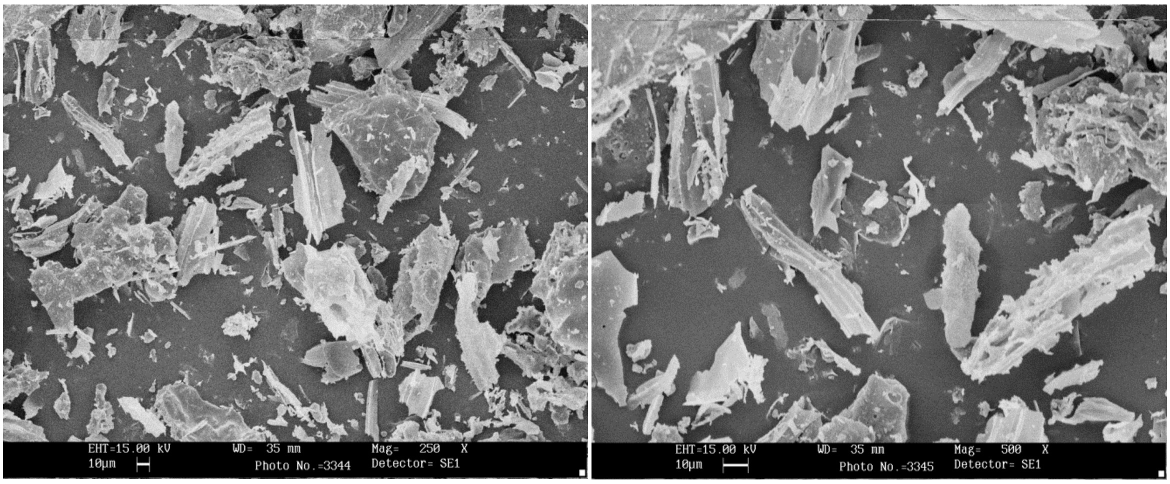
Before (250 X) Before (500 X)



After (250 X) After (500 X)

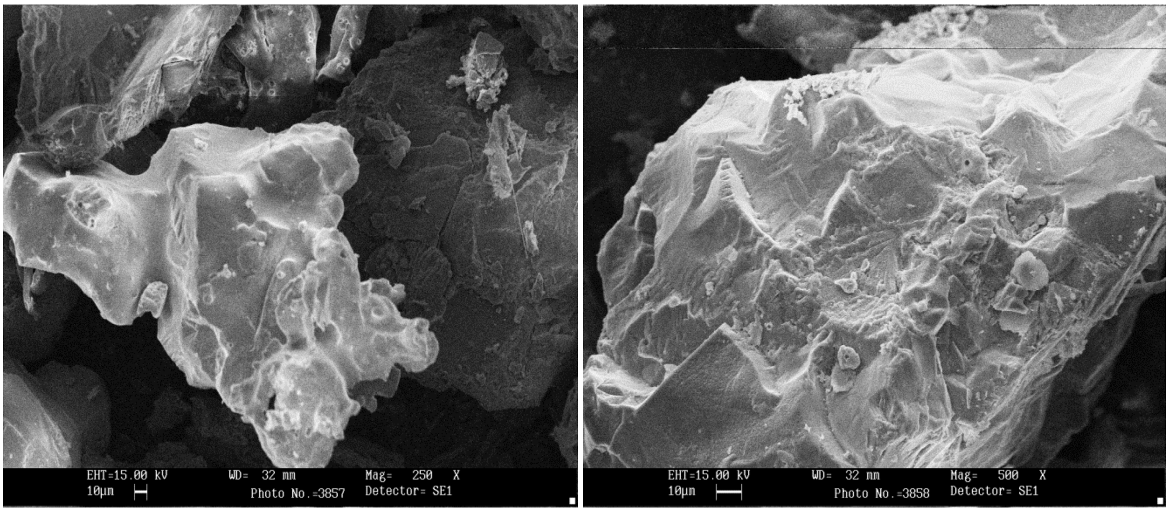
Fig 5.6 SEM of RL

5.1.4.2 FA



Before (250 X)

Before (500 X)

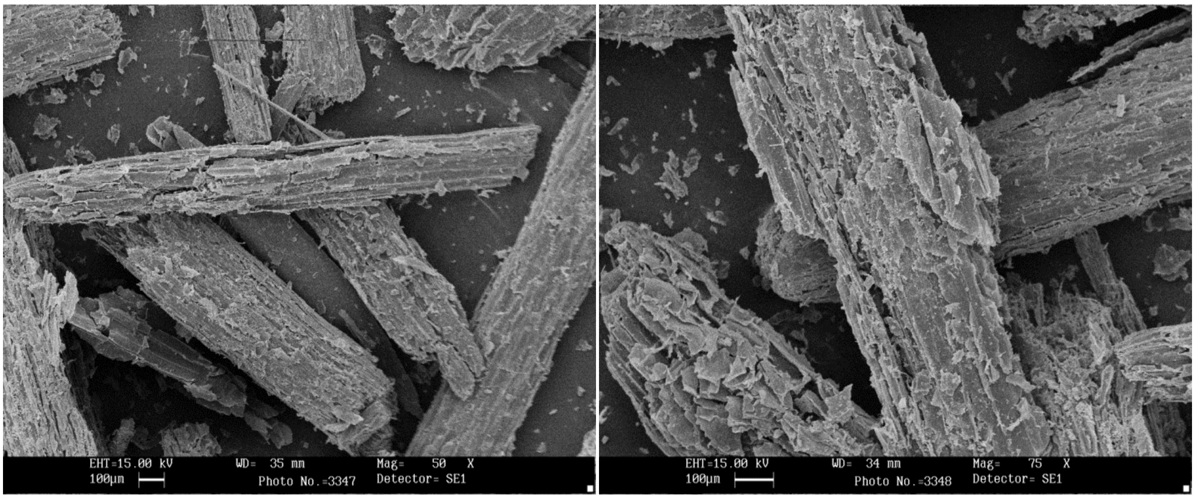


After (250 X)

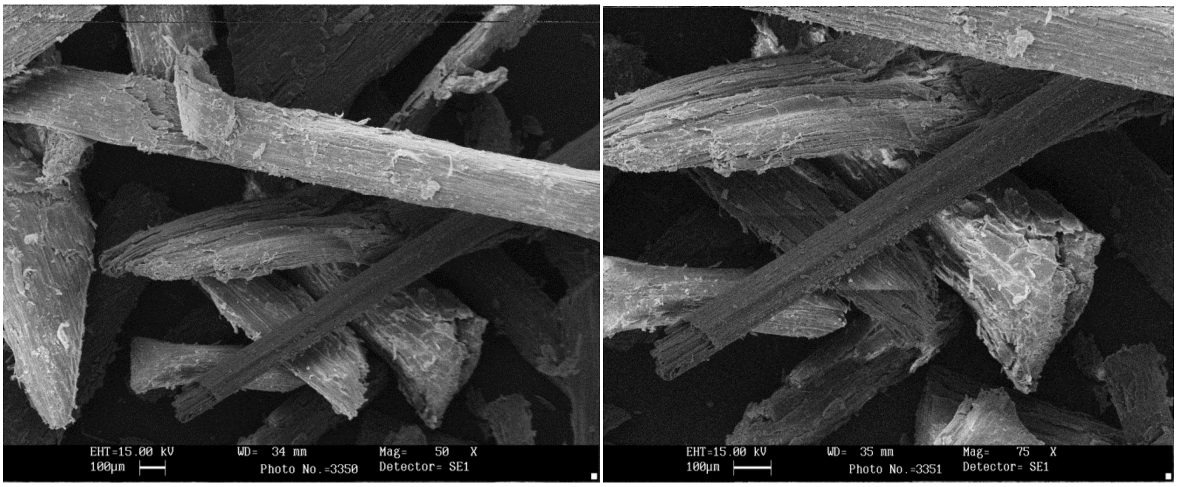
After (500 X)

Fig 5.7 SEM of FA

5.1.4.3 Bagasse



Before (50 X) Before (75 X)



After (50 X) After (75 X)

Fig 5.8 SEM of Bagasse

5.1.5 TGA

5.1.5.1 RL: TGA analysis of RL is shown in fig 5.9 . The TGA analysis was done in a range of 298 K to 1488 K. 6.33 % loss in mass occurred in between 298 K to 773 K which may be due to the oxidation of carbon compounds and silica.

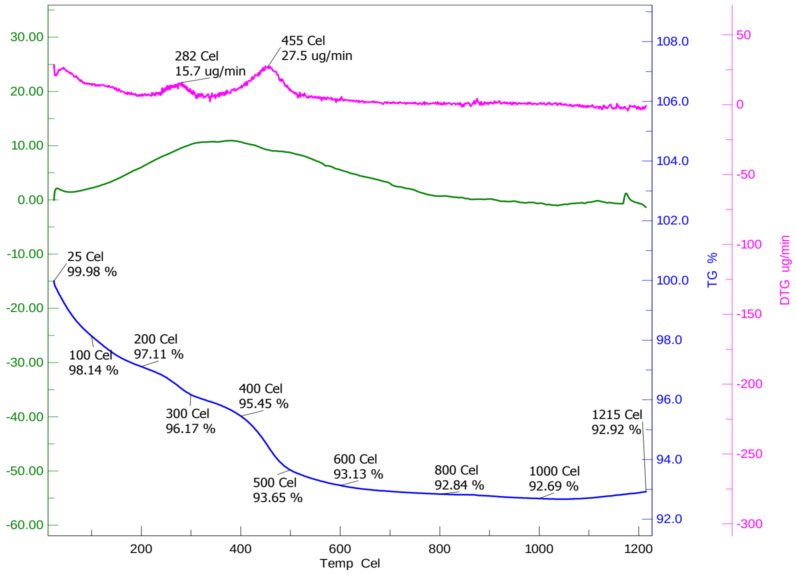


Fig 5.9 TGA of RL

5.1.5.2 Fly Ash

TGA analysis of fly ash is shown in fig . The TGA analysis was done in a range of 302 K to 1484 K. 2.89 % loss in mass occurred in between 302 K to 757 K.

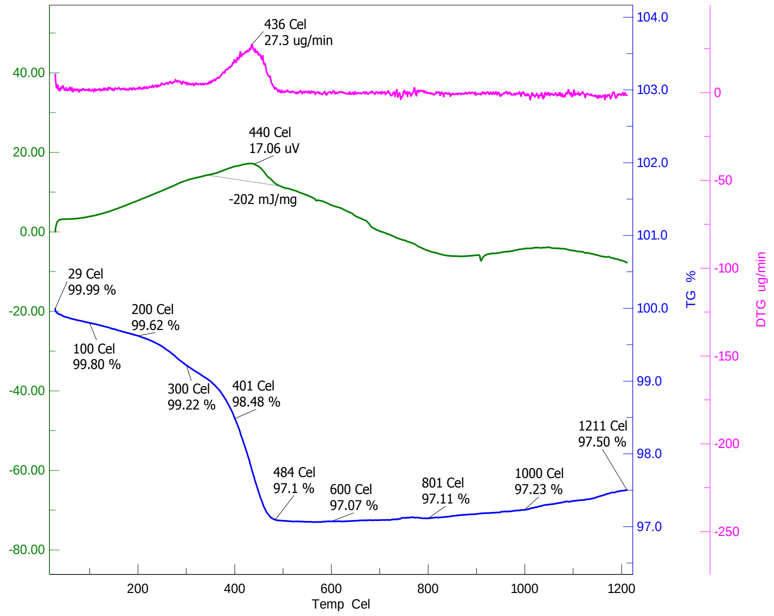


Fig 5.10 TGA of FA

5.1.5.3 Bagasse

TGA analysis of sugarcane bagasse is shown in fig 5.11 . 4.78% loss in mass is observed between 295 K and 373 K due to the loss of moisture. A weight loss of 60.15 % was observed in between 473 K to 597 K because of the degradation of hemicelluloses. Further weight loss of 30 % was observed in between 597 K to 688 K due to the degradation of cellulose. Above 688 K negligible change in mass occurs partly due to completion of cellulose degradation along with the initiation of decomposition of heavier volatiles. Char formation and decomposition of lignin also occurs in this temperature range

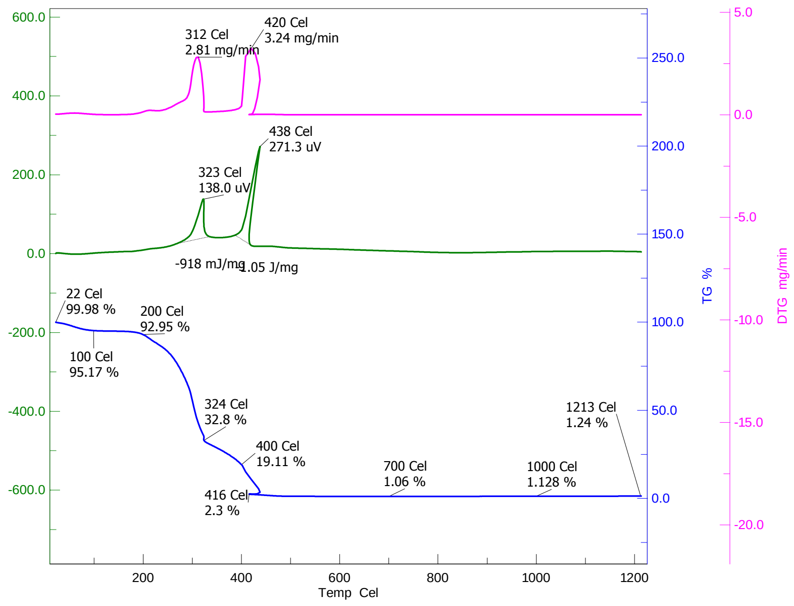


Fig 5.11 TGA of Bagasse

5.2.2 Batch Adsorption Studies

The adsorption studies were carried out in an orbital shaker at an rpm of 150 and a temperature of 305K and the various parameters like contact time, adsorbent dose and pH have been optimized.

5.2.2.1 Effect of pH

In this study the dose and time were kept constant at 10g/l and 4 hr respectively and the pH was varied as 2, 4, 6, 8 and 10. Chromium and Lead performed well in acidic and neutral conditions as compared to the basic conditions. The removal percentage for both the metal ions was least in the case of pH 10. This trend has been noted by Lukman et al., 2013; Reed et al., 1996. Since both Cr and Pb performed well at pH 6; it was the pH that was maintained for further studies. The effect of pH on the metal uptake has been depicted in Fig. based on this experiment it was found out that RL gave the best results compared to FA and bagasse and was chosen as the adsorbent for the current experiment..

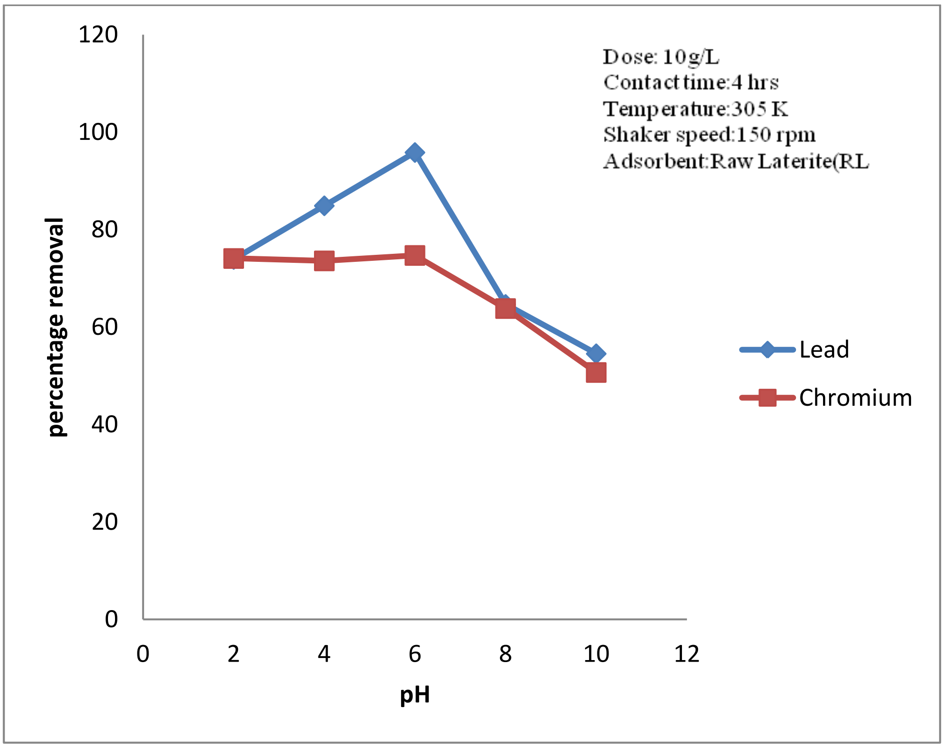


Fig 5.12 pH optimization study of RL

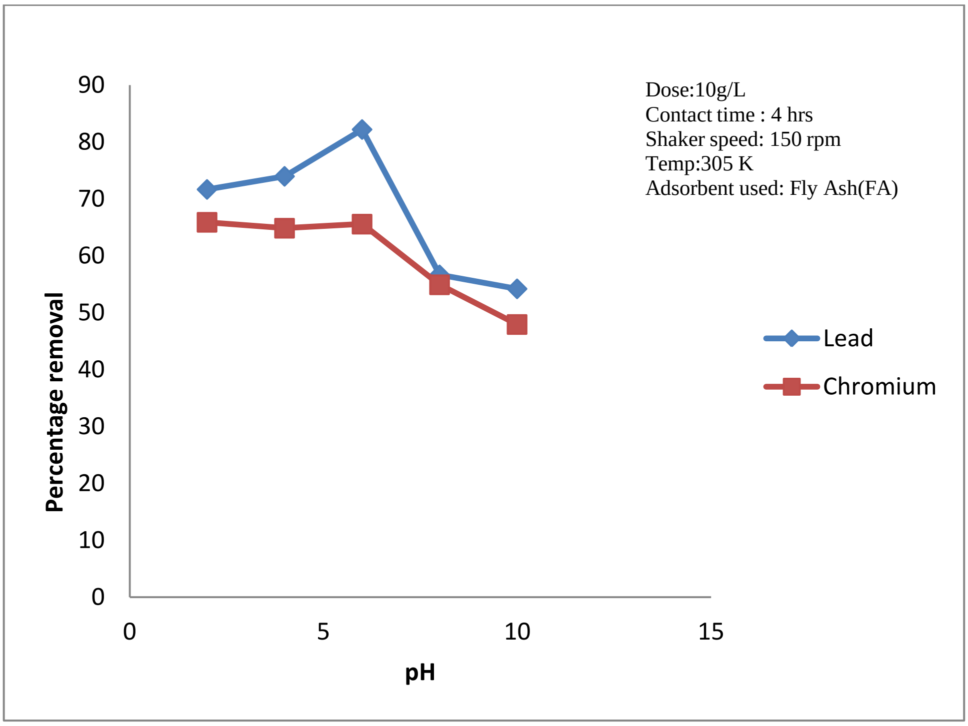


Fig 5.13 pH optimization study of FA

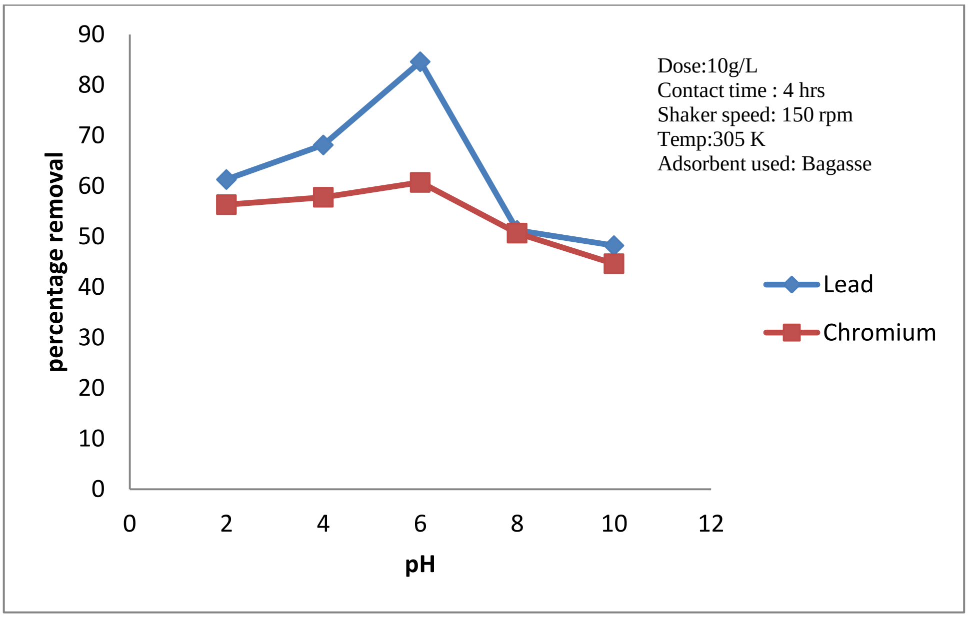


Fig 5.14 pH optimization study of bagasse

5.2.2.2 Effect of adsorbent dose

In this study the contact time was kept constant at 4 hr and the adsorbent dose was varied from 5g/l to 40g/l. The adsorbent dose selected for the present study was 10 g/l as it showed good removal for both lead and chromium. Since the aim of the present study is the simultaneous removal of Cr and Pb hence 10g/l adsorbent dose was chosen as it showed similar removals in less quantity of adsorbent. The dose optimization study is depicted in the following figure

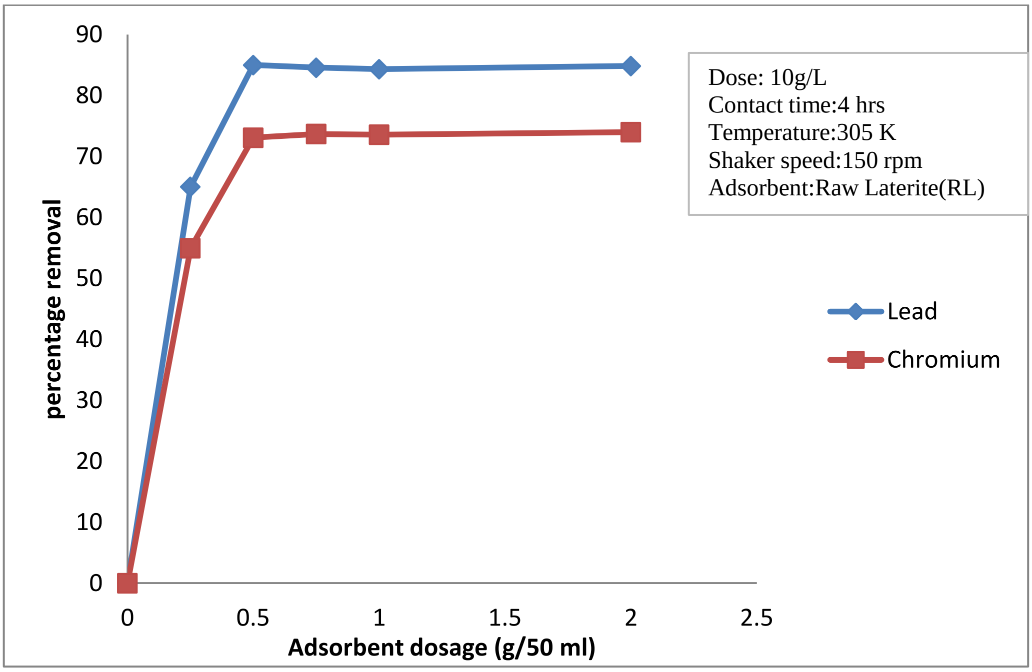


Fig 5.15 dose optimization study of RL

5.2.2.3 Effect of Time

During the time optimization studies it was found that the removal percentage of both Cr and Pb increased with the increase in time but after about four hours the increase observed was almost constant as a result the equilibrium time of adsorption was fixed at 4hr. When compared to the literature the contact time for optimum metal removal by laterite soil varies from 10 min to 24 hr. the contact time of four hours has also been reported by Maji et al, 2007 for removal of arsenic from water. The graph showing the optimization study of time has been depicted in Fig 5.16

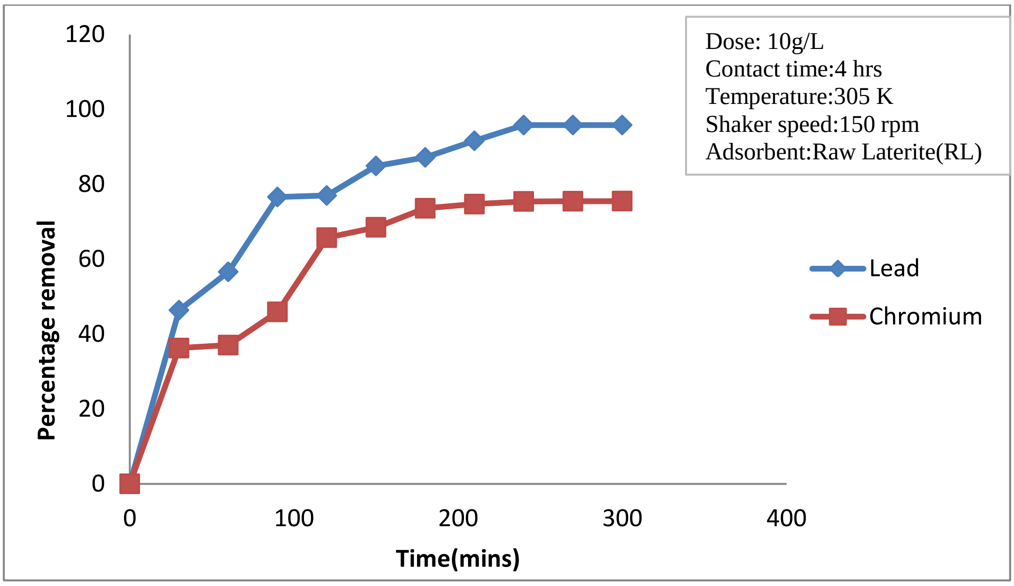


Fig 5.16 time optimization study of RL

5.2.2.4 Effect of initial concentration

In this study the contact time was kept at 4 hr, the dose at 10 g/l and the pH was maintained at 6. The trend observed when the initial concentration was taken in the range of 5, 10, 15 and 20 was that the percentage removal improved minutely with increase in the concentration of the metal solution. The graph depicting the removal percentage for different concentrations has been depicted in Fig 5.20

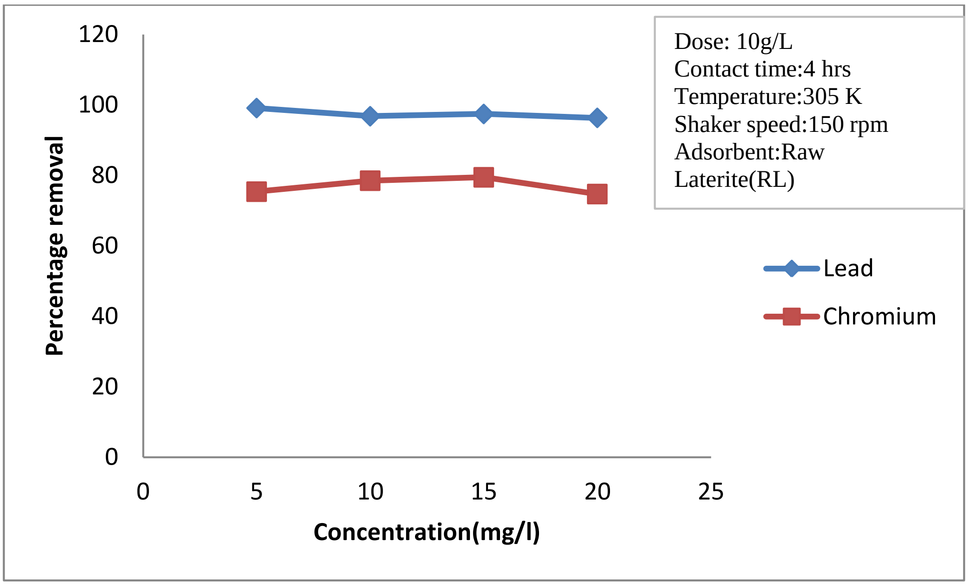


Fig 5.17 initial conc. optimization study of RL

5.2.2.5 Kinetics of the adsorptive study using laterite soil

Two kinetic models have been used to analyze the experimental data. They are pseudo-first order and second order models. The models are represented as:

Pseudo First order

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{\mathrm{K}_1 \mathrm{t}}{2.303}\right)$$

Pseudo Second Order

$$\frac{t}{q_t} = \frac{1}{K_S {q_e}^2} + \frac{t}{q_e}$$

In the present study the pseudo second order model has been found to fit better to the experimental data. The pseudo-second-order kinetic model fits with respect to time for both Cr and Pb. The values of model-predicted or theoretical q_e fitted well with the experimental equilibrium adsorption capacity.

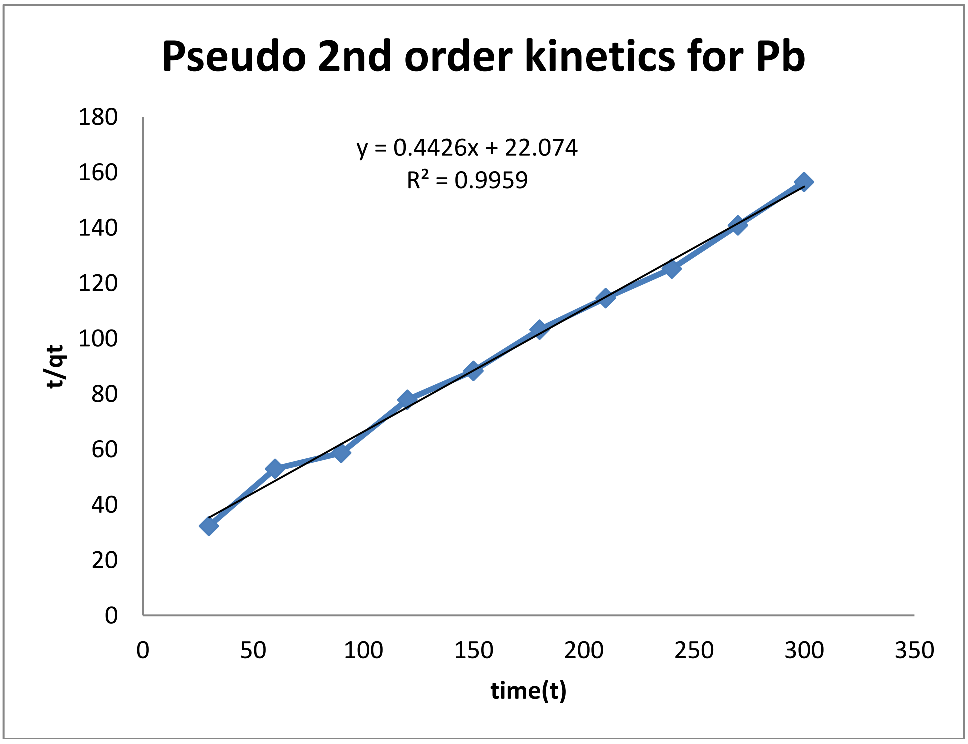


Fig 5.18 pseudo second order kinetics for Pb

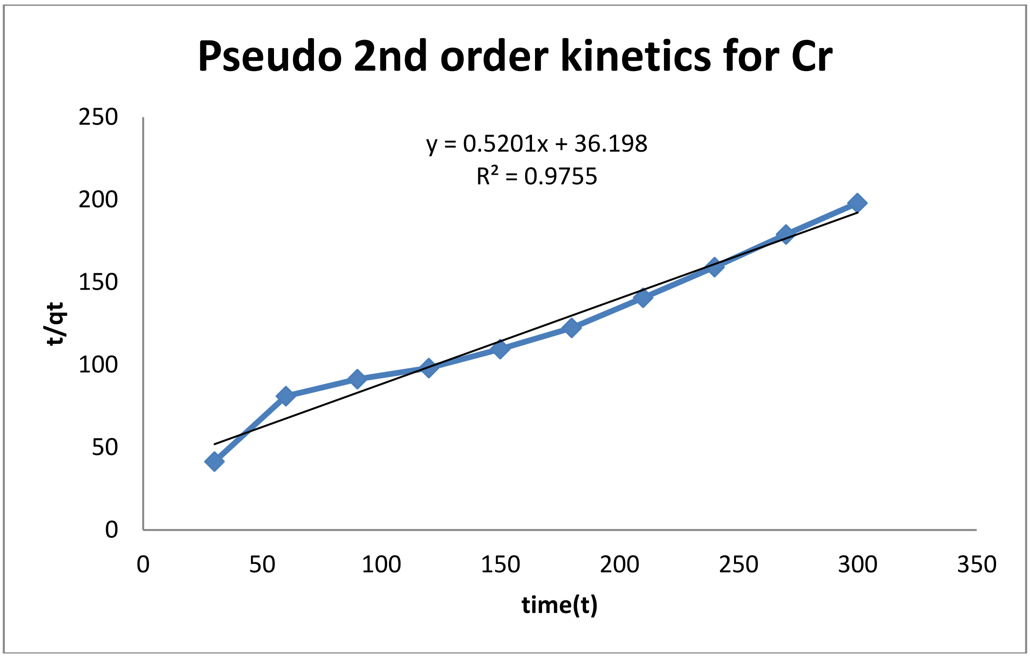


Fig 5.19 pseudo second order kinetics for Cr

Table 5.4 Parameters for pseudo-second order model

For t = 4hrs, C_O=20 mg/L, m=10 g/L, T=305 K		
Parameters	**Chromium**	**Lead**
K_S (g/mg min)	0.00747	0.0089
q_e (mg/g)	1.922	2.259
R^2	0.9755	0.9959

5.2.2.6 Equilibrium study

Equilibrium studies were carried out in order to estimate the conditions for maximum lead and chromium uptake by the laterite soil. The isotherm data was found out by using the Cr and Pb concentrations as 5, 10, 15 and 20 mg/l with a fixed adsorbent dose of 10g/l at three different temperatures of 300, 305 and 315 K.

Experimental data on adsorption can be fitted by using different isotherm models such as Langmuir isotherm and Freundlich isotherm. In the present study both the Langmuir and the Freundlich isotherms were examined, but Freundlich isotherm gave a better fit of the experimental data based on the regression coefficient values.

Freundlich adsorption isotherm is an empirical relation that relates the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact.

The non-linear Freundlich isotherm equation can be written as

$$q_e = K_f C_e^{1/n}$$

Where q_e= amount of adsorbate per unit mass weight of the adsorbent (mg/g)
1/n= adsorption intensity
K_f= adsorption Capacity
C_e= equilibrium concentration of the adsorbate after time (mg/l)

Single component adsorption isotherms

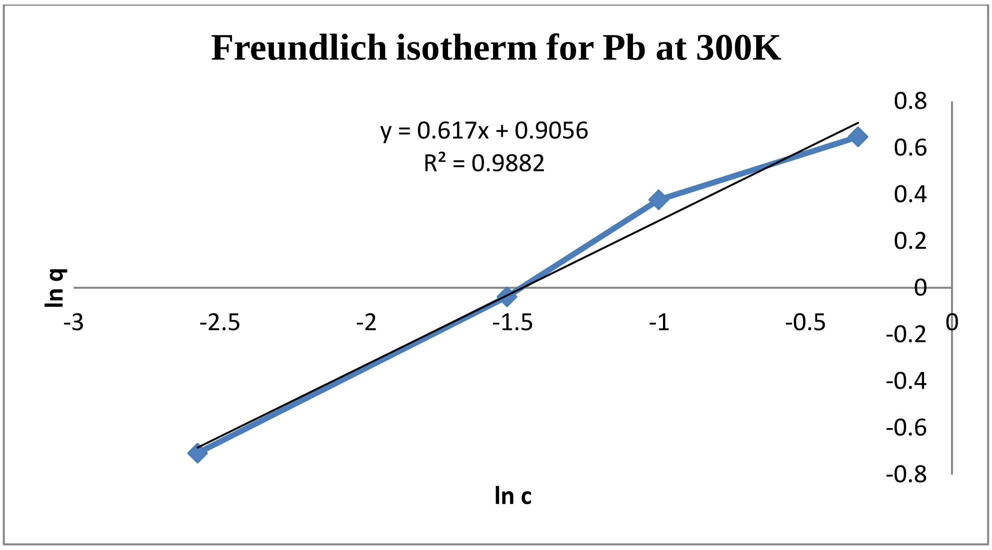


Fig 5.20 Freundlich isotherm for Pb at 300K

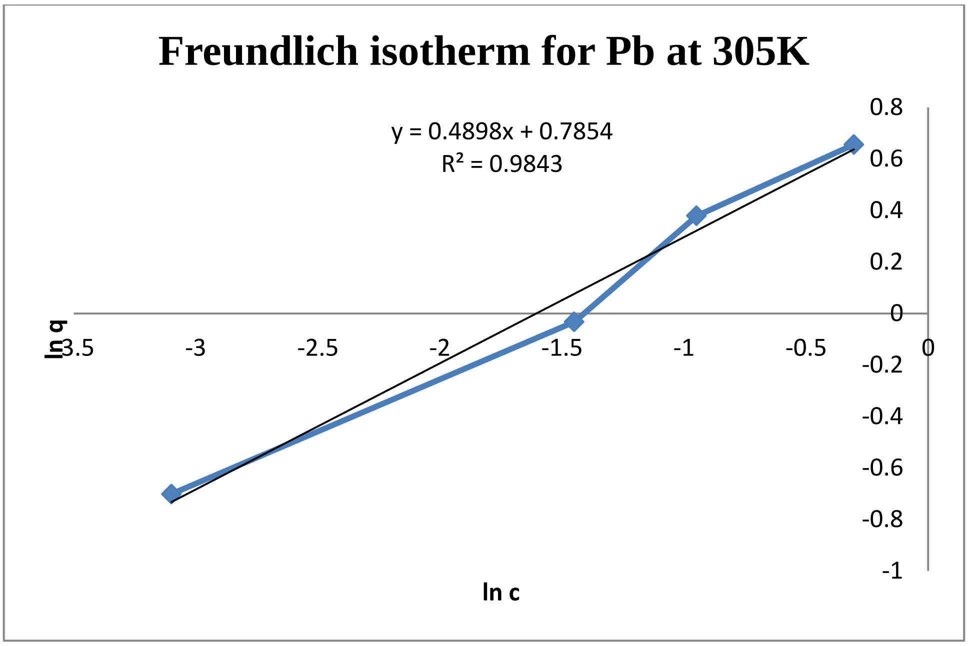


Fig 5.21 Freundlich isotherm for Pb at 305K

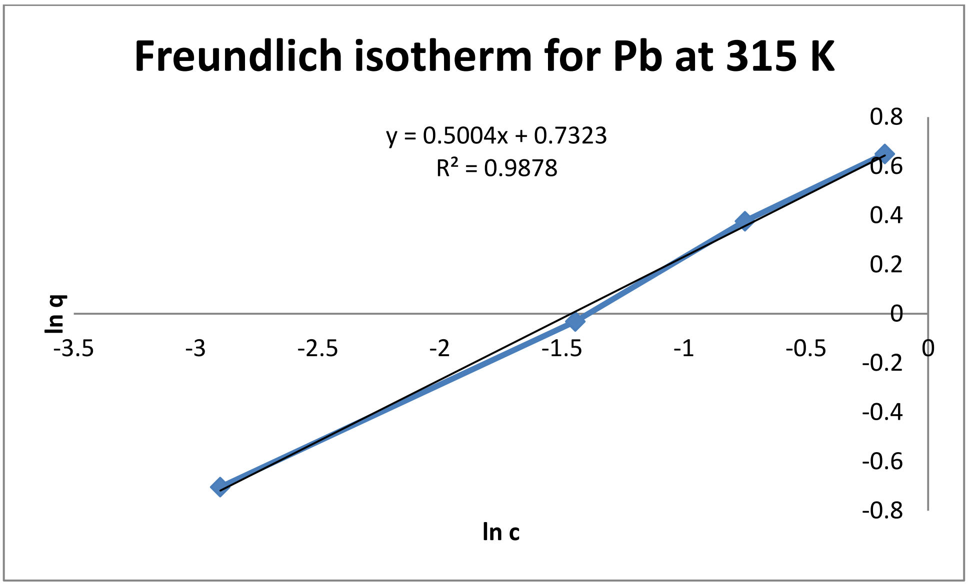


Fig 5.22 Freundlich isotherm for Pb at 315K

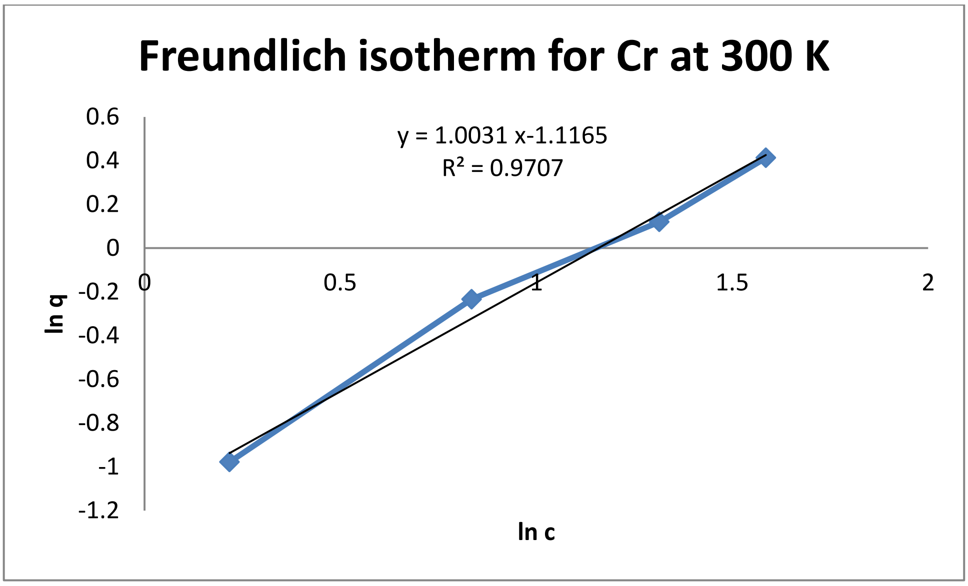


Fig 5.23 Freundlich isotherm for Cr at 300K

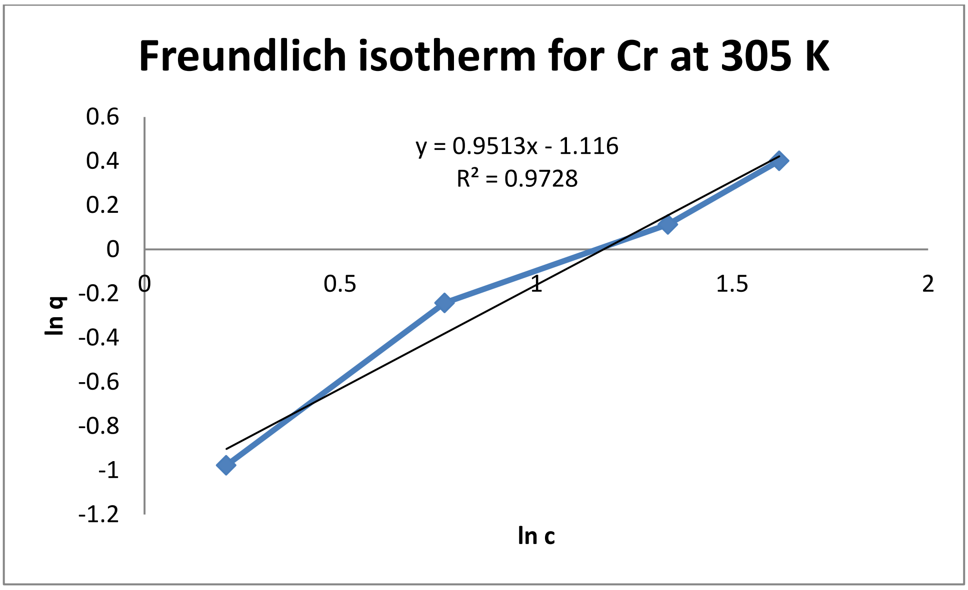


Fig 5.24 Freundlich isotherm for Cr at 305K

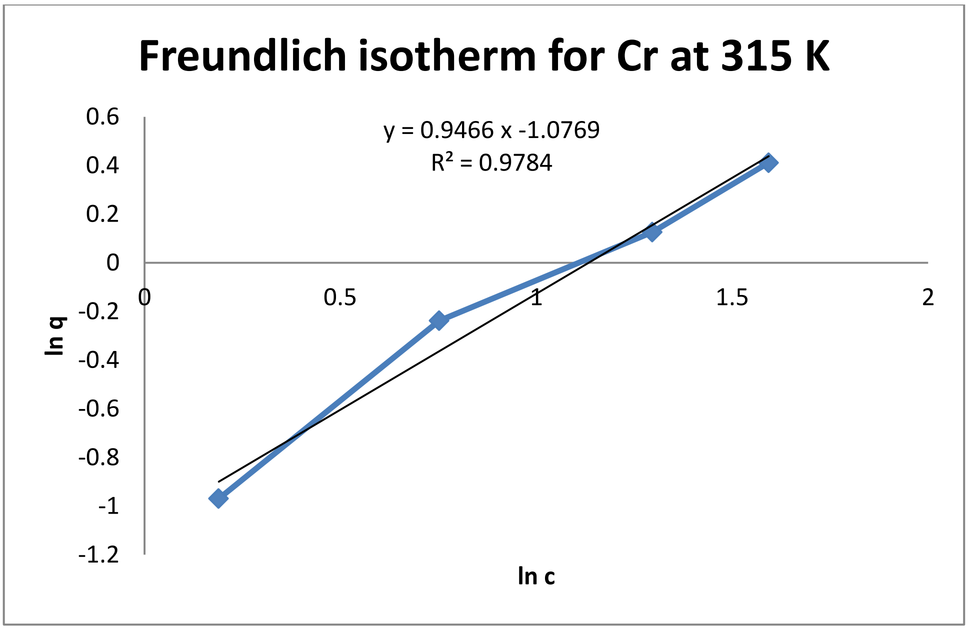


Fig 5.25 Freundlich isotherm for Cr at 315K

The calculated values of constants for Freundlich isotherm constants are given in the following table

Table 5.5 Parameters for adsorption isotherm constants of Cr and Pb on RL

Constants for Chromium				**Constants for Lead**		
Temp (K)	**K_F (mg/l)**	**n**	**R^2**	**K_F (mg/l)**	**n**	**R^2**
300	0.327	0.997	0.9707	2.47	1.6207	0.9882
305	0.3276	1.051	0.9728	2.19	2.042	0.9843
315	0.3406	1.056	0.9784	2.094	1.98	0.9878

5.2.3 Multi- component adsorption:

The simplest approach to describe adsorption equilibrium in a multicomponent system is to extend the models of adsorption isotherms of single component systems. Extended Langmuir model is derived from Langmuir model for single components and Extended Freundlich has been derived from single component Freundlich model. In the present study simultaneous adsorption of Chromium and lead were carried out using raw laterite soil (RL).

The equilibrium solid phase concentration of each adsorbate in a multi-component system and percentage removal of individual adsorbate is calculated from the following equations:

$$q_{e,i} = \frac{(C_{o,i} - C_{e,i})V}{w}$$

$$Rem_i\% = \frac{(C_{o,i} - C_{e,i})}{C_{o,i}} X\ 100$$

Where,

$q_{e,i}$ = solid phase equilibrium concentration of each adsorbate in a dual component mixture (mg/g)

$C_{O,i}$ = initial concentration of each component (mg/L)

$C_{e,i}$ = equilibrium concentration of each component (mg/L)

The results for dual component systems showed good fit to the Extended Freundlich model.

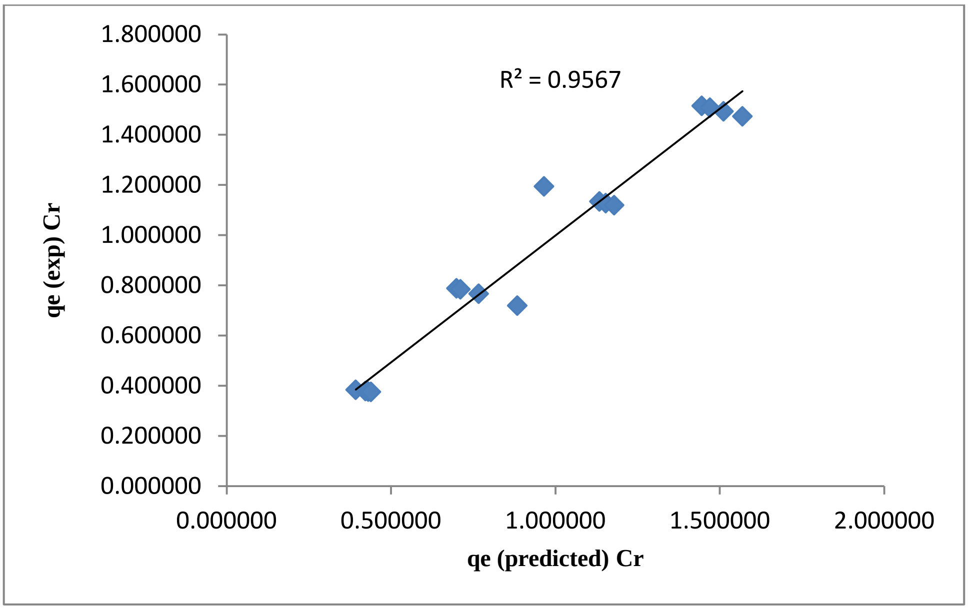


Fig 5.26 predicted and experimental values of qe of Extended Freundlich isotherm model for Cr at 300K

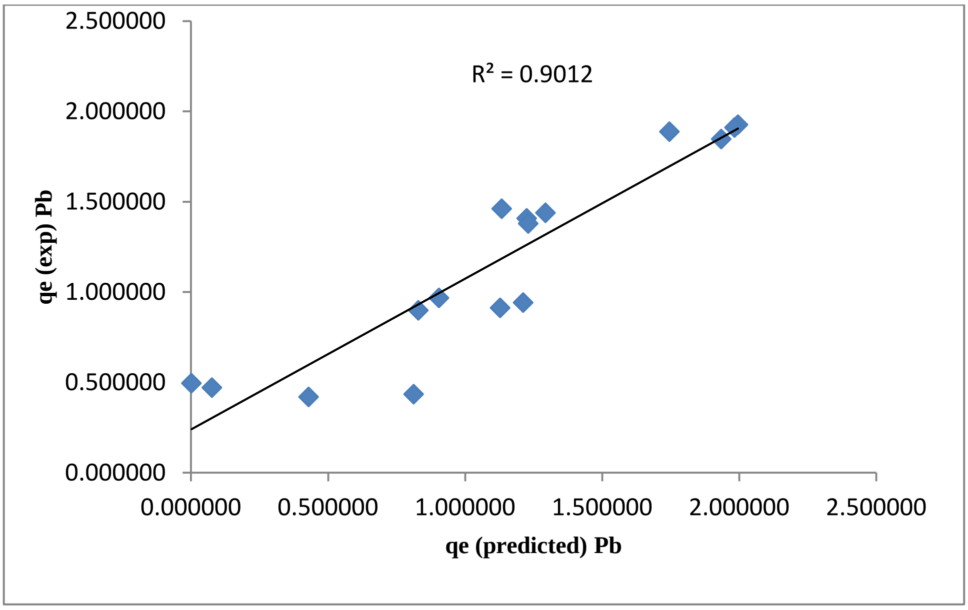


Fig 5.27 predicted and experimental values of qe of Extended Freundlich isotherm model for Pb at 300K

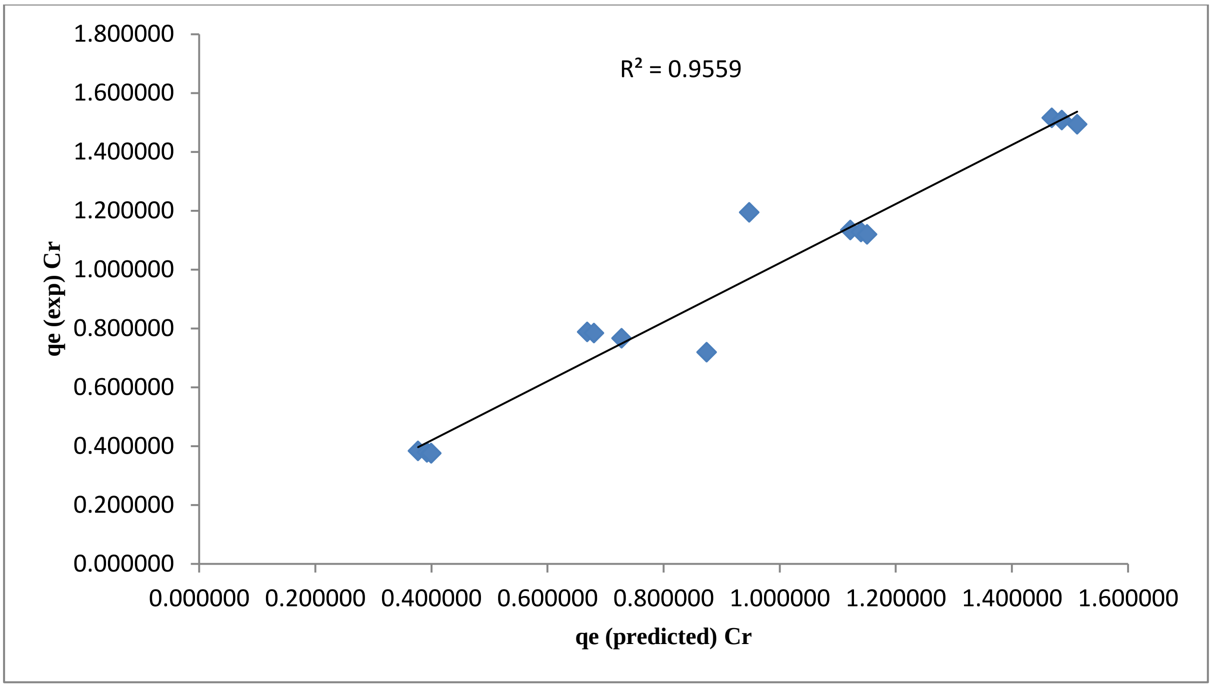


Fig 5.28 predicted and experimental values of qe of Extended Freundlich isotherm model for Cr at 305K

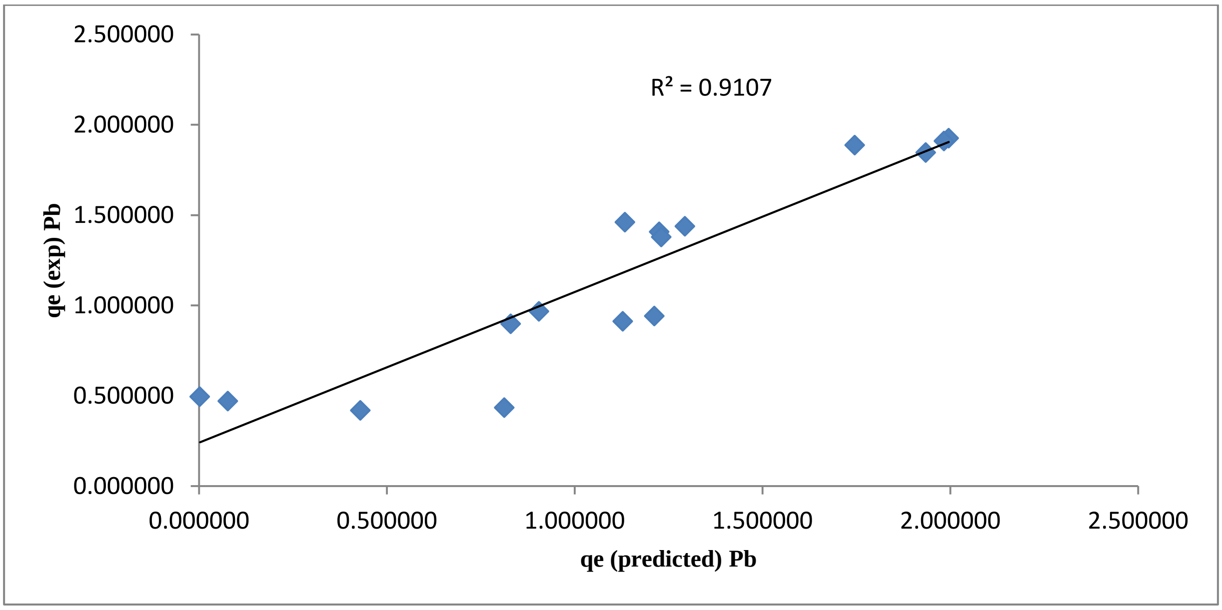


Fig 5.29 predicted and experimental values of qe of Extended Freundlich isotherm model for Pb at 305K

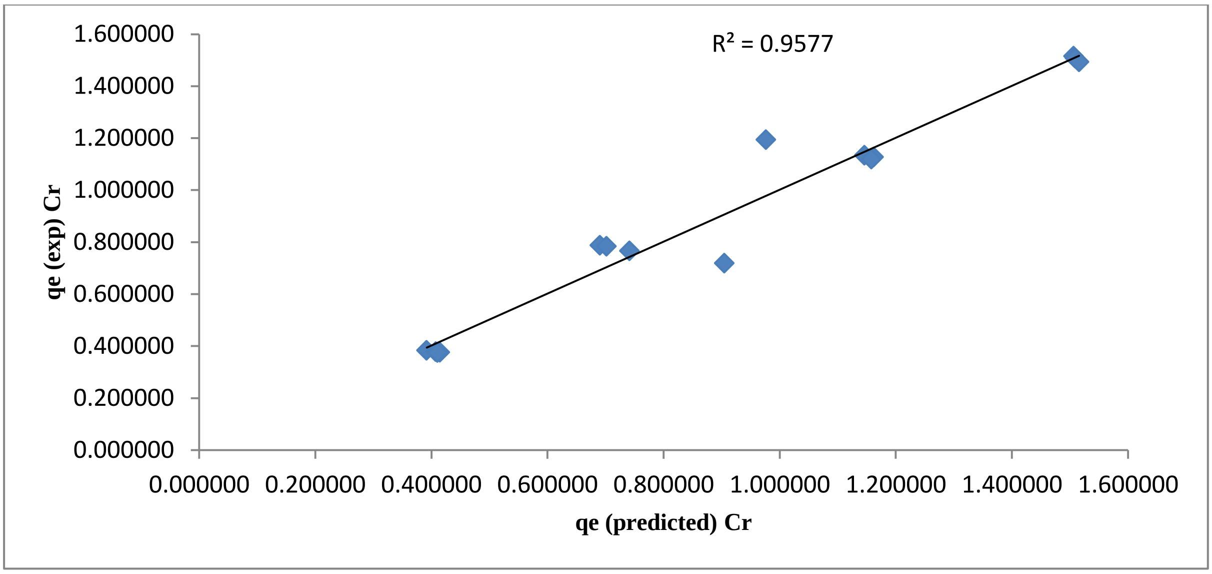


Fig 5.30 predicted and experimental values of qe of Extended Freundlich isotherm model for Cr at 315K

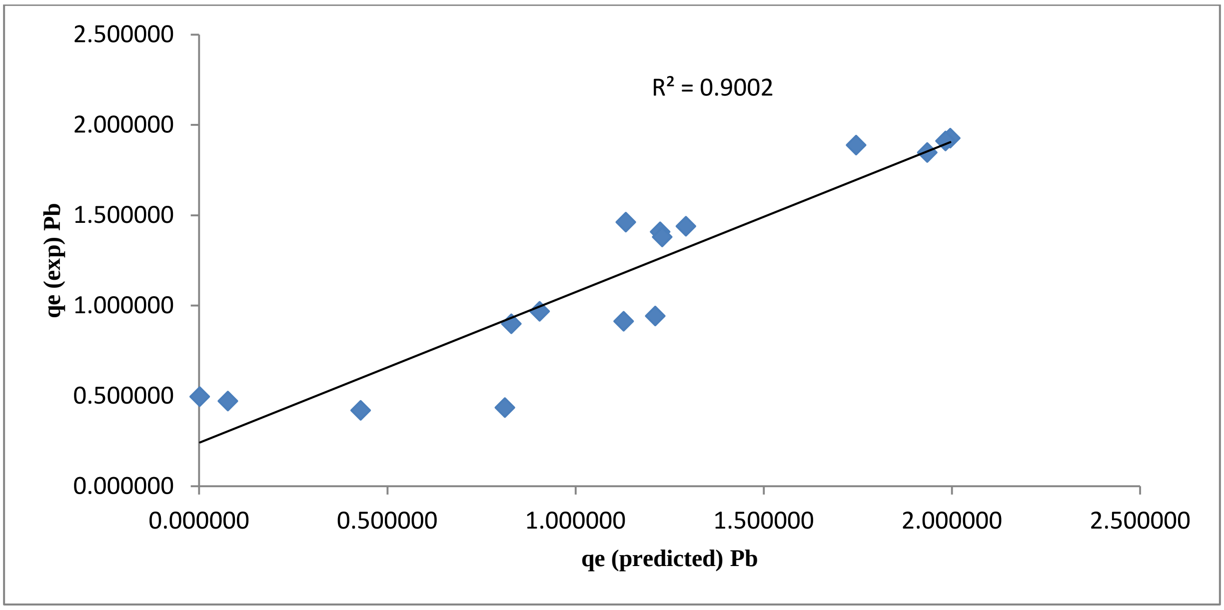


Fig 5.31 predicted and experimental values of qe of Extended Freundlich isotherm model for Cr at 315K

6. Conclusions:

Based upon the experimental work the following conclusions can be drawn:

- Of the three adsorbents, Raw Laterite (RL) demonstrated the best results in terms of removal capacity.
- Raw Laterite (RL) showed best removal at a dosage of 10 g/L, contact time of 4 hours, temperature of 305 K and rpm of 150
- Best removal figures were obtained for both Lead and Chromium at pH 6.
- RL was able to remove around 93% Lead and 74% Chromium from single component systems.
- Experimental data fitted well with Freundlich Isotherm and followed pseudo second order kinetic model.
- Multicomponent removal of lead and chromium showed good results and the values of regression analysis coefficients for predicted and experimental values of solid phase equilibrium concentration of each adsorbate in a dual component mixture followed the same trend.

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