ADSORPTION STUDIES FOR THE REMOVAL OF HEXAVALENT CHROMIUM USING FLY ASH OF 'WASTE TO ENERGY POWER PLANT'

A Dissertation submitted to the Central University of Punjab

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BY

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CERTIFICATE

I declare that the dissertation entitled “ADSORPTION STUDIES FOR THE REMOVAL OF HEXAVALENT CHROMIUM USING FLY ASH OF WASTE TO ENERGY POWER PLANT” has been prepared by me under the guidance of Prof. P. Ramarao, Administrative Guide, Acting Dean, School of Environment and Earth Sciences and Dr. Sunil Mittal, Assistant Professor, Centre for Environmental Science and Technology, Central University of Punjab. No part of this dissertation has formed the basis for the award of any degree or fellowship previously.

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ABSTRACT

Adsorption Studies for the Removal of Cr (VI) using Fly Ash of ‘Waste to Energy Power Plant’

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Chromium is the most common pollutant discharged in industrial effluent and reported to be present beyond permissible limits causing various health problems like carcinogenicity. Therefore, it must be removed from industrial effluent before its discharge. Several physico-chemical methods have been used for the removal of Cr (VI) from industrial effluents. Adsorption using activated carbon is quite efficient for the removal of Cr (VI) from industrial effluents. However, it is a costly process and the regeneration of activated carbon is difficult. Hence, in the present work, efforts have been made to explore the use of fly ash collected from the ‘Waste to Energy Power Plant’ as a low cost adsorbent. In order to maximize the Cr (VI) removal from simulated aqueous solutions, effects of various parameters (adsorbent dose, contact time, pH and initial metal ion concentration) on Cr (VI) adsorption were investigated by batch adsorption experiments. By optimizing the conditions for Cr (VI) adsorption using the fly ash, removal of hexavalent chromium from the aqueous solution (10 µg Cr/ml) was increased from 4% to approx. 99%. This shows that fly ash of agricultural waste burning can be used as an adsorbent for the removal of Cr (VI) at low concentration.

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(Upma Vaid)

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LIST OF ABBREVIATIONS

Sr. No.	Full form	Abbreviation
1.	Raw fly ash material	RM

2.	Washed fly ash material	WM
3.	Raw fly ash after treatment of aqueous solution	TRM
4.	Washed fly material after treatment of aqueous solution	TWM
5.	Laser beam Particle Size Analysis	LPSA
6.	Scanning Electron Microscopy	SEM
7.	Energy Dispersive X-ray Spectroscopy	EDX
8.	Fourier Transformation Infrared Spectroscopy	FTIR
9.	Initial concentration of metal ion (mg/l)	C_o
10.	Equilibrium concentration of solute in bulk solution (mg/l)	C_e
11.	Amount of solute adsorbed per unit weight of sorbent at equilibrium (mg/g)	q_e
12.	Amount of solute adsorbed per unit weight of sorbent at any time (mg/g)	q_t
13.	Time	t
14.	Langmuir constant related to the free sorption energy	b
15.	Chromium removal in Percent	R%
16.	Dimensionless separation factor for Langmuir isotherm	R_L

CHAPTER-1

INTRODUCTION

Chromium (Cr) is a metal of transition series with atomic number 24 and atomic weight 51.996. It has several oxidation states but trivalent and hexavalent states are most stable (Saha *et al.,* 2011). Trivalent chromium is common and occurs in ores like ferrochromite. However, hexavalent chromium is not present naturally, but added in environment due to anthropogenic activities (Zayed and Terry, 2003). Chromium has been reported as most widespread contaminant in nature because of its wide industrial applications like production of steel, chrome plating, anodizing of aluminium, dye and paint production, textile dyeing, tanning of leather, wood preservation, water-cooling etc. (Zayed and Terry, 2003; Altundogan, 2005; Shanker *et al.,* 2005; Yavuz *et al.,* 2006; Owlad *et al.*, 2009; Saha *et al.,* 2011).

In environment, chromium exists in two stable oxidation states; Cr (III) and Cr (VI) (Bishnoi *et al.,* 2004). However, toxicity is mainly caused by hexavalent chromium compounds (Baruthio, 1992). As per Saha *et al.,* 2011, the acute and chronic exposures of hexavalent chromium are 100-folds more toxic than trivalent chromium. This is mainly due to high water solubility, mobility and easy reduction of hexavalent chromium.

In humans and animals, the modes of exposure to chromium are inhalation, contact or ingestion of contaminated food or drinking of water. Inhalation of hexavalent chromium affects the respiratory tract and lead to perforations and ulcerations of nasal septum, bronchitis, impaired pulmonary function, pneumonia, nasal itching and soreness. Ingestion of high amount of hexavalent chromium may affect liver, kidney, gastrointestinal and immune systems. Contact dermatitis, sensitivity, and ulceration of the skin may be caused by dermal exposure to hexavalent chromium (Saha *et al.,* 2011).

Exposure to hexavalent chromium not only affects animals but also to plants. Toxic effects of chromium on plant include alterations in the germination process, growth of roots, stems and leaves. These alterations may lead to decrease in yield by affecting the physiological processes like photosynthesis, water relations and mineral nutrition of the plant. Chromium exposure also leads to metabolic alterations in plants either by directly affecting enzymes or other metabolites or may leads to oxidative stress by affecting their ability to generate reactive oxygen species (Zayed and Terry, 2003; Shanker *et al.,* 2005).

According to Indian Standards, the maximum permissible limit for discharge of Cr (VI) into inland surface waters is 0.1 mg/l and in public sewer is 2.0 mg/l. While, maximum permissible limit for potable water is 0.05 mg/l. Hence, industries must treat their effluents to reduce the Cr (VI) to acceptable levels before discharging into the nearby water bodies.

1.1 METHODS OF CHROMIUM REMOVAL

A number of physico-chemical methods has been used for the removal of chromium from wastewater like ion exchange, chemical reduction and precipitation, electrolysis, ion flotation, membrane processing, electrolytic methods and carbon adsorption (Kumar, 2006; Malaviya and Singh, 2011). All these technologies have some merits and demerits. Ion exchange and various membrane separation processes allow chromium recovery without production of toxic sludge. But these have problems like membrane fouling and high operation and maintenance costs. In industrial sector, precipitation, reduction and adsorption are preferred because these are economic; however, they present the problem of sludge generation and its disposal (Malaviya and Singh, 2011). Major advantages of adsorption system are simple design, easy operation and lesser initial cost for set up (Fadali *et al.,* 2004).

1.2 ADSORPTION

Adsorption is a mass transfer process in which a constituent in the liquid phase is transferred to the surface of solid phase (Metcalf and Eddy, 2004; Artioli, 2008). The constituent which is removed from the liquid phase by transfer to the surface of solid phase is known as adsorbate while solid phase on the surface of which adsorbate accumulate is known as adsorbent (Metcalf and Eddy, 2004). Adsorbate accumulates on the surface of adsorbent due unbalanced surface forces (Eckenfelder *et al.,* 2009).

Adsorption takes place by three methods; physical, chemical and exchange adsorption.

- Physical adsorption is due to weak forces of attraction or Vander Waals' forces of attraction between the molecules of adsorbate and the adsorbent. It results in the condensation of adsorbate in several superimposed layers on the surface of adsorbent. It is usually reversible. The adsorbate may get desorbed to the same extent with the decrease in concentration.

- In Chemical adsorption, the bonds form as the result of stronger forces equivalent to those leading to the formation of chemical compounds. The adsorbate forms a monomolecular layer over the surface of adsorbent. It is irreversible in nature, for desorption heating of material at higher temperature has to be done.
- Exchange adsorption take place as the result of electrostatic forces of attraction between the adsorbate and the sites of opposite charges on the surface of adsorbent (Sawyer *et al.,* 2003).

The adsorption process and extent of adsorption depends upon the different parameters like physico-chemical characteristics of the adsorbent, adsorbate and experimental conditions (Fahim *et al.,* 2006) like pH, temperature, time, absorbate concentration, adsorbent size and dose.

1.3 TYPES OF ADSORBENTS

1.3.1 Commercial adsorbents

Activated carbon, synthetic polymeric and silica based adsorbents are the three types of commonly used commercial adsorbents. However, due to their higher cost synthetic polymeric and silica based adsorbents are rarely used for wastewater treatment. Only activated carbon is preferred for wastewater treatment at present (Metcalf and Eddy, 2004).

Adsorption using activated carbon is quite efficient for treatment of wastewater containing organic compounds, heavy metals and colouring materials. However, activated carbon is costly and there is the problem of regeneration connected with its use (Fadali *et al.,* 2004). Hence, efforts are being made to develop low cost and readily available materials for heavy metal adsorption.

1.3.2 Low-cost adsorbents

Many attempts have been made to develop low-cost adsorbent by using both natural materials and wastes and by-products of many industries either as such or after some minor treatment. The materials used in various studies include non-living biomass of fresh water macrophytes, aquatic weeds, agricultural waste residue, and waste material from various industrial processes.

Using waste material from various industrial processes for treatment of wastewater of other industries is a very good option in environmental and economical terms for the industries. The activity will not only solve the problem of waste management but will also provide ways for its beneficial use. So efforts are being made to find low-cost materials which are abundant and environmentally safe.

The present work describes the batch adsorption characteristics of fly ash from the ‘Waste to Energy Power Plant’, Gidderbaha. The power plant uses a huge quantity of agricultural residues of seasonal crops to produce electricity leaving behind ash. It is suitable to use it as adsorbent because it will not only provide a low-cost adsorbent but also solve the problems of its disposal. The effect of various parameters operating on Cr (VI) adsorption from simulated sample has been investigated through batch adsorption experiments.

CHAPTER-2

REVIEW OF LITERATURE

A lot of research work has been done using different types of low cost materials like sea weeds, aquatic macrophytes, microorganisms, activated sludge, agricultural and industrial waste etc. to find their application in the adsorption of heavy metals in place of the costly adsorbents. Different adsorbents had showed difference in their efficiency for metal removal depending upon their nature and composition and the experimental conditions like temperature, pH, adsorbent dose, presence of other metal ions and Initial concentration of metal ions etc.

The studies of Schneider and Rubio (1999) using non-living biomass of fresh water macrophytes (dried biomass of *Photomogeton lucens*, *Salvinia henzogi* and *Eicchornia crassipes*) showed the adsorption of divalent metal ions like Cr^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. It was found that the dried biomass of *Potamogeton lucens, Salvinia herzogii*, and *Eichhornia crassipes* were excellent biosorbents for these metals. Elangovan *et al.* (2008) also studied the kinetics and mechanism of biosorption of Cr (VI) by different aquatic weeds. They found that Cr (VI) removal capacity of the biosorbents significantly increased after acid treatment, whereas, the Cr (VI) removal capacities of the biosorbents get reduced when treated with alkali.

Biological wastes from agricultural origin are also used as potential adsorbents of Cr and other heavy metals. Dakiky *et al.* (2002) carried out experiments to remove Cr (VI) from industrial wastewater by using different adsorbents like wool, olive cake, sawdust, pine needles, almond shells, cactus leaves and charcoal which are low-cost and abundant. They reported that for the selective removal of Cr (VI), wool was the best among the selected adsorbents at pH 2 with 81% removal efficiency. Later, Demirbas *et al.* (2004) studied the removal of Cr (VI) from aqueous solution using cornelian cherry, apricot stone and almond shell as adsorbent. They concluded that adsorption of Cr (VI) highly depends on pH. For all types of carbon, the optimum pH was reported as 1.0. Sumathi *et al.* (2005) also carried out experiments to remove chromium from tannery effluent using sawdust, rice husk, coir pith and charcoal and vermiculite through batch and column experiments. They determined the adsorption capacities of various substrates using isotherm tests and computing distribution co-efficient. They found that sawdust and coirpith exhibit high adsorption capacity. Cr was removed upto 94% by using a column of coirpith, and it was removed upto 93% by a column containing mixture of coirpith and vermiculite.

Ahalya *et al.* (2007) studied the removal of Fe (III) and Cr (VI) ions from aqueous solutions using the husk of tur dal (*Cajanus cajan*). They studied the effect of parameters like agitation time, adsorbent dosage and pH at different initial Fe (III) and Cr (VI) concentrations. It was found that the biosorptive capacity of the tur dal husk was pH dependent. Optimal pH of the chromium and iron solution was found to be pH 2 and 2.5, respectively. From the infrared spectra of the biomass it was revealed that the uptake of Cr (VI) and Fe (III) ions took place with the involvement of hydroxyl, carboxyl and amide bonds. They concluded that tur dal husk is an excellent material for removing low concentration of metal ions from wastewater.

Pomegranate husk was used by El Nemr (2007) for the removal of Cr (VI) from aqueous solution. The batch experiment was conducted to determine the adsorption capacity of the pomegranate husk. They observed that adsorption capacity has strong dependence on pH. It increased with decrease in pH and the optimum pH value was found to be 1.0. 100% removal of Cr (VI) took place from aqueous solution having initial concentration 25 mg/l of Cr (VI) concentration by the use of 5 g/l pomegranate husk. Another study has been made by Garg *et al.* (2007) on the adsorption of Cr (VI) using sugarcane bagasse, maize corn cob and Jatropha oil cake from aqueous solutions. They investigated the effects of adsorbent dosage, Cr (VI) concentration, pH and contact time on the adsorption of Cr (VI). It was observed that the maximum adsorption take place in the acidic medium at pH 2 with a contact time of 60 minutes at 250 rpm stirring speed. Under similar conditions, Jatropha oil cake had better adsorption capacity than other two materials taken. They concluded that the selected adsorbents can be used as low cost alternatives for the treatment of wastewaters containing low concentrations of chromium in either batch or stirred mode reactors.

Grainless stalk of corn for removal of Cr (VI) and Cr (III) has been used by Bellú e*t al.* (2008). They determined optimum pH 0.84 and 4.6 for the removal of Cr (VI) and Cr (III), respectively. Hasan e*t al.* (2008) used maize bran for the removal of Cr (VI) from aqueous solution by. They observed a maximum uptake of 312.52 mg Cr /g at pH 2.0, temperature 40°C and initial Cr (VI) concentration of 200 mg/L.

They also found that complete desorption of Cr (VI) took place at pH of 9.5. Nameni *et al.* (2008) investigated adsorption of chromium (VI) ions on wheat bran. Results showed optimum contact time for adsorption of chromium by wheat bran was 60 min and optimum pH was 2. . They observed higher chromium adsorption at lower pH, and maximum chromium removal was 87.8 % at pH is 2. At higher initial chromium concentration and lower adsorbent doses adsorption of chromium by wheat bran decreased.

The possibility of using untreated coffee husks for the removal of heavy metals from aqueous solutions was studied by Oliveira *et al.* (2008) and it was found that the sorption efficiency was highest for Cu (II) (89-98%), followed by Cd (II) (65-85%) and Zn(II) (48-79%). Even though equilibrium was not attained in the case of Cr (VI) ions, but still sorption efficiency ranged from 79 to 86%. Sorption performance was found to be inversely proportional to the metal ions concentrations. In the case of Cu (II) and Cr (VI), with the increase in the adsorbent concentration the amount of metal ions sorbed also increased. For the other metal ions increase in the adsorbent concentration did not produce any significant variations. The highest adsorption capacity for each metal ion was observed at different pH value.

Rice hull ash prepared by calcination of rice hull at 500°C under 20 ml air/sec for 50 min was used as adsorbent to remove Cr (III) ion from aqueous solution by Wang and Lin (2008). Rice hull ash thus prepared was not found very efficient. It has been found that by decreasing the rice hull ash dosage the removal of Cr (III) at equilibrium was increased. They determined that increasing the initial chromium concentration or adsorption temperature also increase the removal of Cr (III).

Li e*t al.* (2009) used corn stalk biomass for the removal of Cr (VI) from aqueous solution. Effect of variables such as pH, sorbent dosage and temperature was investigated to determine the optimal experimental conditions for Cr (VI) removal. It was found that during the adsorption process corn stalk powder reduce Cr (VI) to Cr (III) and 97.77% of Cr (VI) removal occurred at 1.0 pH, 30°C temperature, 200 rpm and 3 hours contact time. Increase in adsorption capacity was observed with increase with temperature.

Vinodhini and Das (2009) investigated Cr (VI) adsorption from aqueous solutions on Neem sawdust, Mango sawdust, Wheat shell, Sugarcane bagasse and Orange peel. Out of these, Neem sawdust showed highest Cr (VI) removal efficiency. The concluded that Cr (VI) removal was dependent on the pH of the chromium solution and the optimum pH was 2.0.

Further, Zvinowanda e*t al.* (2009) investigated the possibility of Cr (VI) and Cd (II) ions removal from aqueous solutions by batch adsorption method using maize tassel. It was found that adsorption of both Cr (VI) and Cd (II) highly dependent on pH compared to the other parameters under investigation. Adsorption capacity for Cr (VI) was found to be 79.1 % at pH 2 and contact time of 1h at 25 ºC whereas maximum adsorption capacity for Cd (II) was 88% after exposure time of 1 h at pH range of 5-6 and 25 ºC temperature. They concluded that maize tassel has immense potential for toxic metal ions removal from polluted water and adsorption capacity of tassel was found comparable to those of other commercial adsorbents which are currently in use for the removal of Cr (VI) and Cd (II) from aqueous wastes.

Industries generally have to spend a lot for treatment of effluent and management of solid waste. Various studies have been made to develop low cost adsorbent for the treatment of wastewater using various industrial waste residues. The adsorption behavior of bagasse fly ash, a waste product of sugar industry, as adsorbent for the removal of Cr (VI) from synthetic and actual wastewater has been studied by Gupta *et al.* (1998). They observed decrease in sorption efficiency with increase in pH. They also found that adsorption process using bagasse fly ash follows the Freundlich and Langmuir isotherms for the removal of Cr (VI). Fahim *et al.* (2006) also used activated carbon prepared from waste generated in sugar industry for treatment of tannery wastewater and compared its efficiency with commercial granular activated carbon. They found that the activated carbon prepared from sugar industry waste can be used economically as an efficient technique for Cr (III) removal from tannery wastewaters. Further, Yang *et al.* (2009) also made an attempt to remove Cr (III) and Cr (VI) from aqueous solution by using sugarcane pulp residue, a waste from sugar-refinery, as an adsorbent. They found that there was an increase in removal percentages of Cr (VI) and Cr (III) with increasing dosage of sugarcane pulp residue and temperature and decrease in removal percentages with increasing particle size of sugarcane pulp residue and the initial concentration of chromium ions. pH value influence the removal of Cr (VI) differently from that of Cr (III) removal. An increase in pH values decreased percentage removal of Cr (VI), while the same increased percentage removal for Cr (III). They found that sugarcane pulp residue has higher adsorption capacity for Cr (III) than that for Cr (VI) and concluded that sugarcane pulp residue is more efficient in Cr (III) removal than that for Cr (VI) removal from wastewater.

Waste from various food processing industries has also been used for the removal of Cr (VI). Hossain *et al.* (2005) used black tea leaves as a low-cost adsorbent for the removal of Cr (VI). They conducted batch experiments to evaluate the effects of initial ion concentration, pH and temperature on the removal process. It has been observed that the for 0.1 g/L used black tea leaves, rate constant decreases with increase in the initial ion concentration and increases linearly with temperature increase. In another study exhausted ground coffee waste has been used by Fiol *et al.* (2008). Zubair *et al.* (2008) studied the removal of Cr (VI) and Cr (III) from aqueous solutions by using pulp left after the extraction of juice from *Citrus reticulate.*

Not only waste from agriculture and agriculture based industries have been tested as adsorbent for Cr (VI) but waste from many other industries has also choosen. A study on adsorption of heavy metal ion has been conducted by Srivastava *et al.* (1989) using carbonaceous material developed from the waste slurry generated in fertilizer plants. They found it as a good adsorbent for chromium, mercury and lead, copper and molybdenum but poor adsorbent for cadmium, nickel, cobalt and zinc. Later Singh and Tiwari (1997) also made an attempt to remove Cr (VI) using waste carbon slurry generated in a naphtha-based ammonia plant of the Fertilizer Corporation of India, Gorakhpur as adsorbent. It was found that removal increases with decrease in pH. Maximum removal occurred at pH 2·5.

The adsorption behavior of cement kiln dust as adsorbent to treat tannery effluent containing chromium ions was studied by Fadali *et al.* (2004) and it was found that cement kiln dust has maximum adsorption capacity upto 33 mg/g. After treatment with cement kiln dust chromium concentration in tannery effluent decreased to 0.6 mg Cr/L from initial concentration of 22-mg Cr/L. Malkoc *et al.* (2006) investigated the adsorption potential of pomace, waste generated in olive oil industry, by batch and column experiments. The maximum of Cr (VI) adsorption was observed at pH 2.0. They observed a decreased total Cr (VI) adsorbed and equilibrium Cr (VI) uptake with increasing flow rate and increased total Cr (VI) adsorbed and equilibrium chromium (VI) uptake with increasing inlet Cr (VI) concentration.

A study has been conducted by Gupta *et al.* (2010) on the removal of Cr (VI) from aqueous solution using carbon slurry, produced in generators of fuel oil-based industrial generators as adsorbent. Before using as adsorbent carbon slurry was chemically treated, activated and characterized. They observed maximum removal after 70 min contact time with optimum pH 2.0, optimum dose 4.0 g/L and 303 K temperature.

Adsorption potential of fly ash obtained from a lignite combustion power plant was investigated by Fytianos *et al.* (1997) in batch adsorption experiments for the removal of Cr (VI) from aqueous solutions and tannery wastewater samples. The optimum pH determined was 2 with a contact of 2 hours.

Effect of pH on the removal of metallic cations (Cu^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) from aqueous solution by coal fly ash was studied by Ricou *et al.* (1998). It has been observed that for a fly ash concentration equal to 20 g/l pH increases to 11 which lead to higher removal capacity due to partly to bulk solution precipitation. Further, it has been found that wet fly ash gives smaller adsorption capacity due to lost alkalinity and dissolution of alumina sites. Sorption capacities for metallic ions increase from 10% or 40% to 100% when pH varies from 1 to 10. The removal order of metallic cations was Pb > Cr > Cu > Ni > Zn > Cd.

Studies also showed that structural modification of biosorbent by various processes may affect the removal efficiency. Selvi *et al.* (2001) studied the Cr (VI) removal efficiency of activated carbon prepared by treatment of coconut tree sawdust with concentrated sulphuric acid. They concluded that Cr (VI) adsorption is dependent on pH and the maximum removal take place at lower pH. They also conducted desorption studies and found that with the increase in concentration of sodium hydroxide from 0.01 to 0.1 M percentage of Cr (VI) desorption increases.

Thermally prepared activated rice husk and activated alumina was used by Bishnoi *et al.* (2004) for the removal of Cr (VI) from synthetic solutions. The optimum pH determined for maximum removal of Cr (VI) by activated rice husk was pH 2 and pH 4 for activated alumina. Increase in the dose of both the adsorbents and their contact time lead to increase in amount of Cr (VI) adsorbed.

Garg *et al.* (2004) investigated the Cr (VI) removal capacity of formaldehyde treated sawdust and sulphuric acid treated sawdust carbon of Indian Rosewood, a waste from timber industry. They found that sulphuric acid treated sawdust carbon had higher Cr (VI) adsorption efficiency than formaldehyde treated sawdust. The optimum initial pH determined for Cr (VI) removal by both the adsorbents was 3.0 and the maximum Cr (VI) removal was observed within first 60 min of experiment.

Activated neem leaves were used by Babu and Gupta (2008) in batch adsorption studies for the removal of Cr (VI) from aqueous solutions. They gave heat and concentrated hydrochloric acid treatment to neem leaves for activation. Then, they further treated the activated neem leaves with 100 mmol of copper solution. The maximum Cr (VI) adsorption (99%) was observed at pH in the range of 1-3 at initial concentration 50 mg/l with an adsorbent dose of 10 g/l. Maximum adsorption capacity was determined to be 62.97 mg/g by the application of the Langmuir isotherm to the system. Kinetics study revealed that the adsorption process follows second order kinetics. Namasivayam and Sureshkumar (2008) used coconut coir pith after modification with hexadecyltrimethylammonium bromide for the removal of Cr (VI) from electroplating effluent. The optimum pH required was found to be 2.0 for adsorption of Cr (VI). Later, structurally modified *Zea mays* cob powder was used by Goyal and Srivastava (2009) for the removal of Pb (II), Cd (II), Ni (II) and Cr (III) from single as well as multi-metal ion solutions. Strengthening of functional groups (COO^-) responsible for binding of metal species has been done using acetylation, succination and graft co-polymerization processes. The resultant biomaterial showed enhanced sorption efficiency from 2 to 15% and stability in terms of regeneration cycles from 3 to 5%.

Comparative study of the efficiencies of unmodified and HCl modified coconut husk and teak tree bark for the removal of Cr (VI) and Ni (II) from aqueous solution was done by Kehinde *et al.* (2009) and it was concluded that for Cr (VI) ion HCl modified adsorbents were better adsorbents while for Ni (II) ion the unmodified adsorbents were better adsorbent.

CHAPTER-3

AIM AND OBJECTIVES

The objective of the present study is to explore the use of fly ash from ‘Waste to Energy plant’, Gidderbaha, Distt. Mukatsar as a low cost adsorbent for the removal of hexavalent chromium from aqueous solutions.

In order to achieve the above objective following work was planned:

- ❖ Physical and chemical characterization of the raw and washed fly ash
- ❖ The effect of variation in following parameters on adsorption of chromium
    - adsorbent dose
    - contact time
    - variation in pH and

    - initial metal ion concentration
- ❖ Calculation of adsorption efficiency by mass balance
- ❖ Calculation of adsorption capacity by plotting adsorption isotherm

CHAPTER-4

MATERIALS AND METHODS

4.1 MATERIALS

Fly ash from ‘Waste to Energy plant’, Gidderbaha was selected as adsorbent for the adsorption studies.

All the chemicals used in experimental work were of analytical grade and were procured from Lobachemie Pvt. Ltd., Mumbai. Potassium dichromate was used for preparation of stock solution of Hexavalent chromium as adsorbate. Other chemicals used for the estimation of metal ion were Sulfuric acid, Phosphoric acid, 1, 5-diphenylcarbazide, Acetone etc. All the solutions were prepared using distilled water.

4.2 INSTRUMENTS

4.2.1 Electronic Weighing Balance

Sartorius Model TE64 with least measurement 0.1 mg was used for all type of weighing purposes like weighing salts to prepare solutions and weighing of adsorbent doses.

4.2.2 Ultra Violet and Visible (UV-VIS) Spectrophotometer

The metal ion concentration was determined spectrophotometrically using UV-VIS double beam spectrophotometer (Systronics-2202) to determine the concentration of chromium in the solution.

4.2.3 pH meter

pH meter (systronics) was used to measure the pH wherever required.

4.3 CHARACTERIZATION OF THE ADSORBENT

For characterization of the selected material i.e. to find out particle size of adsorbent, surface morphology, its composition and the available functional groups Laser beam Particle Size Analysis (LPSA), Scanning electron microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDS) and Fourier transformation infrared spectroscopy (FTIR) studies were carried out.

4.3.1 Particle Size Analysis

Particle size Analysis of the raw and washed fly ash was conducted using Laser Beam Particle Size Analyzer (Mastersizer 2000, Malvern instruments Ltd.) using Hydro 2000MU (A) accessory in the size range 0.100 to 1000.00 µm. Water was used as dispersant for analysis.

4.3.2 SEM-EDX Analysis

Surface structure and elemental composition of the fly ash was analyzed by Scanning Electron Microscopy (ZEISS EVO 40 EP) and Energy Dispersive X-ray Analysis (BRUKER LN_2 Free X-Flash 4010 SDD Detector), respectively using Quantax 200 analytical software.

SEM-EDX analysis of the raw and washed fly ash samples was carried out before and after treatment of aqueous solution (60 µg Cr /ml) at initial pH 1.0. All the four samples were dried in an oven at 70ºC for 3-4 hours. For the analysis, samples were mounted on a stainless steel stub using a double- sticky carbon tape.

4.3.3 FTIR Analysis

To find out the functional groups that may be responsible for the binding of metal ions Fourier Transform Infrared spectroscopy was performed using a Fourier Transform Infrared spectrometer (Nicolet 6700 FT-IR, Thermo Scientific) for both raw and washed fly ash before and after treatment of aqueous solution (60 µg Cr/ml) at initial pH 1.0. All the four samples were dried in an oven at 70ºC for 3-4 hours. Samples for FTIR were prepared by employing KBr dilution technique.

4.4 METHODOLOGY

4.4.1 Collection of the material

Fly ash was collected from Waste to Energy Plant, Gidderbaha. Initial composition of the waste which was burnt comprised of 70-80% gram straw, 10-15% cotton straw, 5-10% wheat straw and small percentage of leaves. Coal was used for efficient burning.

This was chosen to be used as adsorbent because this is easily available in this area, have no cost and further do not have any use. There is even a problem to dump this.

4.4.2 Preparation of the Adsorbents

A part of the material was directly heated in the oven for 7-8 hours at 105 ºC and then sieved using sieve shaker with mesh of size 300 µ. The ash particles of less than 300 µ were taken and stored in polythene bags for further use. This was labeled as raw fly ash (RM).

Another part of the material was washed with hot distilled water in 1:5 ratios in a 5 l beaker. The mixture of material and hot water were stirred at approx. 170 rpm for two hours. After each washing the material was separated from the water using Whatman filter paper no. 1. The entire process of shaking with distilled water, settling and filtration was repeated many times till the mixture attained a constant pH.

After washing ash was left for sun drying and then heated in oven at 70˚C till complete drying and then sieving was done using sieve shaker. The ash particles of less than 300 µ were taken and stored for further use. This was labeled as washed fly ash (WM).

4.4.3 Preparation of Adsorbate

A stock solution of 500 µg Cr/ml water was prepared by dissolving 1.414 g of Potassium dichromate in 1l of distilled water. The stock solution was then diluted with the distilled water to obtain the desired concentrations.

4.4.4 Adjustment of pH

pH of the solutions was adjusted using 1N H_2SO_4 or 1 N NaOH.

4.4.5 Determination of hexavalent chromium

A stock solution of hexavalent chromium having concentration 500 µg Cr/ml was prepared by dissolving 1.414 g of Potassium dichromate. Analysis of hexavalent chromium was done by using 3500-Cr B Colorimetric Method given in Standard Method for Examination of Water and Wastewater (Eaton, 2005).

Reagents:

(i) Phosphoric acid (concentrated)

(ii) Sulfuric acid (concentrated)

(iii) Sodium hydroxide (1N): Dissolved 40 g NaOH in 1l distilled water.

(iv) Diphenyl carbazide (DPC) solution: Dissolved 250 mg 1,5-diphenylcarbazide in 50 ml acetone.

Procedure:

80 ml of chromium solution was taken in nesslers cylinder. To this added 5 drops of H_3PO_4 followed by adjustment of pH to 1.0 ± 0.05 using 1N H_2SO_4. The final volume was made 100 ml using chromium solution. To each nesslers cylinder, 2 ml of DPC was added and the solution was mixed thoroughly. Further, the solution was kept undisturbed for 5 to 10 minutes for colour development. The colour developed was read on UV-Vis at 540 nm absorbance.

Preparation of calibration Curve

A graph was plotted between known concentrations of Cr (VI) ions and absorbance at a particular wave length. This curve was used to calculate unknown concentrations.

4.4.6 Procedure for Adsorption Experiments by Batch Adsorption Method

(a) To Study the Effect of Adsorbent Doses

200 ml of 10 µg Cr/ml aqueous solution was taken in each conical flask. To these flasks added varying doses (10 g, 20 g, 30 g, 40 g/l) of adsorbents under study. The flasks were shaken for 2 hours at 200 rpm and left undisturbed for 22 hours to achieve the equilibrium state. After 24 hours, the adsorbent was separated by filtration through Whatman filter paper no. 1 and aqueous phase concentration of metal ions was analyzed by using method as per **4.4.5.** The experiment was repeated 3 times for both raw and washed fly ash and the results are represented as average of three.

(b) To Study the Effect of pH

10 µg Cr/ml aqueous solutions having pH of 1, 2, 3, 4, 5 were prepared using sulphuric acid. Then 200 ml of 10 µg Cr/ml was shaken for 2 hours at 200 rpm after addition of 10g/l fly ash and left for 22 hours to attain equilibrium. After 24 hours the mixture was filtered through Whatman filter paper no. 1 and aqueous phase concentration of metal ion was analyzed by using method as per **4.4.5.** The experiment was repeated 3 times for both raw and washed fly ash and the results are represented as average of three.

(c) To Study the Effect of Contact Time

10 g/l fly ash was added to 200 ml of 10 µg Cr/ml metal ion solution having pH1.0. Different sets of flasks were shaken for different time intervals (5 min, 30 min, 60 min and 90 min) at 200 rpm. The adsorbent was separated immediately by filtration after shaking using Whatman filter paper no. 1 and aqueous phase concentration of metal ion was analyzed by using method as per **4.4.5.** The experiment was repeated 3 times for both raw and washed fly ash and the results are represented as average of three.

To Study the Effect of Initial Metal Ion Concentration

Solutions of 10 µg, 20 µg, 40 µg, 60 µg and 80 µg Cr/ml were made by diluting the stock solution. The pH of all the concentrations was adjusted to 1.0. These solutions were further used in this experiment. 10 g/l fly ash was added to 200 ml of aqueous solution having pH 1.0. The flasks were shaken for 90 minutes at 200 rpm and left to achieve equilibrium. After 24 hours the adsorbent was separated by filtration through Whatman filter paper no. 1 and aqueous phase concentration of metal ion was analyzed using method as per **4.4.5.** The experiment was repeated 3 times for both raw and washed fly ash and the results are represented as average of three.

4.4.7 Data Analysis

From the data collected as above, percent removal and adsorption capacity of the sorbent was determined. Mass balanced equation was applied to calculate adsorption capacity of the sorbent.

Mass balance equation:

$$q_e = \frac{\left(C_0 - C_e\right) V}{S}$$

Where,

q_e = Metal uptake by sorbent after equilibrium, mg/g

C_o = Initial concentration of metal ion, mg/l

C_e = Final Concentration of metal ion after adsorption has occurred, mg/l

V = Volume of liquid treated, l

S = Mass of solid sorbent, g

Percentage Cr (VI) removed:

The percentage of Cr (VI) ions removed (R %) was calculated using following equation:

$$R\ \% = \frac{\left(C_0 - C_e\right)}{C_0} * 100$$

4.4.8 Adsorption Isotherms

Characteristics (solubility, molecular weight, molecular structure and polarity etc.), concentration of the adsorbate and temperature are the factors on which amount of adsorbate adsorbed by an adsorbent depends.

Mostly the quantity of material adsorbed by the adsorbent is studied as a function of concentration at constant temperature. The resultant function from such a study is called an adsorption isotherm. Developing adsorption isotherm is a relatively simple

method to determine the feasibility of using an adsorbent for a particular application.

Data obtained in adsorption experiments is usually described by different equations which were developed by Langmuir, Freundlich and Brunaur - Emmet – Teller (BET) isotherm etc.

Development of Adsorption Isotherms

The linear form of Langmuir isotherm was applied on the data generated in study of variation in initial ion concentration.

The Langmuir adsorption isotherm is based on following assumptions:

- Adsorbent surface always have fixed number of accessible sites and all such sites have same energy.
- Nature of adsorption is reversible. Equilibrium stage appears when the rate of adsorption of molecule onto the adsorbent surface become equal

  to the rate of desorption of molecules from the surface.

Langmuir isotherm can be applied only when the adsorbate coverage is limited to one molecular layer.

Langmuir isotherm is expressed by the following equation:

$$\theta = \frac{(q_e)}{q_m} = \frac{(b\ C_0)}{(1+bC\ e)}$$

Where,

θ = fractional coverage

$b = k_a/k_d$

k_a = constants for adsorption

k_d = constants for adsorption and desorption

q_m = quantity of adsorbate required to form a single monolayer on unit mass of adsorbent, mg/g and

q_e = amount adsorbed on unit mass of the adsorbent at equilibrium, mg/g

The above equation can be rearranged as below:

$$\frac{(C_e)}{q_e} = \frac{1}{b\ q_m} + \frac{1}{q_m} * C_e$$

Where,

C_e = equilibrium concentration of solute in bulk solution (mg/l)

b = Langmuir constant related to the free sorption energy (l/mg)

This is a Linear equation for Langmuir isotherm and if the Langmuir equation is obeyed by the adsorption equilibrium, plot of (C_e/q_e) vs. C_e should be a straight line. Values of q_m and b can be derived from slope and the intercept of the trend line.

Further, Langmuir Equation also predict that whether the process is favourable or not on the basis of dimensionless separation factor. R_L can be derived using equation:

$$RL = \frac{1}{(1+bCe)}$$

where, value of R_L represents the following adsorption characteristics:

$R_L > 1$: unfavourable adsorption;

RL = 1: linear adsorption;

0 < RL < 1: favourable and

$R_L = 0$: irreversible adsorption.

4.4.9 Adsorption Kinetics

The linear form of Lagergren pseudo-first order and pseudo-second order adsorption kinetic model was applied to the data given in **table 5.2.3** for raw and washed fly ash.

The linearized form of pseudo-first order Lagergren equation can be expressed as

$$\log(q_e - q_t) = \log q_e - \frac{K_{1,ads}}{2.303} * t$$

and linearized form of pseudo-second order Lagergren equation is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} * t$$

Where,

q_e = mass of metal adsorbed at equilibrium (mg/g)

q_t = mass of metal adsorbed at time t (mg/g)

$k_{1,ads}$ = the pseudo first-order reaction rate of adsorption (per minute)

$h = k_2 q_e^2$

k_2 = the pseudo-second-order rate constant of adsorption mg/g $\min^{-1}$.

CHAPTER-5

RESULTS and DISCUSSION

5.1 CHARACTERIZATION OF THE MATERIAL

Physical and chemical characterization of the material was done using various techniques like Laser Beam Particle Size Analysis, FTIR and SEM-EDX. Following results has been obtained by these analysis techniques:

5.1.1 Particle size Analysis

Particle size analysis revealed that that in case of both raw and washed fly ash, major fraction lies in the range of 1-150 µm which is 92.40 % and 93.33 %, respectively. The specific surface area of raw and washed fly ash is. 0.404 m^2/g and 0.381 m^2/g, respectively whereas uniformity of raw and washed fly ash is 0.867 and 0.741, respectively.

Table 5.1.1: Particle size distribution of Raw fly ash and Washed fly ash

S.No.	**Size (µm)**	**% Volume**	
		Raw fly ash	**Washed fly ash**
1	**<1**	1.47	1.35
2	**1-50**	54.39	49.92
3	**50-100**	26.62	31.28
4	**100-150**	11.39	12.13
5	**150-200**	4.10	3.77
6	**200-250**	1.10	0.90
7	**250-300**	0.88	0.61
8	**>300**	0.05	0.04

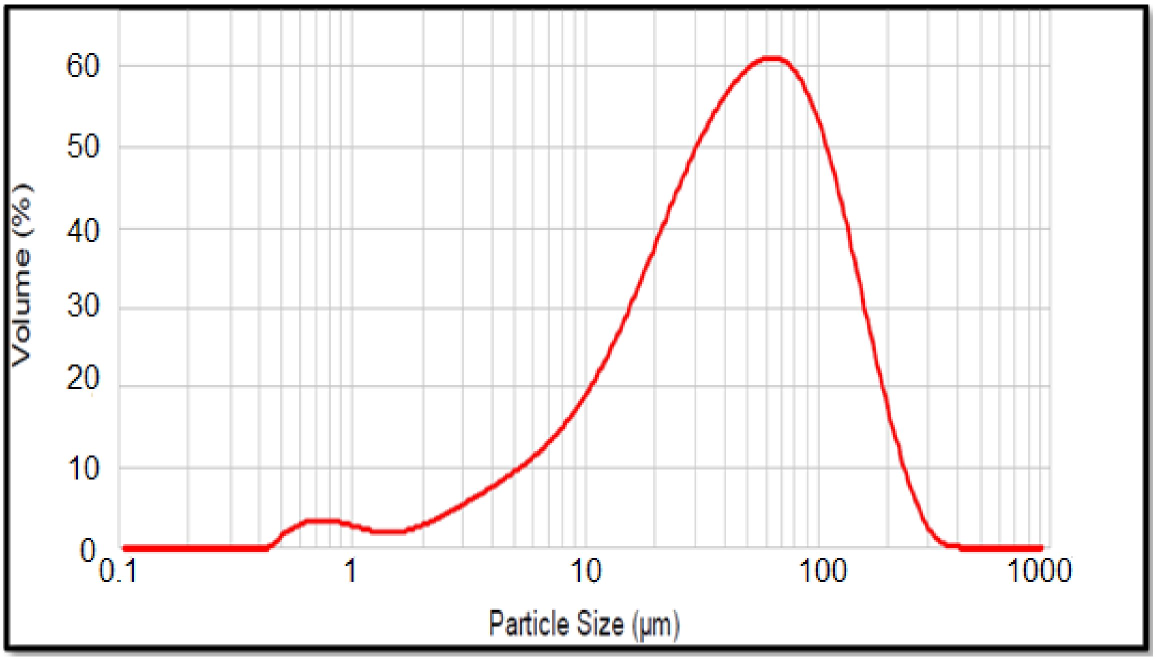

Figure 5.1.1 (a): Particle size distribution of Raw fly ash

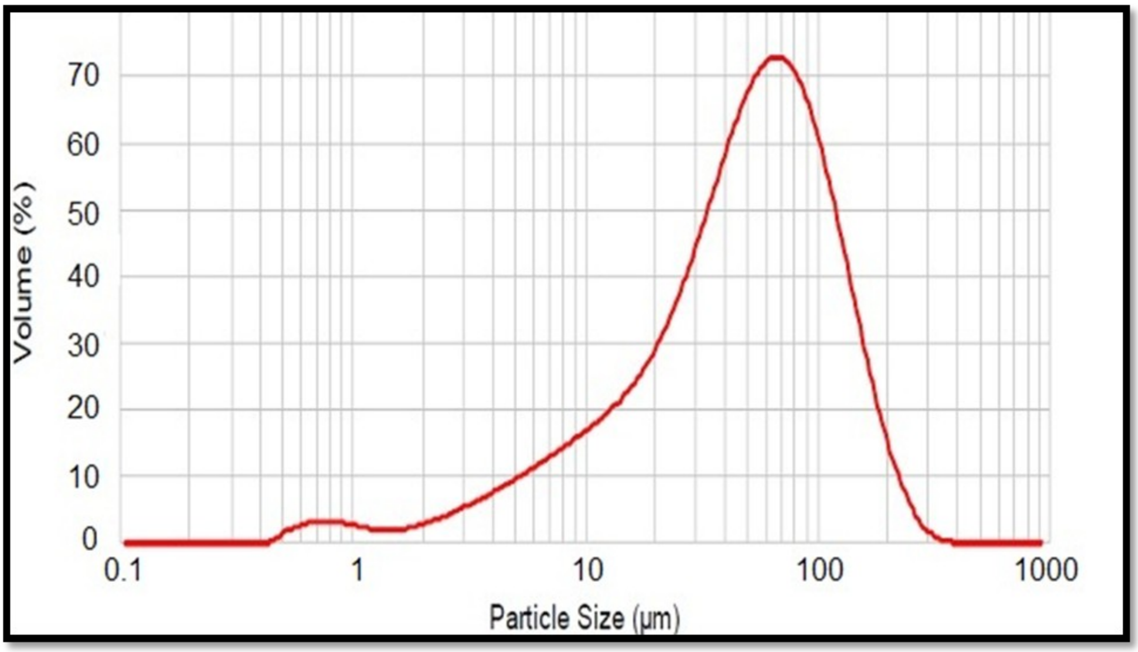

Figure 5.1.1 (b): Particle size distribution of Washed fly ash

5.1.2 SEM-EDX Analysis

Electron micrographs and EDX spectra of raw and washed fly ash before and after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH 1.0) are shown below. The micrographs show the heterogeneous morphology of the adsorbent.

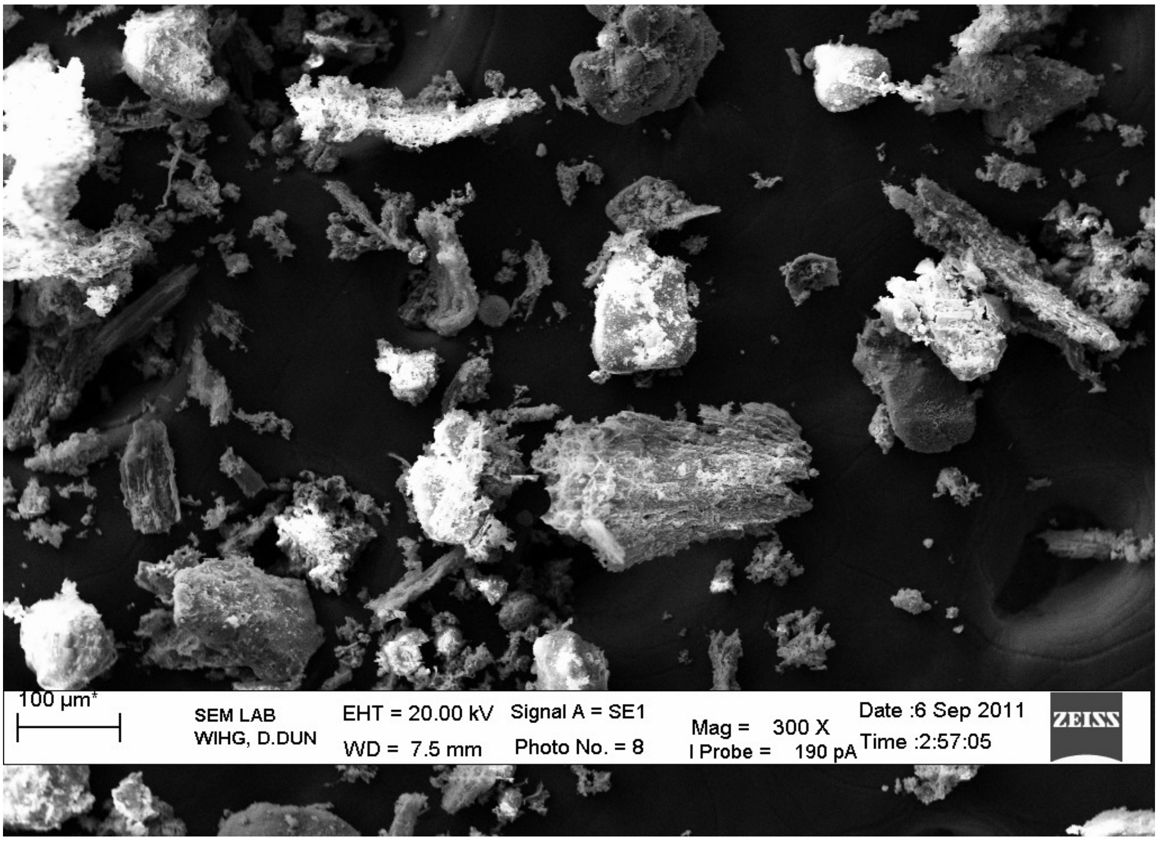

Figure 5.1.2 (a): Electron micrograph of Raw fly ash

Figure 5.1.2 (b): EDX spectra of Raw fly ash

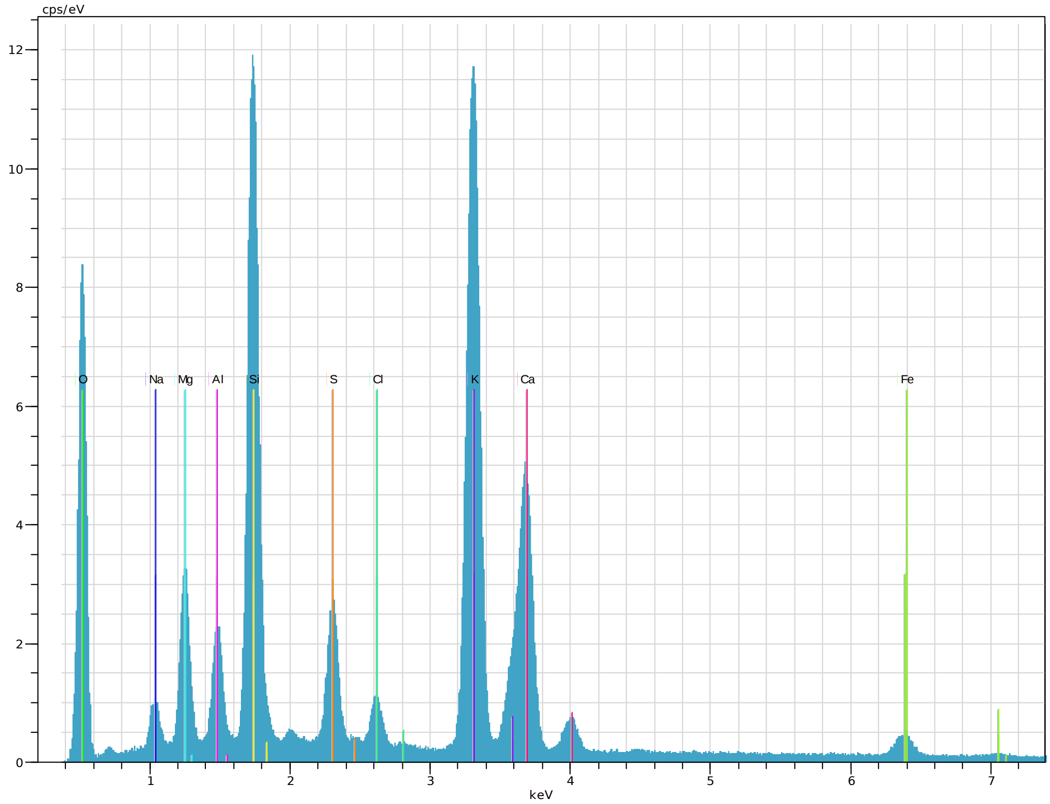

Figure 5.1.2 (c): Electron micrograph of Washed fly ash

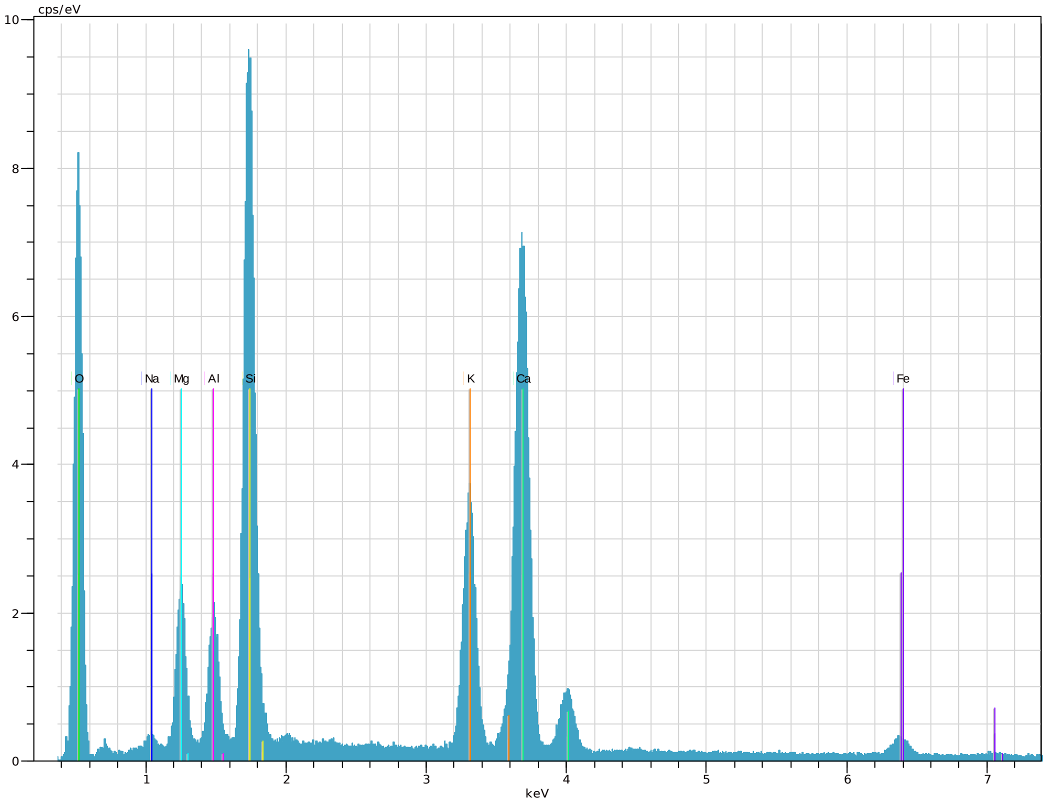

Figure 5.1.2 (d): EDX spectra of Washed fly ash

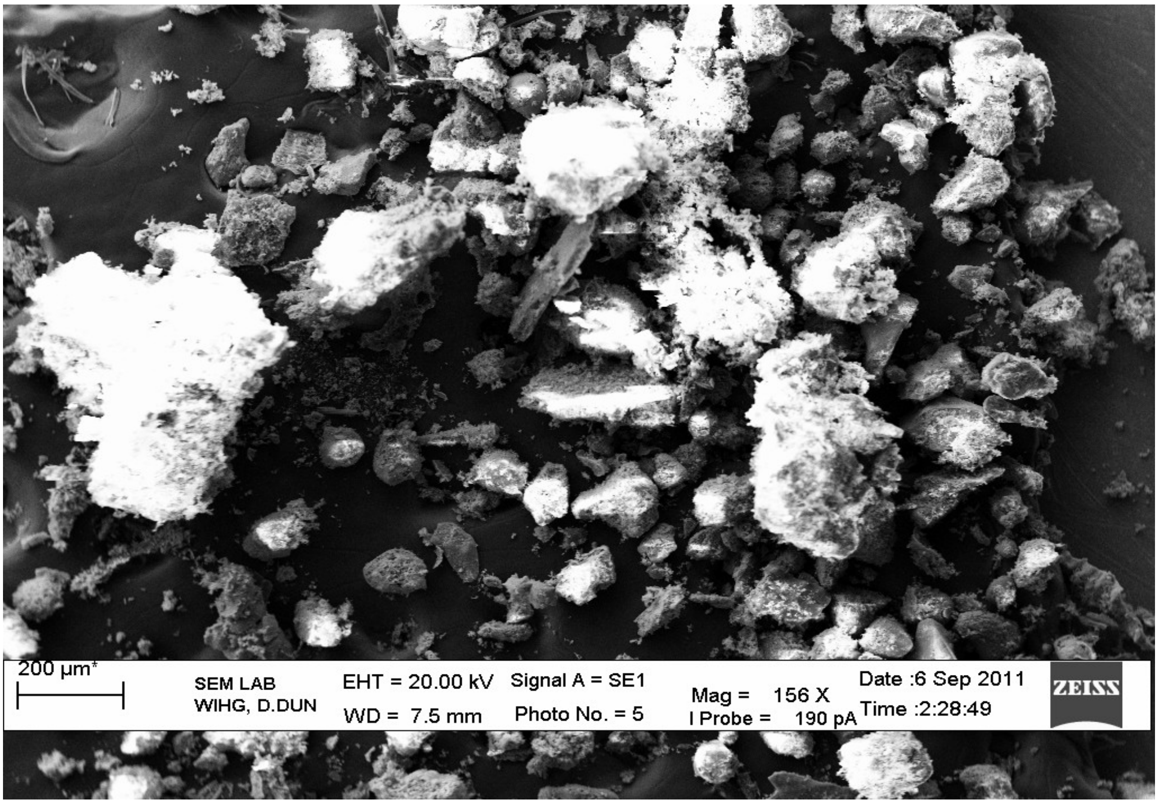

Figure 5.1.2 (e): Electron micrograph of Raw fly ash after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

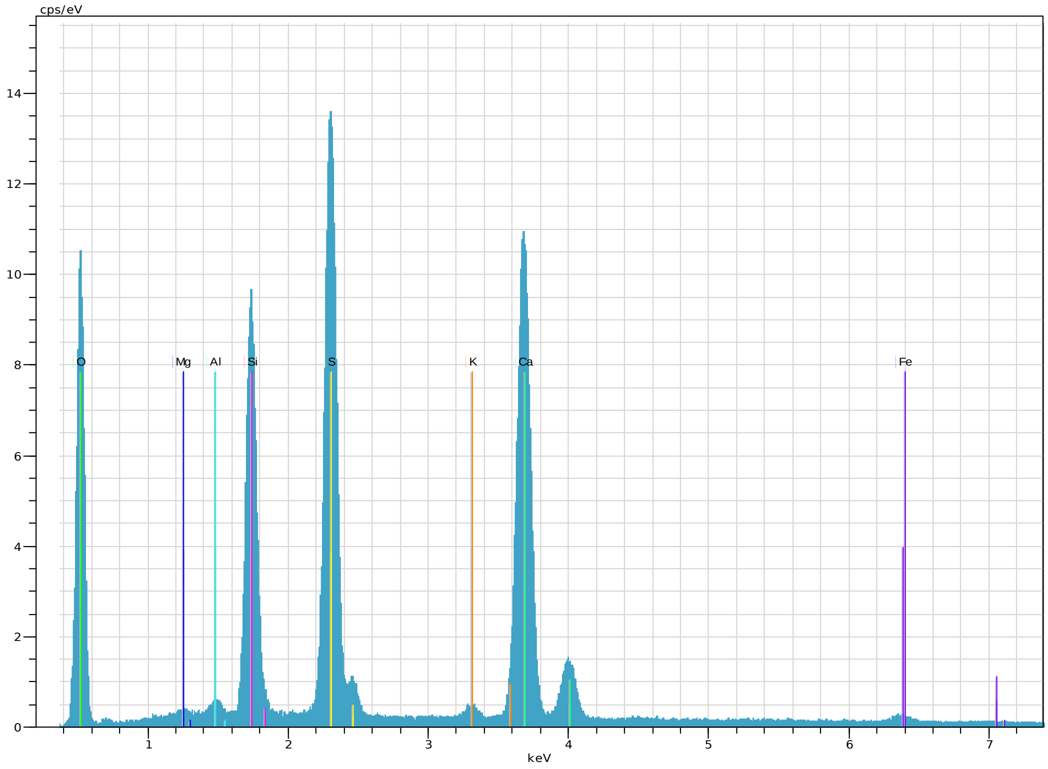

Figure 5.1.2 (f): EDX spectra of Raw fly ash after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

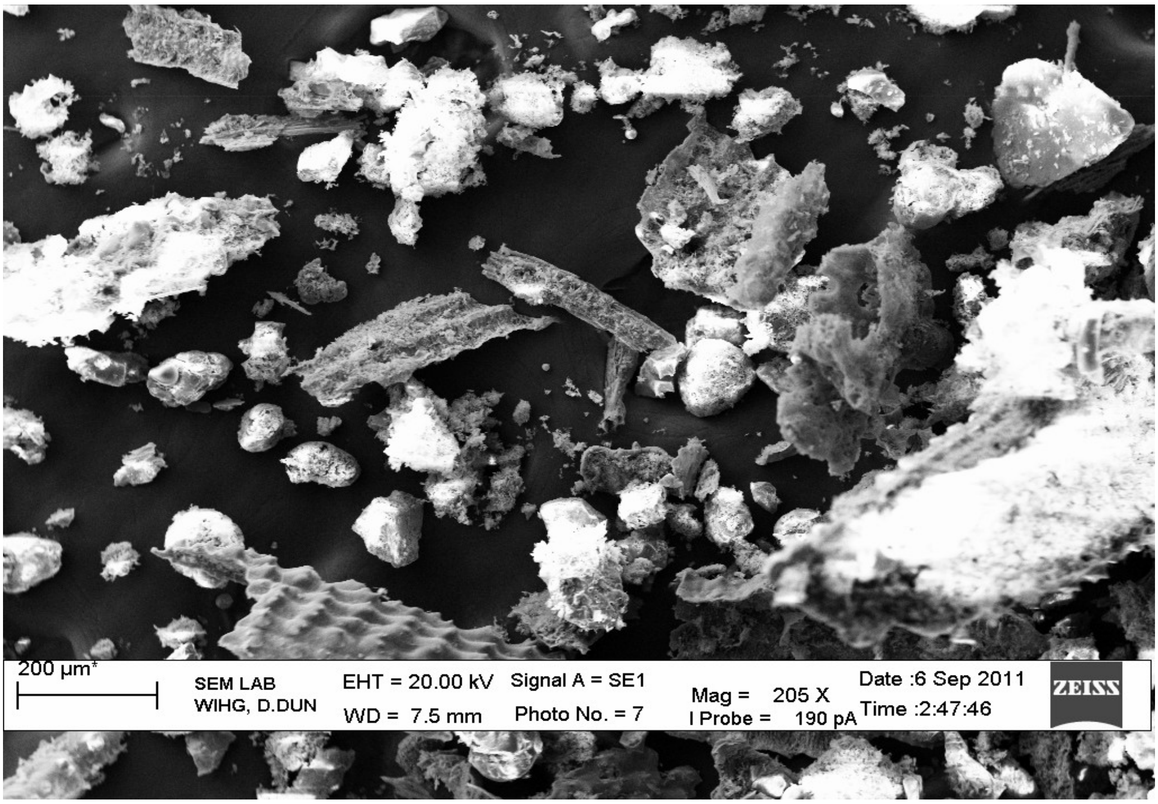

Figure 5.1.2 (g): Electron micrograph of washed fly ash after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

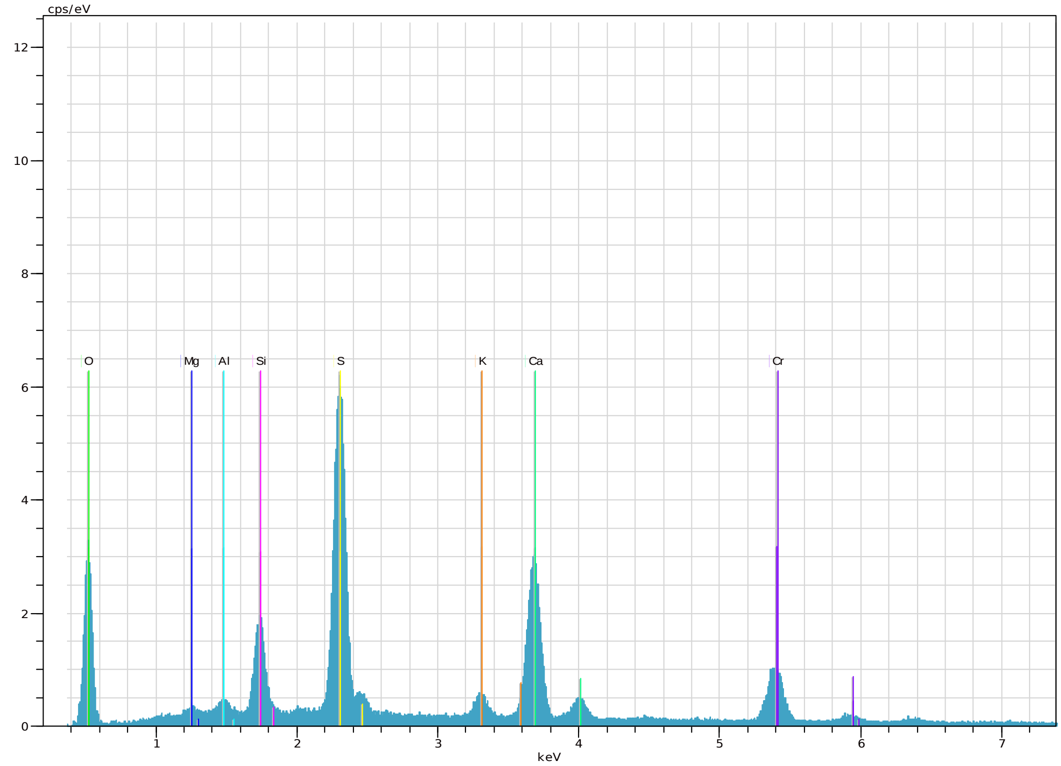

Figure 5.1.2 (h): EDX spectra of washed fly ash after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

The elemental distribution of raw and washed fly ash obtained by EDX shows high percentage level (3-60%) of Carbon, Magnesium, Silicon, Potassium, Calcium and Oxygen and lower percentage of Sodium, Aluminium and Iron. Sulphur and Chlorine are also present in lower percentage (<2%) in raw fly ash samples but are absent in washed fly ash. They may have washed away with water during washing of the material. Raw and washed samples after treatment of aqueous solution also showed the presence of chromium which indicate adsorption, but at the same time significant amount of sulphur also appeared due to sulphuric acid used for maintaining pH. Some variation in the percentage composition is observed after treatment of aqueous solution.

Table 5.1.2: Elemental Composition of Raw and Washed Fly Ash before treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

Element	**Percent composition**			
	RM	**WM**	**TRM**	**TWM**

Carbon	6.34	8.49	3.29	50.05
Sodium	1.32	0.25	--	--
Magnesium	3.20	2.67	0.01	0.12
Aluminium	1.64	1.71	0.09	0.17
Silicon	8.01	7.64	5.61	1.11
Sulfur	1.75	--	9.84	4.54
Chlorine	0.52	--	--	--
Potassium	10.69	3.47	0.19	0.50
Calcium	4.72	7.87	10.51	2.83
Iron	0.79	0.63	0.70	--
Oxygen	61.04	67.27	69.76	39.35

5.1.3 FTIR Analysis

FTIR spectra of raw and washed fly ash samples before and after treatment of 60 µg Cr /ml aqueous solution having pH 1.0 were studied in the range 4000- 400 cm^{-1}. The FTIR spectra of all the four samples are as shown in figures below [**Figure 5.1.3 (a), Figure 5.1.3 (b), Figure 5.1.3 (c)** and **Figure 5.1.3 (d)**]. These reveal some important functional groups that may be responsible for the binding of metal ions as illustrated in **table 5.1.3 (a)** and **table 5.1.3 (b)** for raw and washed material respectively.

All the four spectra shows the presence of silica and trace amount of carbon which is in agreement with the results drawn from EDX. Presence of sulphate is shown by all except washed fly ash sample. It may be washed away with water during washing of the material. Treated samples of raw and washed fly ash also showed the presence of sulphates that appeared due to sulphuric acid used for maintaining pH.

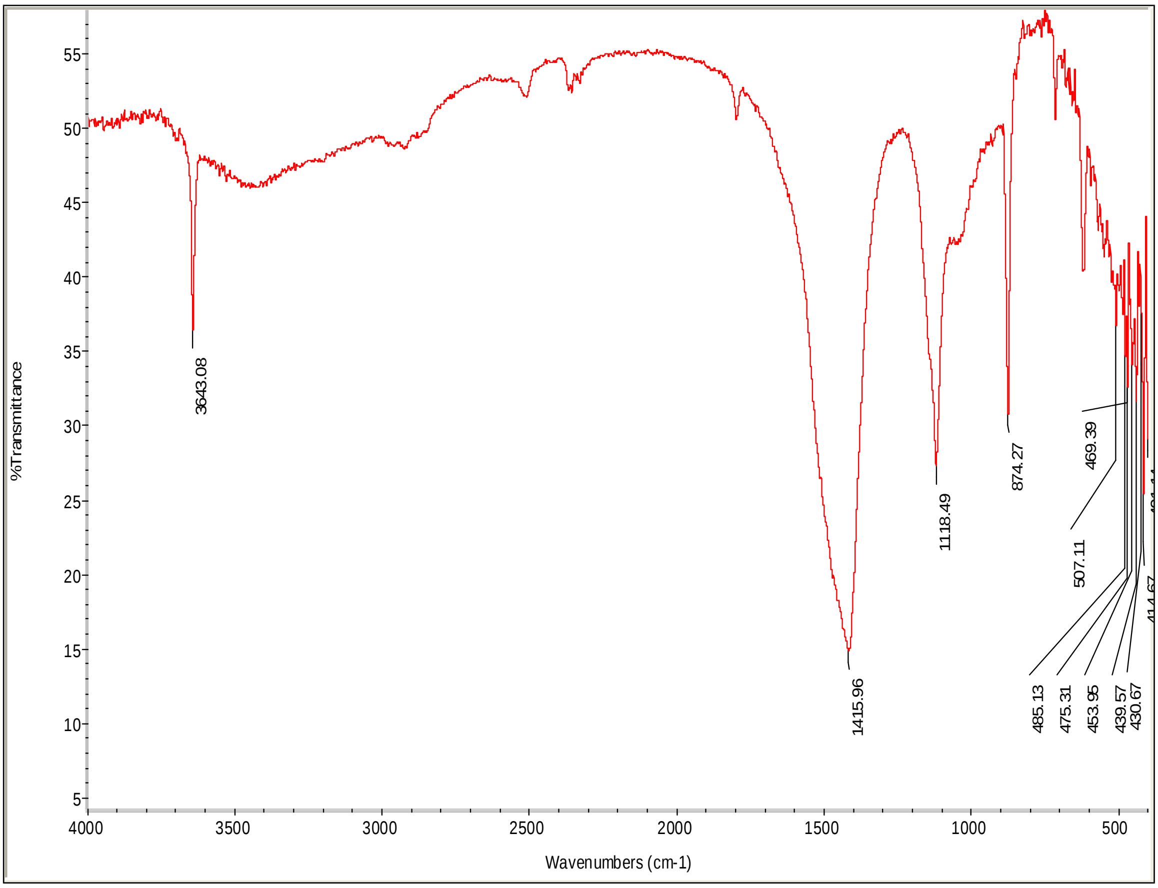

Figure 5.1.3 (a): FTIR spectra of Raw fly ash

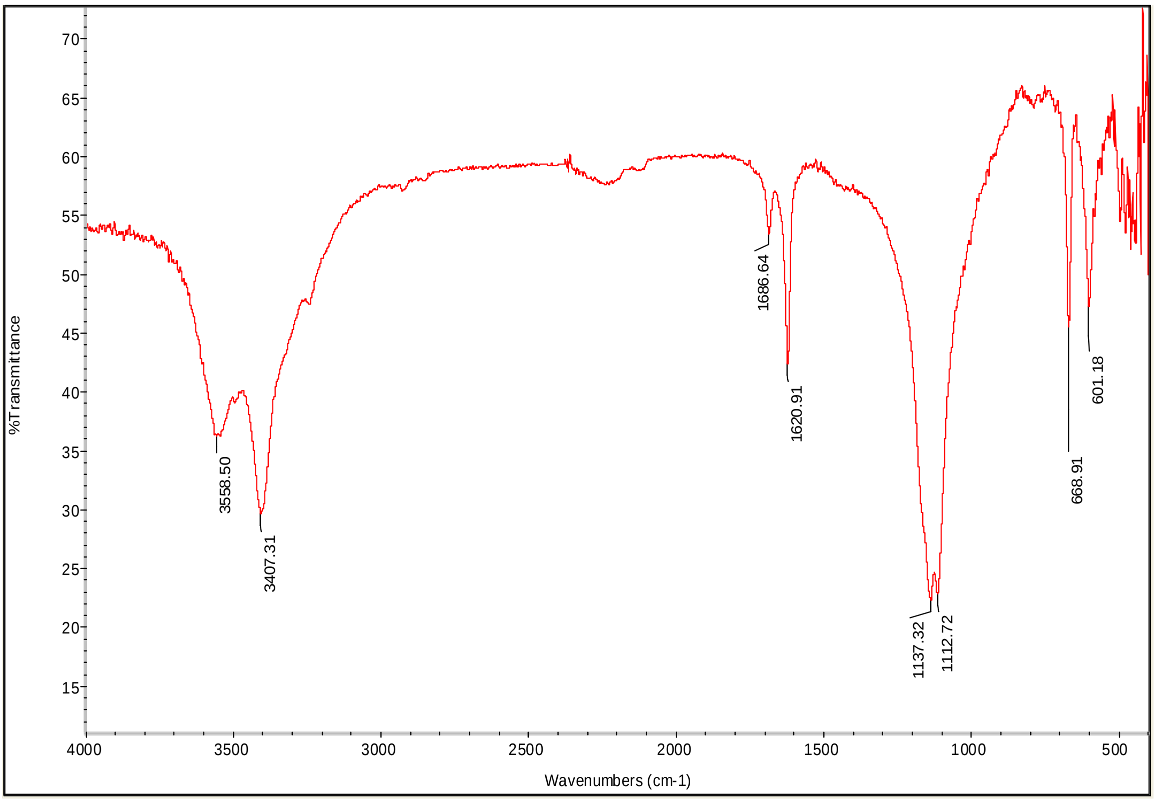

Figure 5.1.3 (b): FTIR spectra of Raw fly ash after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

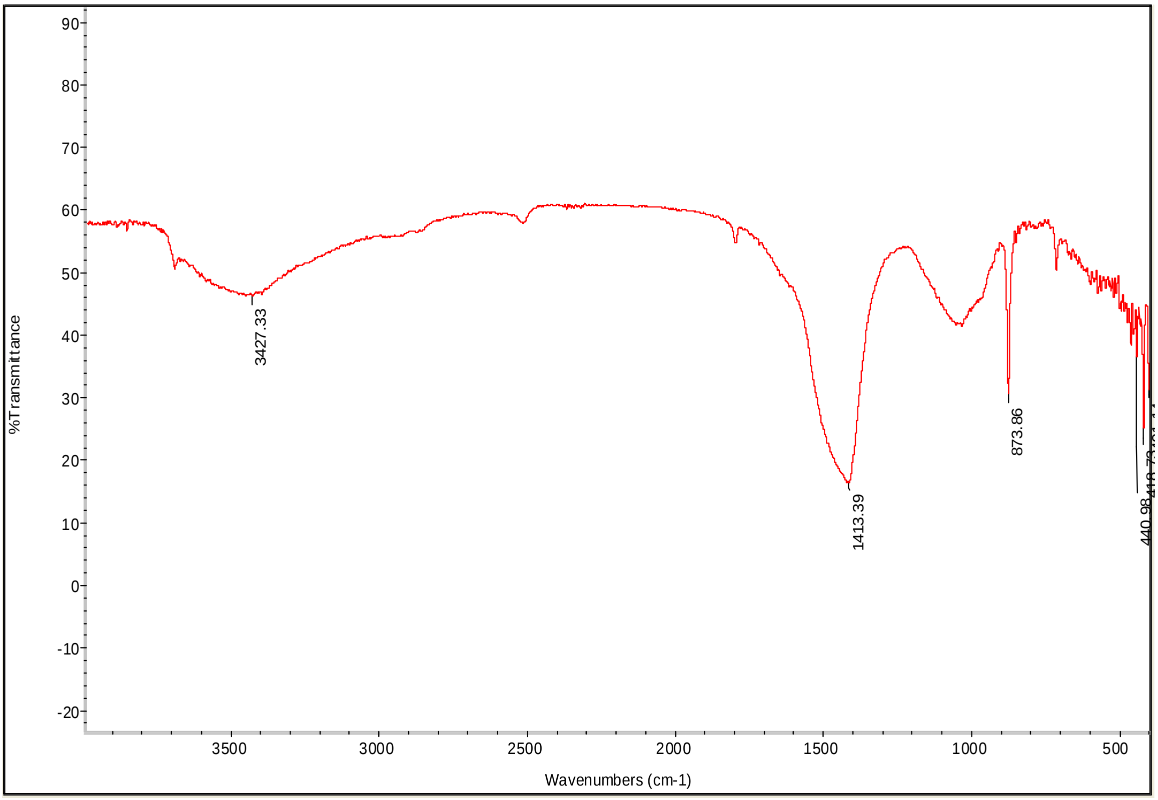

Figure 5.1.3 (c): FTIR spectra of Washed fly ash

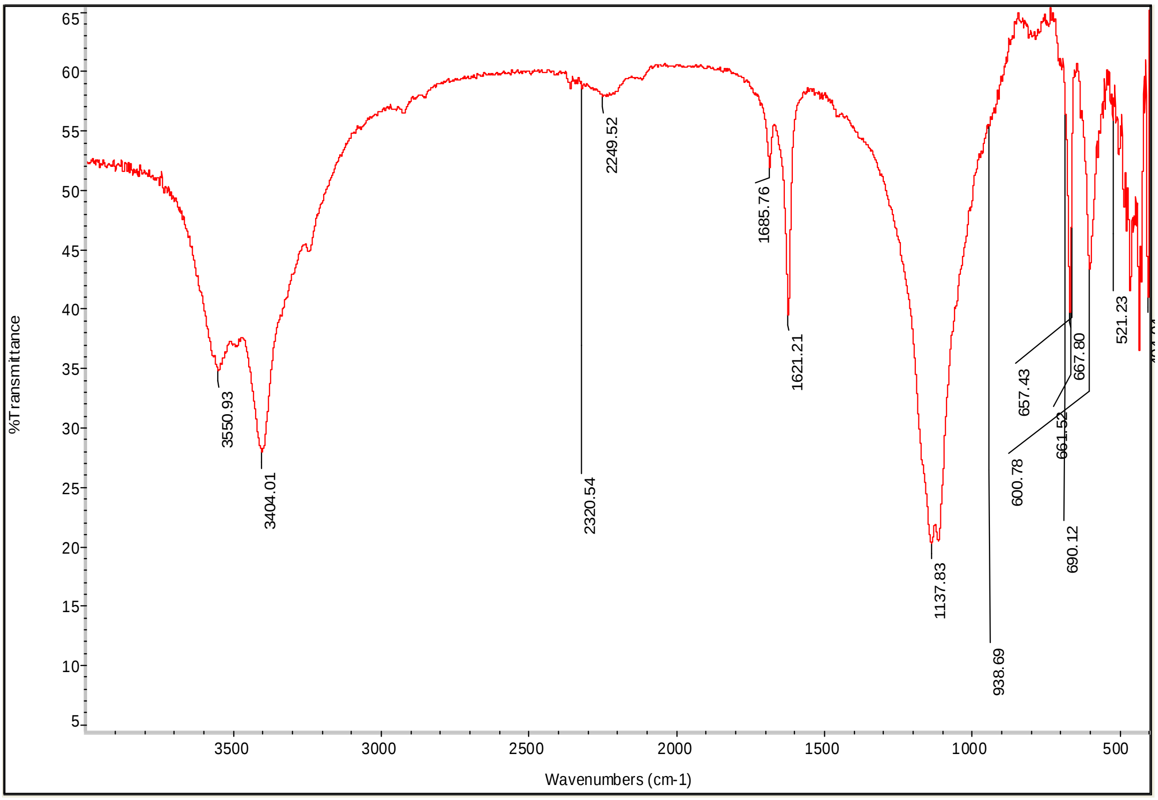

Figure 5.1.3 (d): FTIR spectra of Washed fly ash after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

Table 5.1.3(a): IR bands of some identified peaks and their corresponding groups in Raw fly ash before and after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH)

S.No.	Wave number (cm^{-1})	Possible Functional group
Before Treatment		
1.	3643.08	SiO-H streching
2.	1415.96	-C-H streching
3.	1118.49	S-O streching
4.	874.27	=C-H bending
5.	475.31	Si-O-Ca band
6.	453.95	Si-O band
After Treatment		
7.	3558.50	SiO-H stretching
8.	3407.31	SiO-H stretching
9.	1686.64	C=O stretching
10.	1620.91	C=C stretching
11.	1137.32	S-O stretching
12.	1112.72	S-O stretching
13.	668.91	S-O bending

Table 5.1.3(b): IR bands of some identified peaks and their corresponding groups in washed fly ash before and after treatment of aqueous solution (60 µg/ml Cr (VI) solution at initial pH-1.0)

S.No.	Wave number (cm^{-1})	Possible Functional group

Before Treatment		
1.	3427.33	SiO-H stretching
2.	1413.39	-C-H (bending)
3.	873.86	=C-H (bending)
4.	440.98	-Si-O
After Treatment		
5.	3550.93-3404.01	SiO-H stretching
6.	1621.21	Carbonate
7.	1137.83	S-O stretching
8.	667.80	S-O bending
9.	661.52	S-O bending
10.	657.43	S-O bending

5.2 BATCH ADSORPTION STUDIES

Batch experiments were carried out using 250 ml conical flasks to find optimum pH, contact time, and adsorbent dose to achieve maximum removal of hexavalent chromium by the raw flyash and washed flyash. All the experiments were carried at room temperature (25±1°C). The pH was adjusted using conc. sulphuric acid.

5.2.1 Effect of Adsorbent dose:

To investigate the effect of adsorbent dose on adsorption of hexavalent chromium, doses of 10, 20, 30 and 40 g/l of fly ash were added to volumetric flasks having 10 µg/ml aqueous solution of chromium with 2h shaking and 24 hour equilibration time at 25±1ºC (for details refer **4.4.6 (a)** of Chapter 4). The results obtained are shown in **table 5.2.1** and **figure 5.2.1**.

Table 5.2.1: Effect of adsorbent dose on % Chromium removal and its uptake

(Initial ion conc.=10 µg/ml, Adsorbent dose=10 g/l, Contact time= 2 hrs, pH=5.5, Temperature=25±1ºC)

Adsorbent dose (g/l)	RM			WM		
	Concentration at equilibrium C_e (mg/l)	% Chromium removal	Chromium uptake q_e (mg/g)	Concentration at equilibrium C_e (mg/l)	% Chromium removal	Chromium uptake q_e (mg/g)
10	9.60	4.00	0.040	9.95	2.50	0.025
20	9.40	6.00	0.030	9.82	3.80	0.019
30	9.14	8.60	0.029	9.57	5.50	0.018
40	8.99	10.10	0.025	9.31	6.50	0.016

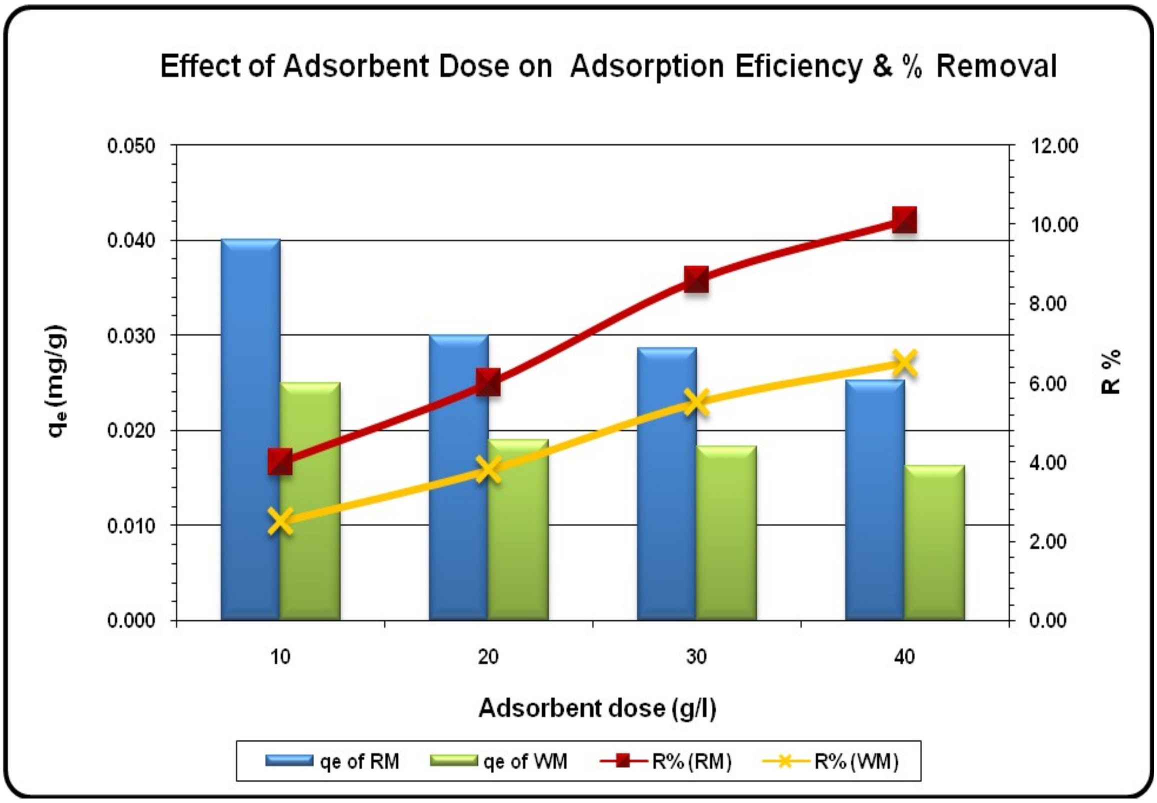

Figure 5.2.1: Effect of adsorbent dose on % Chromium removal and its uptake

The results showed that percent removal of Cr (VI) ions increased from 4.0 to 10.1% with raw flyash while the removal varied from 2.5 to 6.5% in case of washed fly ash with increase of adsorbent dose from 10 to 40 g/l. Increase in percent removal was due to increase in surface area and adsorption sites. On the other hand, a decrease in the Chromium ion uptake (q_e) was observed in both cases with increase of adsorbent dose. The decrease in Chromium ion uptake (q_e) may be due to availability of lesser number of Cr (VI) ions per unit mass of the fly ash due to which the active sites may remain unsaturated during the adsorption process.

Similar trend of increase in percent removal of Chromium ions and decrease in the Chromium ion uptake (q_e) with increase of adsorbent dose was observed by El Nemr (2007); Babu and Gupta (2008) for the removal of Cr (VI).

5.2.2 Effect of pH:

To study the effect of pH on adsorption efficiency, experiments were conducted in the pH range 1-5 at 25ºC with initial ion concentration of 10 µg/ml Cr (VI), adsorbent dose of 10 g/l, 2h shaking and 24 hour equilibration time (for details refer **4.4.6 (b)** of Chapter 4). The results of percent removal and adsorption efficiency of raw and washed fly ash are given in **table 5.2.2** and **figure 5.2.2**.

Table 5.2.2: Effect of pH on % Chromium removal and its uptake
(Initial ion conc.=10 µg/ml, Adsorbent dose=10g/l, Contact time= 2 hrs.,
Temperature= 25±1ºC)

pH	**RM**			**WM**		
	Conc. at equilibrium C_e (mg/l)	**% removal**	**Chromium uptake q_e (mg/g)**	**Conc. at equilibrium C_e (mg/l)**	**% removal**	**Chromium uptake q_e (mg/g)**
5	9.18	8.20	0.082	9.76	2.40	0.024
4	9.12	8.80	0.088	9.73	2.70	0.027
3	9.02	9.80	0.098	9.37	6.30	0.063
2	1.86	81.40	0.814	1.54	84.60	0.846
1	0.14	98.60	0.986	0.13	98.70	0.987

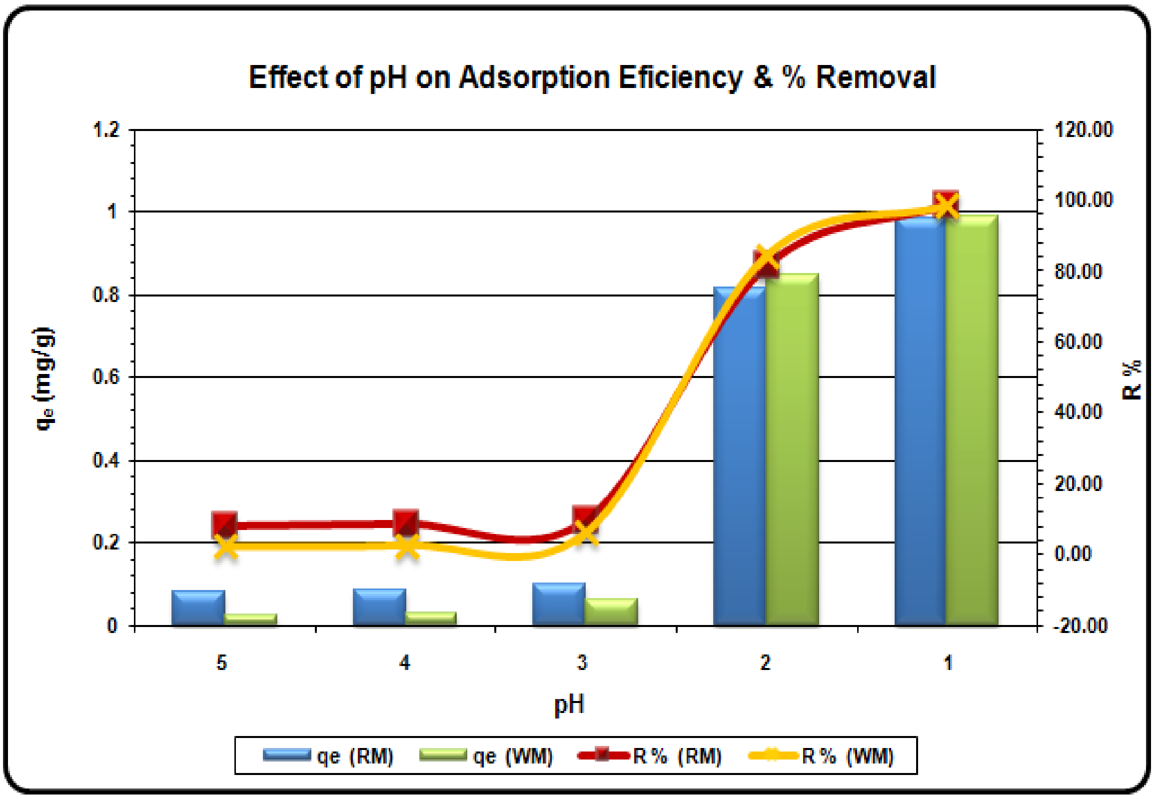

Figure 5.2.2: Effect of pH on % Chromium removal and its uptake

Results showed an increase in the Chromium ion uptake and its percent removal with the decrease in pH. Both the adsorbents showed the similar trend. In case of raw fly ash the adsorption at pH 5 was 8.2% which increased to 81.4% at pH 2. On further reducing the pH the adsorption further increased and reached nearly 98.6% at pH 1. Similarly, the adsorption increased from nearly 2.4% at pH 5 to 98.7% at pH 1 in case of washed fly ash. Likewise, Chromium uptake efficiency also increased with decrease in pH from 5 to 1 with both materials. The results were not studied at lower pH as this increased the use of sulphuric acid relatively high. So, on the basis of above results the optimum pH for Cr adsorption was found to be 1.0 because at this pH both adsorption efficiency and removal percentage are maximum for both the materials.

pH of solution is the most important parameter among all other parameters as it determines the adsorption efficiency (Selvi *et al.,* 2001; Demirbas *et al.,* 2004; Yavuz et *al.*, 2006; Ahalya *et al.,* 2007; El Nemr, 2007; Vinodhini and Das, 2009; Zvinowanda *et al.*, 2009). It influences the speciation of metal ions and the charges on the sorption sites (Lee *et al*., 1998; Marques *et al*., 2000; Gao and Wang, 2007).

The maximum removal of hexavalent chromium at lower pH could be justified using the fact that in the acidic medium Cr (VI) exists in the form of $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, etc. and at lower pH the adsorbent surface may get protonated. This protonation of the adsorbent surface facilitate the greater uptake of the oxyanions of Cr (VI) due to increased forces of attraction (Hasan *et al.,* 2008). With the increase in pH, protonation of the surface also get reduced and consequently, there is decrease in uptake of oxyanions (Selvi *et al.,* 2001). Further, at higher pH, there is a competition between OH^- ion and oxyanions (El Nemr, 2007).

5.2.3 Effect of Contact Time:

Effect of contact time was studied by shaking the aqueous solution of 10 µg Cr/ml with 10g/l adsorbent dose at four different time intervals i.e. 5, 30, 60 and 90 minutes, keeping all other parameters like adsorbent dose, pH and temperature constant (for details refer **4.4.6 (c)** of Chapter 4). The results showing the effect of contact time on percent Chromium removal by raw and washed flyash is given in **table 5.2.3** and **figure 5.2.3**.

Table 5.2.3: Effect of contact time on % Chromium removal
(Initial ion conc.=10 µg/ml, Adsorbent dose=10 g/l, pH =1, Temperature= 25±1ºC)

Contact time (min.)	RM		WM	
	Final Conc. C_e (mg/l)	% removal	Final Conc. C_e (mg/l)	% removal
5	3.01	69.90	2.58	74.20
30	0.93	90.70	0.90	91.00
60	0.26	97.40	0.17	98.30
90	0.19	98.10	0.14	98.60

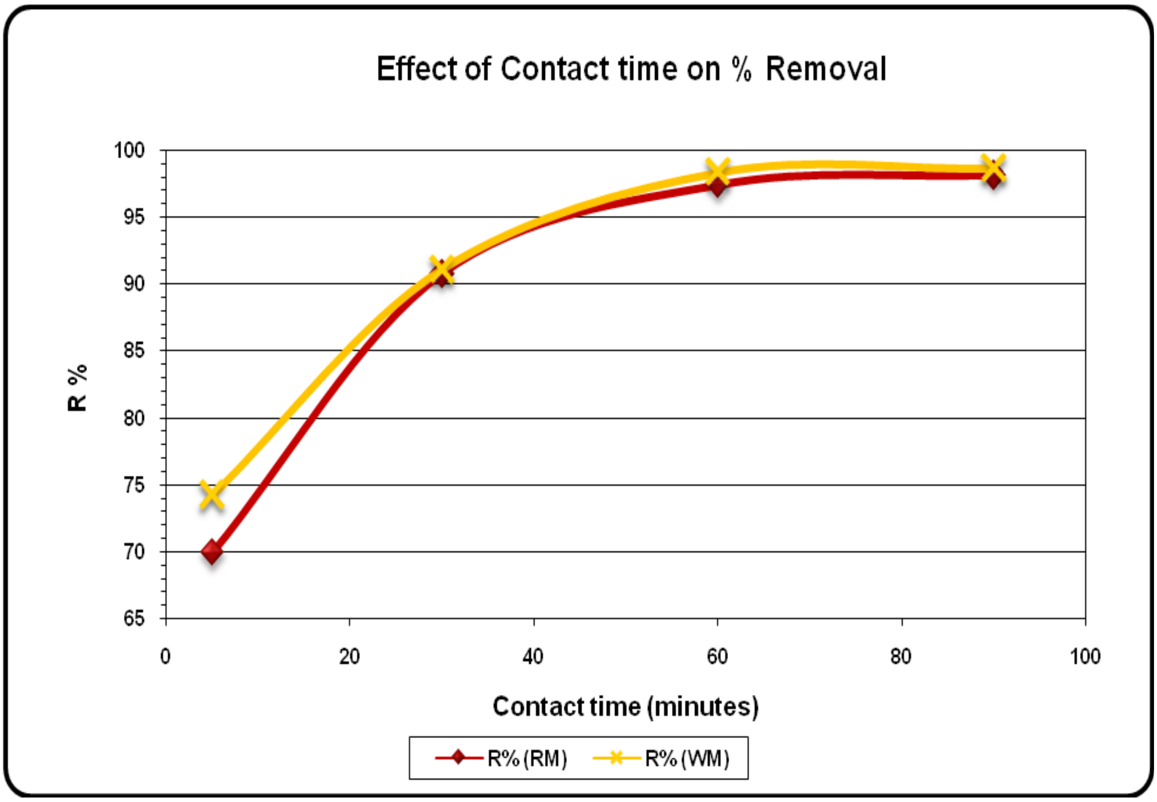

Figure 5.2.3: Effect of contact time on % Chromium removal

From **figure 5.2.3**, it is clear that the rate of Cr (VI) adsorption was faster in the initial stage and then became slow after first 30 minutes till the attainment of equilibrium. It has been found that 69.9 % and 74.2 % Chromium ion removal took place in first 5 minutes with raw and washed flyash, respectively. When contact time was increased from 5 to 90 minutes, the percentage removal of chromium ions was also increased from 69.9 to 98.1% and from 74.2 to 98.6% for raw and washed flyash, respectively.

According to Babu and Gupta (2008), solute transfer from the solution to the solid includes two steps. Firstly, diffusion occurs through the fluid film around the adsorbent particle and then, through the pores diffusion occurs to the internal adsorption sites. There is large concentration gradient between the film and the solid surface at the starting of the adsorption process and therefore, there is faster transfer of solute onto the solid surface. It may be because of this reason that it took only 5 minutes to attain percentage removal of Cr (VI) up to 69.9%. With the passage of time, due to predominance of intra-particle diffusion, Cr (VI) ions took more and more time for transfer from solid surface to internal adsorption sites through the pores.

5.2.4 Effect of Initial Ion Concentration:

A series of experiments was performed by varying the initial ion concentration of aqueous solution between 10-80 µg Cr/ml keeping all other parameters constant (for details refer **4.4.6 (d)** of Chapter 4). The results obtained are given in **table 5.2.4** and **figure 5.2.4**.

Table 5.2.4: Effect of initial ion concentration on % Chromium removal and uptake (Adsorbent dose=10 g/l, pH =1, Contact time= 90 min, Temperature= 25±1ºC)

C_o (µg/ml)Initial ion Conc.	RM			WM		
	equilibrium C_e (mg/l)Conc. at	removal%	q_e (mg/g)Chromium uptake	equilibrium C_e (mg/l)Conc. at	% removal	q_e (mg/g)Chromium uptake
10	0.14	98.60	0.986	0.13	98.70	0.987
20	8.60	57.00	1.140	6.36	68.20	1.364
40	27.18	32.05	1.282	24.80	38.00	1.520
60	46.40	22.67	1.360	42.78	28.70	1.722
80	67.10	16.13	1.290	63.08	21.15	1.692

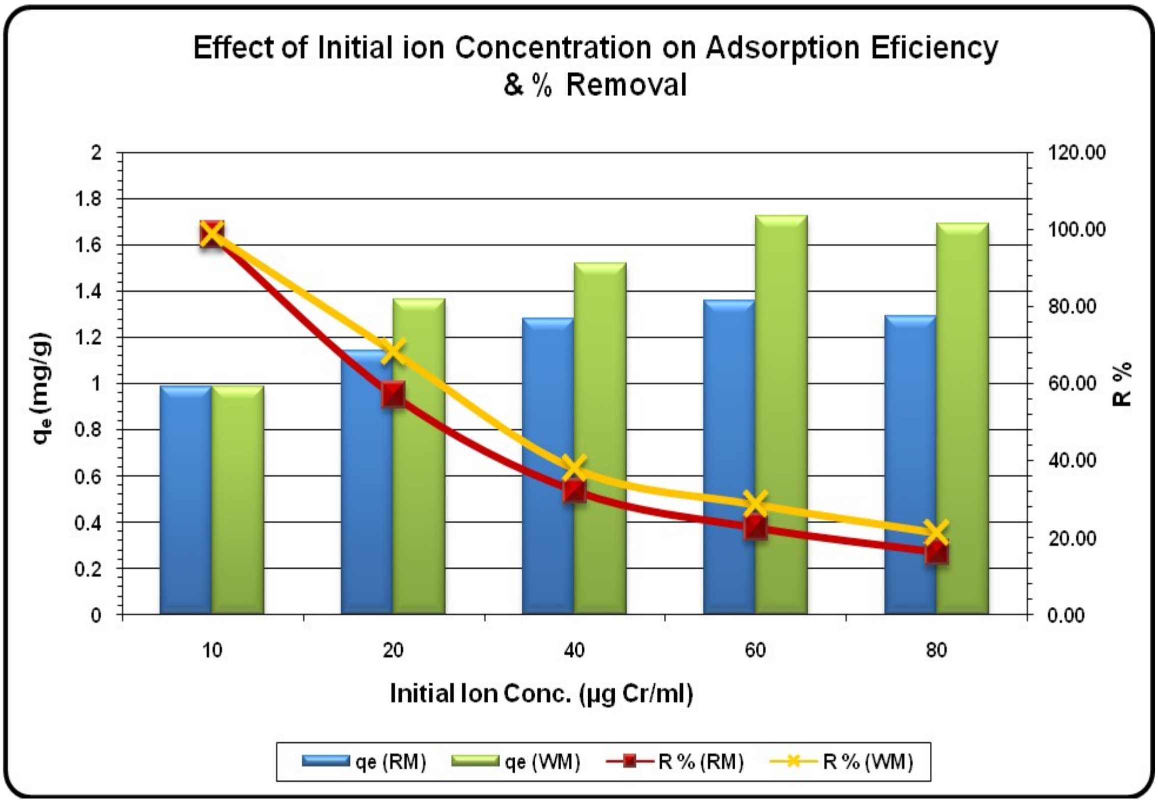

Figure 5.2.4: Effect of initial ion concentration on % Chromium removal and its uptake

From the above graph it is evident that Chromium ion uptake increases with increase in initial chromium ion concentration of aqueous solution. When initial metal ion concentration of Cr (VI) in aqueous solution was increased from 10 to 80 µg Cr/ml, percentage removal was decreased from 98.60 to 16.13% and from 98.70 to 21.15% for raw and washed fly ash, respectively. Increase in the number of Cr (VI) ions for the same amount of adsorbent may be the reason for this (Babu and Gupta, 2008). The Chromium ion uptake increased with increase with in initial ion concentration upto an initial ion concentration of 60 µg Cr/ml. Because increase in Cr (VI) ions leads to complete utilization of adsorption surface and available active sites which was otherwise not possible in low concentration (Babu and Gupta, 2008). But a decrease in chromium ion uptake was observed after 60 µg Cr/ml. That may be due to the saturation of the adsorbent at that concentration. Same trend was observed for both the adsorbents.

5.4 ADSORPTION KINETICS

Adsorption data given in **table 5.2.3** for raw and washed fly ash was fitted in the the Lagergren pseudo-first order and pseudo-second order adsorption kinetic model. **Figure 5.4.1** and **figure 5.4.2** are showing linear fit diagram of Lagergren pseudo-first order adsorption kinetic plot for raw and washed fly ash with correlation coefficient of 0.979 and 0.976 respectively. **Figure 5.4.3** and **figure 5.4.4** are showing linear fit diagram of Lagergren pseudo-second order adsorption kinetic plot for raw and washed fly ash, both with correlation coefficient of 0.999. From these linear plots values of q_e and rate constants were obtained. A comparison between both adsorption kinetic models is given in **table 5.4.1**.

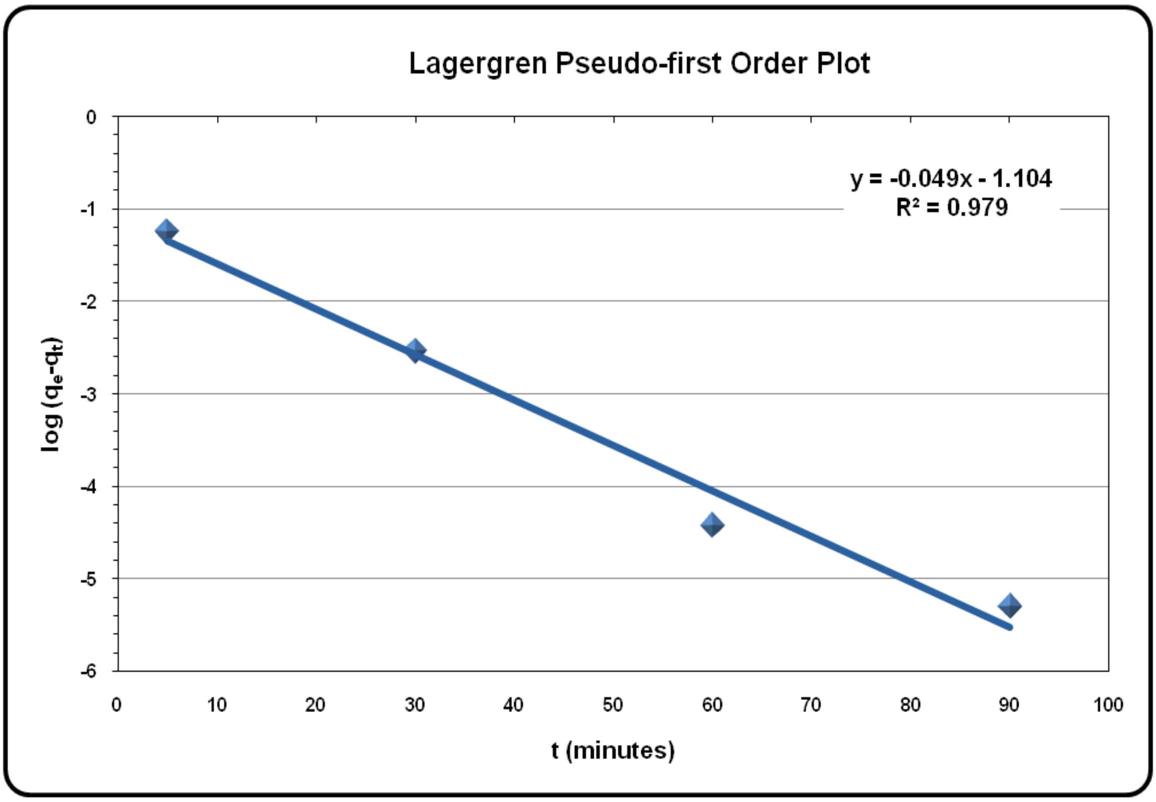

Figure 5.4.1: Lagergren Pseudo-first order Adsorption kinetic plot for Raw fly ash

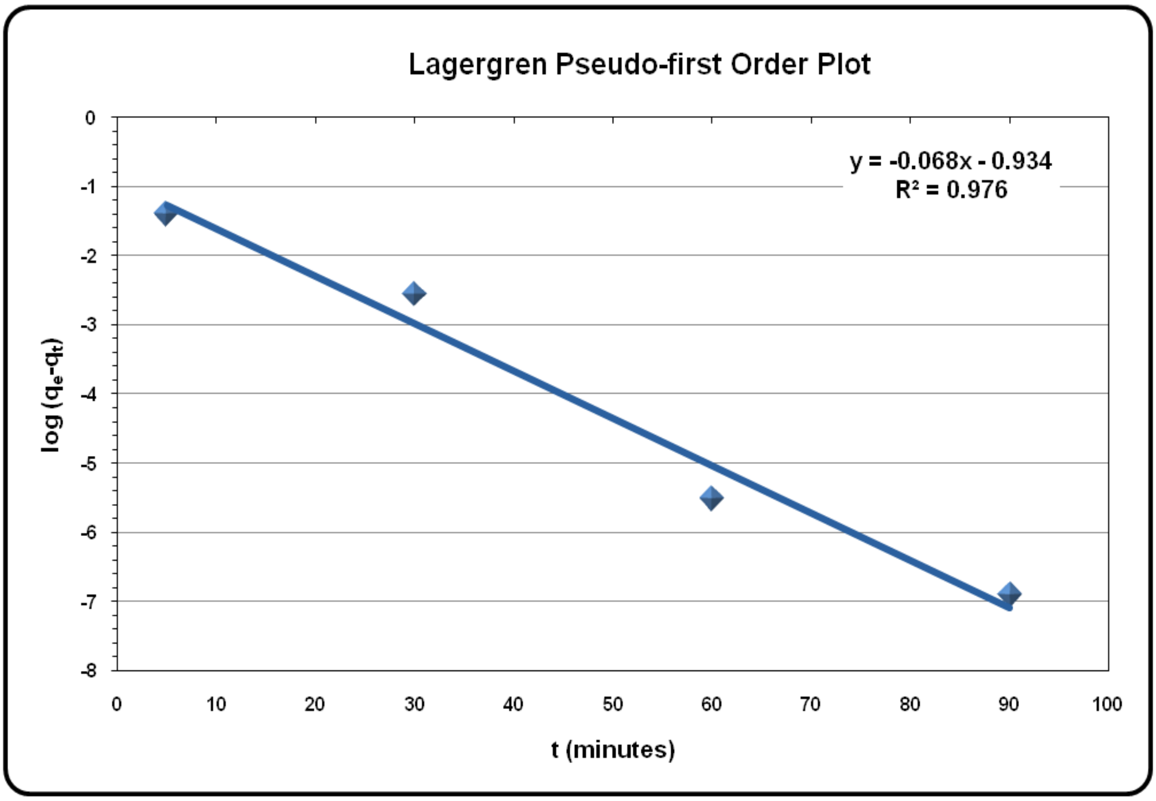

Figure 5.4.2: Lagergren Pseudo-first order Adsorption kinetic plot for Washed fly ash

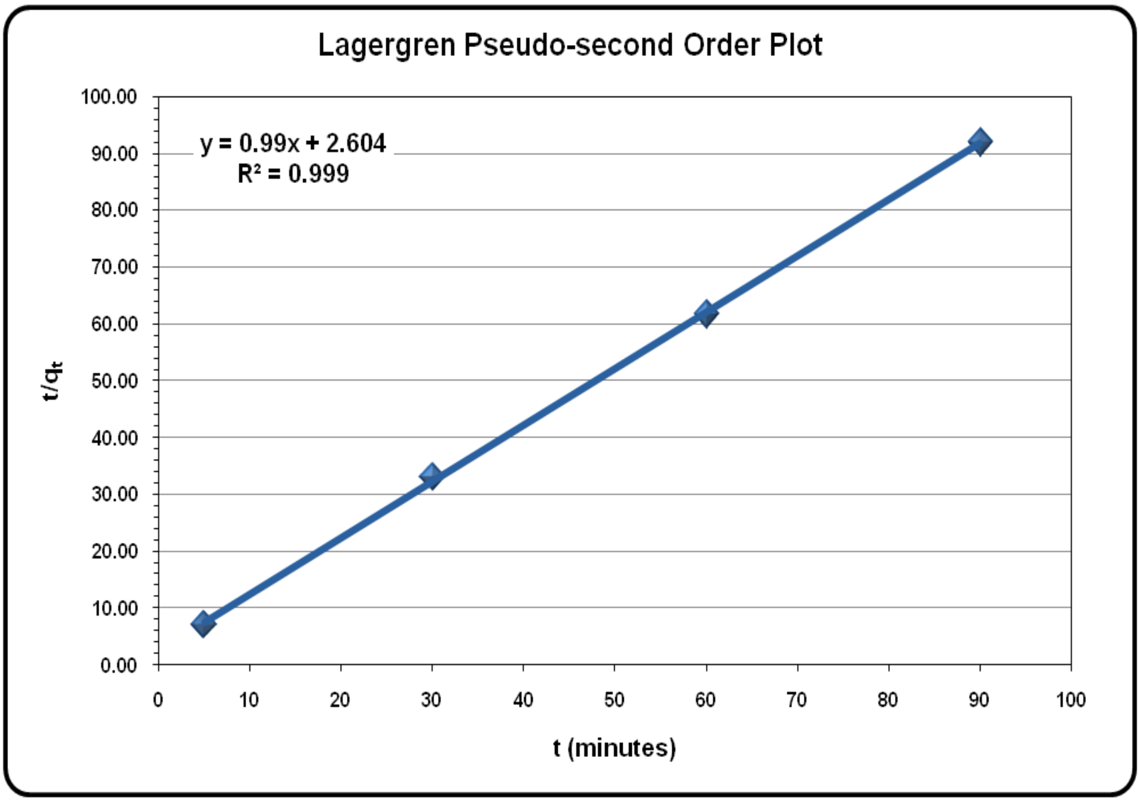

Figure 5.4.3: Lagergren Pseudo-second order Adsorption kinetic plot for Raw fly ash

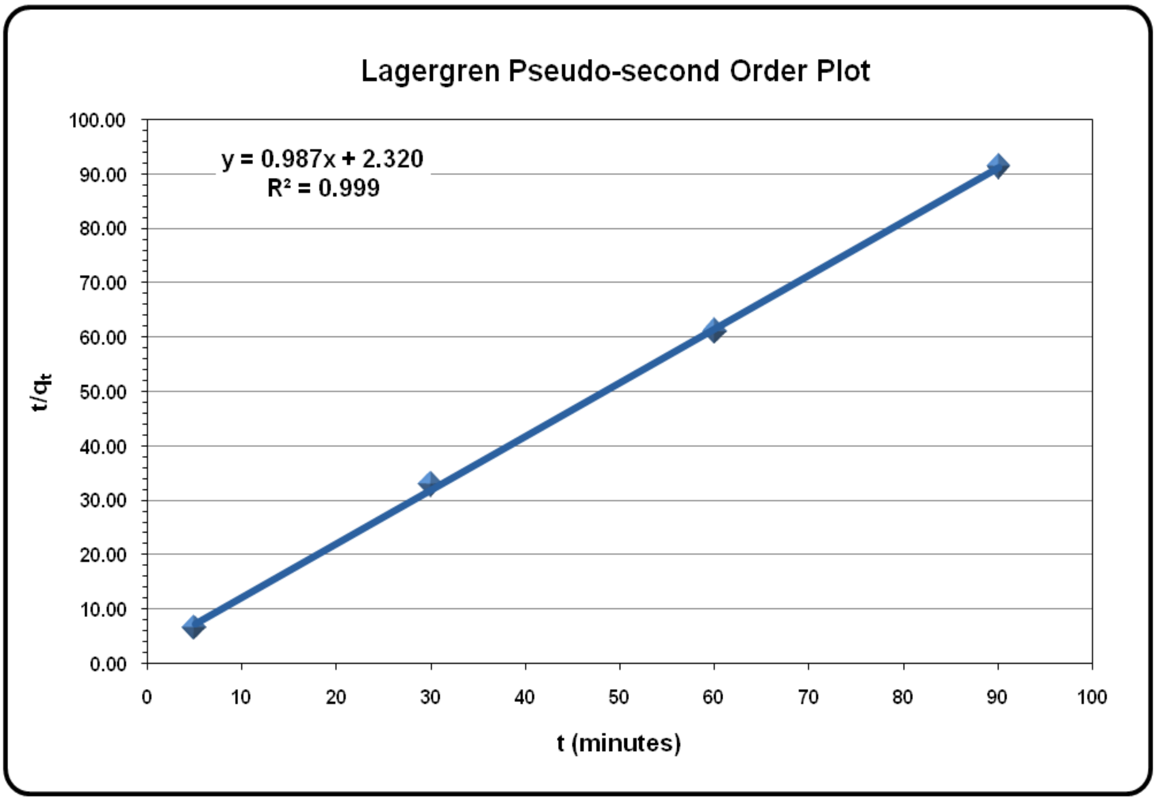

Figure 5.4.4: Lagergren Pseudo-second order Adsorption kinetic plot for Washed fly ash

Table 5.4.1: Comparison between Lagergren Pseudo-first order and Pseudo-second order Adsorption kinetic plot

Adsorbent	**Exp. q_e (mg/g)**	**Pseudo-first order kinetic model**			**Pseudo-second order kinetic model**		
		q_e (mg/g)	**$K_{1,ads}$ (min^{-1})**	**R^2**	**q_e (mg/g)**	**$K_{2,ads}$ (min^{-1})**	**R^2**
RM	0.986	0.137	0.1128	0.979	1.01	0.384	0.999
WM	0.987	0.102	0.1566	0.976	1.02	0.431	0.999

From the **table 5.4.1**, it is evident that coefficient of correlation is high for pseudo-second order kinetic model and the values of q_e drawn for the same model is in agreement with experimental q_e for both raw and washed fly ash.

CONCLUSION

Fly ash collected from the ‘Waste to Energy Power Plant’, Gidderbaha, Distt. Mukatsar was investigated for the removal of Cr (VI) from aqueous solution by carrying out batch adsorption experiments and the following important conclusions are withdrawn from the experimental results:

- Percentage removal increases and adsorption capacity decreases with increase in adsorbent amount. Increase in percent removal is due to increase in surface area and adsorption sites. On the other hand, decrease in the Chromium ion uptake (q_e) is due to availability of lesser number of Cr (VI) ions per unit mass of the fly ash.
- Adsorption of Cr (VI) on the selected adsorbent is highly dependent on pH. The adsorption increased from 8.2 % at pH 5 to 98.6% at pH 1 in case of raw fly ash and 2.4% at pH 5 to 98.7% at pH 1 with washed fly ash**.** Hence**,** optimum pH for Cr (VI) adsorption was found to be 1.0.
- Kinetics of Cr (VI) adsorption on fly ash follows pseudo-second order reaction. The rate of Chromium adsorption on fly ash is very fast in the initial stage and then became slow after first 30 minutes, equilibrium is reached after 24 hours.
- Equilibrium adsorption data was well fitted in Langmuir isotherm model which substantiate monolayer adsorption of Cr (VI) on both raw and washed fly ash. The calculated value of separation factor (R_L) in both cases confirmed favorable adsorption of Cr (VI).

At last, it can be concluded that fly ash of agricultural waste burning can be used as adsorbent for Cr (VI) at low concentration. It has low cost and easy availability in all agricultural areas. It will not only cut down the cost of effluent treatment but will also provide a beneficial use of fly ash. Hence, it is beneficial to use fly ash of agricultural waste burning as adsorbent both economically and environmentally.

However, no work is complete in itself; there is always a heavy scope to work further and to get knowledge. As in this report consideration is given only to adsorption of Chromium at very lower concentration and at small scale by batch adsorption method. There is a further scope to widen the area of study by considering more heavy metals or carrying out experiments at large scale through continuous process.

SUMMARY

Chromium is the most widespread contaminant in nature because of its extensive usage in industrial applications. Chromium has been reported beyond permissible limits in ground and tap water samples collected from villages along the polluted wastewater drains of Punjab due to discharge of untreated industrial effluent containing chromium and other heavy metals. Intake of Cr (VI) beyond the permissible limit leads to various health problems because it is highly toxic and carcinogenic. Therefore, it must be removed from industrial effluent before its discharge.

A number of physico-chemical methods have been used for the removal of Cr (VI) from wastewater. Adsorption using activated carbon is quite efficient for the treatment of wastewater. However, activated carbon is costly and the regeneration of activated carbon is associated with problems. Hence, efforts are being made to develop low cost and readily available materials for Cr (VI) adsorption. The present work is undertaken to study the adsorption characteristics of fly ash collected from the 'Waste to Energy Power Plant', which uses a huge quantity of agricultural waste to produce electricity and leaving behind ash. This was chosen to be used as adsorbent because this is easily available in this area, have no cost and further do not have any use.

The effect of various parameters i.e. adsorbent dose (10-40 g/l), contact time (5-90 minutes), variation in pH (1-5) and initial metal ion concentration (10-80 µg/ml) on Cr (VI) adsorption from simulated aqueous solutions using raw and washed fly ash was investigated by batch adsorption experiments. It was found that adsorption of Cr (VI) on the selected adsorbents was highly dependent on pH. Maximum adsorption was observed by adding 10 g/l of adsorbent at pH 1.0 for contact period of 90 minutes and maintained at 200 rpm. Thus, by optimizing the process conditions of the fly ash, the removal of hexavalent chromium from the industrial effluents can be maximized.

The adsorption process of Cr (VI) by both raw and washed fly ash was tested using Langmuir isotherm model. Linear fit diagram of Langmuir adsorption model with high correlation coefficient of 0.998 and 0.997 for raw and washed fly ash, respectively. High value of correlation coefficient confirmed the monolayer

adsorption of Cr (VI) on the adsorbent surface. The adsorption capacity to form a monolayer (q_m) was found to be 1.319 and 1.727 mg/g for raw and washed fly ash, respectively. Further, the dimensionless equilibrium parameter, R_L was found to be between 0.042 to 0.954 for raw fly ash and 0.021 to 0.911 for washed fly ash. In both the cases value lies between 0 and 1 which indicate favourable adsorption.

Further, the adsorption process using fly ash of 'Waste to Energy Plant' follows a pseudo-second order kinetic model and the values of q_e drawn for the same model is in agreement with experimental q_e for both raw and washed fly ash.

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