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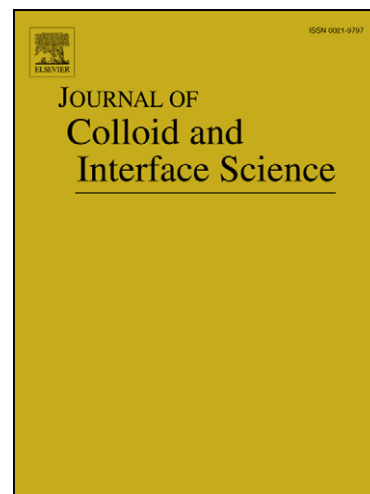
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Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material

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Abstract

Low cost fertilizer industry waste material called carbon slurry, produced in generators of fuel oil based industrial generators was converted into an effective and efficient adsorbent for the removal of hexavalent chromium (VI) from aqueous solutions. The waste was chemically treated, activated, characterized and used for the adsorption of chromium. The work involves batch experiments to investigate the effect of contact time, pH, temperature, concentration and adsorbent dose on the extent of adsorption by carbon slurry. The maximum adsorption was found at 70 min., 2.0 pH, 4.0 g/L dose, 303 K temperature. Maximum adsorption capacity (15.24 mg/g) of Cr(VI) on carbon slurry was observed at 100 mg/L initial Cr(VI) concentration. Langmuir and Freundlich adsorption isotherm models were applied to analyze adsorption data, and both were found to be applicable to this adsorption system, in terms of relatively high regression values. Thermodynamic parameters showed that the adsorption of Cr(VI) onto carbon slurry was feasible, spontaneous and exothermic under studied conditions. Kinetics of adsorption was found to follow pseudo second order rate equation. Column studies have been carried out to compare these with the batch capacities. The recovery of Cr(VI) and chemical regeneration of the spent column have also been tried. In all, the results indicated that the adsorbent used in this work proved to be effective material for the treatment of chromium bearing aqueous solutions.

Keywords: Carbon slurry; Hexavalent chromium; Adsorption isotherm models; Thermodynamic parameters; Kinetics

1. Introduction

Chromium is generated from various industrial processes like electroplating, leather tanning, wood preservations, manufacturing of dye, paint and paper and petroleum refining processes [1]. The effluents from these industries contain both Cr(VI) and Cr(III) in concentrations ranging from tens to hundreds of milligram per liters. However, hexavalent form is five hundred times more toxic than the trivalent one and human toxicity of Cr(VI) includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage [2]. Because of these differences, the discharge of Cr(VI) to surface water is regulated to below 0.05 mg/L by the U.S. EPA, while total Cr, including Cr(III), Cr(VI), and its other forms, is regulated to below 2 mg/L [3].

The conventional chromium treatment method consists of four steps:

1. Reduction of Cr(VI) to Cr(III).
2. Precipitation of Cr(III) as Cr(OH)₃ at high pH.
3. Settling of the insoluble metal hydroxide.
4. Disposal of the dewatered sludge.

Due to major shortcomings of conventional treatment methods including the high cost of safely disposing the sludge, expensive chemicals necessary for Cr(VI) reduction, and incomplete reduction of Cr(VI), adsorption processes are considered to be the appropriate method. Adsorption, an effective and versatile method for removal of heavy metals is when combined with suitable desorption step solves the problem of sludge disposal [4]. A number of low cost adsorbents have been used earlier for the removal of toxic pollutants from waste waters [5-10]. During recent years, among them various naturally available adsorbents like wool, olive cake, sawdust, pine needles, almond shells,

cactus leaves, charcoal used tyres, soot, hazelnut shell, coconut shell charcoal, banana peel, seaweed, dead fungal biomass, cyanobacterium and green alga were used for removal of chromium [11- 19]. However, many of these naturally available adsorbents have low chromium adsorption capacity and slow process kinetics. Thus, there is the need to develop innovative low cost adsorbents useful for both industries and environment.

Since in India large numbers of fertilizer plants are working to produce fertilizer, and they use oil as a fuel to generate energy. But, due to incomplete combustion of fuel in generator, fertilizer plants produces large amount of solid waste product called carbon slurry. This waste product also creates disposal management problem. In this work efforts have been made to put this solid waste to use by converting it into a suitable adsorbent material. Earlier researchers have reported on carbon slurry promising results for the removal of dyes Vertigo Blue 49, and Orange DNA 13, chlorophenols, fluoride, and of pesticides [20-23]. Use of carbon slurry has also been reported for some metal ions viz. on Hg^{2+} , Pb^{2+} and Cu^{2+} [24, 25], but still there is lots of scope available to use this waste, carbon slurry, for the removal of other heavy metal ions from waste waters. In the same sequence in this investigation, adsorption studies for the removal of hexavalent chromium from aqueous solutions by carbon slurry are carried out.

2. Materials and Methods

Fertilizer plants in India generate large amounts of carbon slurry waste due to incomplete combustion of oil fuel. This slurry is stored in large tanks and allowed to dry. The dried cake material, available at very cheap rate, was procured from National

Fertilizer Limited, Panipat (India) and powdered. It was found to consist of small, black and greasy granules form. Raw material obtained from plant was initially hydrophobic in nature but when activation performed it will be changed into hydrophilic.

All reagents used were of AR grade either from Merck, Germany or SD Fine Chem. Ltd., India and solutions were prepared using Milli-Q water. Standard solution of Cr(VI) (1000 mg/L) for atomic adsorption spectrometry was obtained from Merck, Germany. To adjust the pH, 0.1 N HCl and 0.1N NaOH solutions were used and 30% w/v analytical grade H₂O₂ manufactured by S.D. Fine, India, was used to activate carbon slurry. HNO₃ utilized in column studies was supplied by Merck, Delhi, India.

2.1. Equipment

The pH measurements were made using a pH meter (model cyber scan 510, Singapore). The chromium solutions were analyzed using an atomic adsorption spectrophotometer model Z- 7000 (Hitachi, Japan) at a wavelength of 357.9 nm. LEO 435 VP (Leo Elektronenmikroskopie GmbH, Germany), scanning electron microscopy was used for the scanning of carbon slurry. Infra red spectra of the samples were recorded on a FTIR, Spectrophotometer model –1600, (Perkin Elmer, USA).

2.2. Preparation of adsorbent

The raw material was obtained in the form of small, spherical carbonaceous, black, greasy granules from the fertilizer industries. Firstly, it was powdered and treated with hydrogen peroxide for 24h at room temperature to oxidize the adhering organic material, and then heated to 473 K in air until the emission of black soot was completely stopped. Now material was cooled and activated in muffle furnace for 2h at 723 K in the presence of air. The activated product obtained was about ~90% which is further treated

with 1.0M HCl solution to remove remaining ash content and then washed with doubled distilled water, thereafter it was dried in an oven at 373 K, 24h. The dried product is referred to as carbonaceous adsorbent and was sieved to obtain different particles sizes corresponding to 100-150, 150-200 and 200-250 British Standard Sieve (BSS) mesh and stored in vacuum desiccators.

2.3. *Batch adsorption studies*

. Adsorption was determined by batch method, which permits convenient evaluation of parameters that influence the adsorption process. In batch method, a fixed quantity of carbon slurry is mixed continuously with a specific volume of solution or waste and constantly agitated at 303 ± 2 K, until the equilibrium was reached. At the end of adsorption, 1 ml sample was collected and centrifuged at 1500 rpm for 10 min. on a centrifuge. The filtrate was collected in polythene tubes and diluted before analysis. The concentration of remaining Cr(VI) ions in the adsorption medium was determined using an atomic adsorption spectrophotometer model Z- 7000 (Hitachi, Japan) at a wavelength of 357.9 nm. Before determination of the total quantity of chromium Cr(VI) in the adsorption medium, Cr^{3+} and Cr^{2+} were converted to Cr(VI) using KMnO_4 . The adsorption capacities were then obtained by mass balance calculations.

For adsorption isotherms, a series of 25 ml glass tubes were filled with 10 ml Cr(VI) solution of varying concentrations (10-100 mg/L), maintained at desired temperature and pH. Then equal amount of activated carbon slurry was added into each test tube. The amount of carbon slurry used for Cr(VI) solutions was 4.0 g/L, after the optimum uptake time (70 min) the concentrations of chromium ion was calculated by taking the difference in their initial and final concentrations. In each experiment constant

shaking of the solution was performed by using magnetic stirrer. All the experiments were repeated three times and average values were reported. The standard deviation was found to be $\pm 1.8\%$.

Kinetic studies of adsorption by fertilizer waste were also carried out at two initial chromium concentrations (50 and 100 mg/L) at 303 K wherein the extent of adsorption was analyzed at regular time interval.

2.4. Column studies

Adsorption isotherms are used for some primary studies and obtaining the operational parameters before running more costly experiments. Hence, the practical applicability of the product for column operations has also been studied to obtain some parameters necessary for a factual design model. A glass column (30 × 1.5 cm) filled with a known amount of carbon slurry (mesh size 100-150 B.S.S.) was used. Effluent flow was adjusted with a clip at the bottom of the column. The column runs were carried out up to the point where the break through capacity was consumed.

2.5. Regeneration

Regeneration of adsorbent as well as recovery of adsorbate material is quite important, therefore, the same have been achieved by using 1% HNO₃. For this the desorption studies were conducted using different desorbing agents like 1% HNO₃, HCl, 0.3 M NH₄OH, NaCl and deionized H₂O. The adsorbent loaded with Cr(VI) metal ion was placed in the desorbing medium and was constantly stirred on a rotatory shaker at 100 rpm for an hour at 303 K. Desorption ratio is given as the amount of metal ions desorbed to the amount of metal ions adsorbed multiplied by 100. Simultaneous regeneration of adsorbent was also tried.

3. Results and discussion

3.1. Characterization of the prepared adsorbent

The carbon slurry was chemically analyzed and it was found to be organic in nature; i.e., it contains constituents such as carbon (78.93%), oxygen (19.41%), Al (1.16%), and F (0.49%). Carbon (due to the presence of coke particles) is the prominent component of carbon slurry. The organic content generally imparts porosity to the adsorbent as observed in the SEM results which is highly porous in nature (fig.1). This is reflected in the surface area of the adsorbents which were found to be 388 m²/g (calculated by our laboratory workers) for carbonaceous adsorbent, as the carbon content decreases, the surface area correspondingly decreases [26,27]. On the basis of surface area, the carbonaceous adsorbent is expected to be a useful material for the removal of metal ions.

FIGURE 1

The samples of carbonaceous adsorbent was stirred with deionized water for 2 h and left for 24 h to see any interaction. It was seen that in carbonaceous adsorbent, the pH of water was lowered, which indicates it as carbonaceous adsorbent as per Steenberg classification [28] comes under “L” type carbon. IR spectrum of the sample of carbonaceous adsorbent taken indicates the presence of two prominent bands lying at 1634 and 3420 cm⁻¹. The first peak may be assigned to the presence of a carbonyl group, and the latter one may be assigned to the presence of the OH group.

3.2. Adsorption studies

Adsorption of Cr(VI) on a low cost fertilizer industry waste material, carbon slurry, was studied as a function of pH, temperature, dose, metal ion concentration and adsorbent particle size. The adsorption data were fitted to different isotherms.

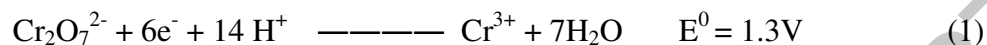
3.2.1. Effect of pH

Hexavalent chromium removal by the fertilizer waste at 303 K temperature and an initial calculated metal ion concentration of 50 and 100 mg/L was found to be pH-dependent as shown in fig 2. Equilibrium chromium sorption was favoured by acidic pH range of 1-3 and maximum adsorption by the carbon slurry was observed at pH 2.0. Thus, the results showed that the uptake of Cr(VI) rises from 8.5 (pH 1.0) to 14.8 mg/g (pH 2.0) and then starts to decrease. Accordingly, the optimum pH for the maximum uptake of Cr(VI) was found at 2.0.

Figure 2

This could be explained that since Cr(VI) exists in the form of oxyanions such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , etc. in acidic medium and the lowering of pH causes the surface of the adsorbent to be protonated to a higher extent and as a result a strong attraction exists between these oxyanions of Cr (VI) and positively charged surface of the adsorbent. Hence, the uptake increases with increasing pH from 1.0 to 2.0 of the solution. Whereas at high pH there will be abundance of negatively charged hydroxyl ions in aqueous solution, causing hindrance between negatively charged ions $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , etc and negatively charged adsorbent, resulting in decrease of adsorption.

Thus during adsorption of Cr(VI) on the surface of carbon slurry there was adsorption of Cr(VI) as well as Cr(III). Reduction of Cr(VI) into Cr(III) is also clear from the aqueous chemistry of Cr(VI) at low pH value:



For the determination of Cr(VI), its supernatant was separated from the reaction mixture and divided into two parts. In one part equilibrium concentration of the Cr(VI) was measured by prescribed method. Whereas second part was heated up to 125-140 °C with powerful oxidizing reagent such as KMnO_4 . The concentration of Cr(VI) is then measured, which shows higher equilibrium concentration. Reason is that, KMnO_4 oxidize all the Cr(III) into Cr(VI), present in the solution, which was formed at the surface of carbon slurry during the adsorption process at very low pH. Similar type of observation was also reported by some other workers [29,30].

3.2.2. *Effect of contact time*

Fig. 3 shows the comparative data of the effect of contact time on the extent of adsorption of Cr(VI) on the carbon slurry at 50 and 100 mg/L initial chromium concentration at pH 2.0 and temperature 303 K. It has been observed that the metal adsorption rate is high at the beginning and then decreases slowly till saturation levels were completely reached at equilibration point (70 min.). The data obtained from this experiment were further used successfully to evaluate the kinetics of the adsorption process.

Figure 3

3.2.3. *Effect of particle size*

The adsorption of Cr(VI) on carbon slurry at pH 2, and 100mg/L was investigated at three particle sizes, 100–150, 150–200, and 200–250 mesh, respectively, as shown in fig. 4. It was found that the adsorption capacity increases with decrease in particle size of the adsorbent as there is increase in surface area. But it may be possible that Cr(VI) ion are not able to penetrate to some of the interior pores of the particles, especially when their sizes are large. The access to all pores is facilitated in small size particles. Similar results were also obtained by McKay et. al. [31]. Particles size 100-150 mesh show maximum adsorption capacity.

Figure 4

3.2.4. Effect of adsorbent dose

To determine the effect of adsorbent dose, different amounts (1-10 mg/L) of adsorbent was suspended in 10 ml chromium solution in which the concentration of chromium was 100 mg/L under optimized conditions of pH and contact time. The effect of adsorbent dose on the amount of chromium (VI) adsorbed in mg/g and extent of removal of chromium for the adsorbent is shown in fig. 5. The amount of adsorbent significantly influenced the extent of chromium (VI) adsorption. The extent of Cr(VI) removal was found to be 3% for 0.5 g/L of adsorbent. It greatly increased to 65% for 4 g/L of adsorbent, respectively. However, it has been observed that there was only a slow change in the extent of Cr(VI) adsorption for carbon slurry, when the adsorbent dose was over 4 g/L. Furthermore, higher adsorbent dose result in lower adsorption capacity ($q_e = 2$ mg/g at 1 g/L dose for carbon slurry) value at a fixed Cr(VI) concentration (100 mg/L) as shown in fig. 5. At low dose, all types of sites are entirely exposed and the adsorption

on the surface is saturated faster, showing a higher q_e value. But at higher adsorbent dose, the availability of higher energy sites decreases with a larger fraction of lower energy sites occupied, resulting in a lower q_e value. Thus, an optimum dose of 4g/L is selected for all the experiments. Similar type of result has also been observed by other researchers also [14,15].

Figure 5

3.2.5. *Effect of Cr(VI) concentration*

The effect of Cr(VI) concentration on carbon slurry was investigated at different chromium concentrated solutions and results are shown in fig. 6. This plot show that the time for equilibrium adsorption remains unchanged, and shows maximum adsorption at 100mg/L. Similar type of observations were obtained while studying the adsorption of dyes [32].

Figure 6

3.3. *Adsorption Isotherm Modelling*

Temperature effect experiments were performed at pH 2.0, initial Cr(VI) concentration 100mg/L, 0.4g adsorbent and at various temperatures of 303, 313 and 323 K. It was observed that the uptake (mg/g) of chromium ion decreases from 14.7, 13.8 to 12.8 with the rise in temperature from 303, 313 to 323 K (fig. 7). This result also shows that the adsorption was exothermic in nature.

Figure 7

The results obtained from adsorption isotherms were analyzed with Langmuir and Freundlich models as discussed earlier [12]. The plots of $1/q_e$ vs $1/C_e$ (Langmuir plot) and $\ln q_e$ vs $\ln C_e$ (Freundlich plot) [figures not shown] were drawn at three different temperatures and the Langmuir and Freundlich adsorption constants and the regression

correlation coefficient obtained are given in Table 1. The values of regression coefficients obtained from these models were used as the fitting criteria to find out these isotherms. It was found that both the plots depicted the linearized form of the isotherms at all temperatures and the extremely high correlation coefficients ($R^2 = 0.98, 0.99$), thus indicating both monolayer and heterogenous surface conditions. Also, from the Langmuir adsorption constant q_e , the adsorption capacity of Cr(VI) on carbon slurry was observed as 15.24 mg/g at 303 K which decreased with the increase in temperature. When compared with several other low cost adsorbents, the present low cost adsorbent from fertilizer waste i.e. carbon slurry was found to show comparable hexavalent chromium adsorption (15.24 mg/g).

3.4. *Thermodynamic study*

To study the thermodynamics of adsorption of Cr(VI) on low cost adsorbent carbon slurry, thermodynamic constants such as enthalpy change ΔH° , free energy change ΔG° and entropy change ΔS° were calculated using equations described in our earlier work [18]. The values of these parameters are given in Table 2. A perusal of Table 2 indicated that the enthalpy change ΔH° is negative (exothermic) due to decrease in adsorption on successive increase in temperature. Further, negative ΔG° values indicate thermodynamically feasible and spontaneous nature of the adsorption process and positive value of ΔS° reveals the increased randomness at the solid-solution interface during the fixation of the Cr(VI) on the active sites of the adsorbent.

3.5. *Kinetic study*

The mathematical representations of Pseudo first- and second- order kinetic models are given in equation 2 and 3.

$$\log (q_e - q_t) = \log q_e - \frac{k_{1,ads}}{2.303} t \quad (2)$$

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_e the equilibrium sorption uptake at time $t = \text{infinity}$ and q_t (mg/g) is the amount of adsorbed chromium on the adsorbent at time t and $k_{1,ads}$ (/min) and $k_{2,ads}$ (g/mg/min) are the rate constant of first-order and second order adsorption. The adsorption rate constant (k_1) for chromium sorption was calculated from the slope of the linear plot of $\ln (q_e - q_t)$ versus time. In the latter case, kinetic data were plotted between t/q_t against t as shown in fig. 8. The kinetic rate constants obtained from first and second-order pseudo kinetic model are given in Table 3. The values of correlation coefficient R^2 for the pseudo-second-order adsorption model is relatively high (>0.9979), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo-first-order are not satisfactory. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of chromium ion on carbon slurry.

Figure 8

3.6. Comparison with other adsorbents

Table 4 compares maximum adsorption capacities obtained in this study with some other values reported in the literature. The adsorption capacity for chromium using carbon slurry, a waste from the fertilizer industry, is of the same order of magnitude or greater than that has been found using similar adsorbents [33- 37].

3.7. Column studies

The results obtained from adsorption batch experiments were used to remove chromium metal ion by column. The flow rate was varied to achieve the maximum removal of the adsorbate and it was found that the maximum uptake of chromium was achieved at flow rate 1.0 ml/min. About 92–93% chromium is removed at lower flow rates (1.0 ml/ min), while this decreases with increased flow rate. The plots of C/C_o versus time or volume, for a constant flow rate, depict the increase in the ratio of effluent to influent concentration as the zone moves through the column.

The breakpoint on the curve has been adopted by various workers differently to determine the breakthrough capacity of the column [38, 39]. The calculation [29] of breakthrough capacity, exhaustion capacity and degree of column utilization have been evaluated from breakthrough curve as given in fig. 9 was found to be 28.0 mg/g for chromium, which is greater than in the batch experiments (15.24 mg/g). The high column capacity may be due to the fact that a continuously large concentration gradient occurred at the interface zones as it passes through the column, while the concentration gradient decreased with time in the batch experiments.

Figure 9

Regeneration and recovery of the column is a very important aspect in wastewater treatment processes and, therefore, desorption of chromium was tried with a number of eluents like, deionized water, ammonium hydroxide, sodium chloride, hydrochloric acid, nitric acid, etc. and it was found that the desorption of the metal ion occurred by 1% HNO_3 . The column was allowed to pass 1 % HNO_3 at a flow rate of 1.0 ml/min for about 2 h and then again allowed to pass deionized water at the same flow rate. It was observed

that the column loses about 3% capacity after the first run and about 10–15% after more than five runs. Therefore, the column can be used for at least five runs without any problem. It is very important to mention here that carbon slurry, a waste from fertilizer industry, is an easily available, inexpensive material, and its cost is very low in comparison to the cost of regeneration.

4. Summary

The batch studies conducted in the present study provides significant information regarding adsorption of chromium on carbon slurry in terms of optimum pH and adsorbent dose for maximum removal of Cr(VI) from the aqueous solution. The studies indicate that carbon slurry is an effective adsorbent for Cr(VI) removal. The maximum Cr(VI) adsorption capacity has been found to be 15.244 mg/g Cr(VI) of dry weight of adsorbent at an carbon slurry dose of 4.0 g/L in 70 min. of contact time with initial Cr(VI) concentration of 100 mg/L, 303 K temperature and optimum pH of 2.0. The Langmuir and Freundlich adsorption model were used for the mathematical description of the adsorption of Cr(VI) ions onto carbon slurry and it was found that the adsorption equilibrium data fitted well to both the models. The adsorption of chromium ions on the carbon slurry follows second order adsorption kinetics and 5% HNO₃ efficiently desorbed metal from the metal-loaded adsorbent. The studies on column operations show that the product can also be used on an industrial scale. Metal ions adsorbed on the column of this material can be quantitatively eluted with HNO₃. The exhausted column can be chemically regenerated by treating it with HNO₃ and no dismantling is required. Other salts present in effluents do not cause any disturbing effects. The advantage of high metal adsorption capacity, proves that the carbon slurry has the potential to be used as an

efficient and economic adsorbent material for the removal of chromium from aqueous phase.

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References

- [1] L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, *J. Hazard. Mater.* 123 (2005) 223–231.
- [2] US Department of Health and Human Services, Toxicological Profile for Chromium. Public Health Service Agency for Toxic substances and Diseases Registry, Washington, DC, 1991.
- [3] World Health Organization (WHO), Guidelines for Drinking-water Quality, Vol:1, 3rd ed., Recommendations, Geneva, 2004, pp. 334.
- [4] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (1999) 2469–2479.
- [5] A. Mittal, L. Kurup, V.K.Gupta, Use of waste materials- Bottom ash and De-Oiled soya as potential adsorbents for the removal of Amaranth from aqueous solutions, *J. Hazard. Mater.* 117 (2005) 171-178.
- [6] V.K. Gupta, I. Ali, Suhas, V.K. Saini, Removal of chlorophenols from wastewater using red mud: An aluminum industry waste, *Environ. Sci. Tech.* 38 (2004) 4012-4018.
- [7] V.K. Gupta, S. Sharma, Removal of zinc from aqueous solutions using bagasse fly ash – a low cost adsorbent, *Indust. Eng. Chem. Res.* 42 (2003) 6619-6624.
- [8] V.K.Gupta, C.K. Jain, I. Ali, S. Chandra, Removal of lindane and malathion from wastewater using bagasse fly ash - A sugar industry waste, *Water Res.* 36 (2002) 2483-2490.
- [9] V.K.Gupta, S.K.Srivastava, R. Tyagi, Design parameters for the treatment of phenolic wastes by carbon columns (obtained from fertilizer waste material), *Water Res.* 34 (2000) 1543- 1550.

- [10] V.K. Gupta, A. Rastogi, M.K. Dwivedi, D. Mohan, Process development for the removal of zinc and cadmium from wastewater using slag – A blast furnace waste material, *Sep. Sci. Technol.*, 32 (1997) 2883-2912.
- [11] J. Lakatos, S.D. Brown, C.E. Snape, Coals as sorbents for the removal and reduction of hexavalent chromium from aqueous waste streams, *Fuel* 81 (2002) 691–698.
- [12] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, *Chem. Eng. J.* 84 (2001) 95–105.
- [13] S.H. Hasan, K.K. Singh, O. Prakash, M. Talat, Y.S. Ho, Removal of Cr(VI) from aqueous solutions using agricultural waste ‘maize bran’, *J. Hazard. Mater.* 152 (2008) 356-365.
- [14] D. Park, Y.S. Yun, J.M. Park, Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics, *Process Biochem.* 40 (2005) 2559–2565.
- [15] M. Kobya, Adsorption, kinetic and equilibrium studies of Cr (VI) by hazelnut shell activated carbon, *Adsorp. Sci. Technol.* 22 (2004) 51–64.
- [16] J. R. Memona, S. Q. Memonb, M.I. Bhangera, A. El-Turkic, K. R. Hallamc, G. C. Allenc, Banana peel: A green and economical sorbent for the selective removal of Cr(VI) from industrial wastewater, *Colloid Surfaces B: Biointer.* 70 (2009) 232–237.
- [17] Z. A. Zakaria, M. Suratman, N. Mohammed, W.A. Ahmad, Chromium(VI) removal from aqueous solution by untreated rubber wood sawdust, *Desalin.* 244 (2009) 109–121.
- [18] V.K.Gupta, A.Rastogi, Sorption and desorption studies of chromium(VI) from nonviable cyanobacterium *Nostoc muscorum*, *J. Hazard. Mater.* 154 (2008) 347-354.

- [19] V.K.Gupta, A.Rastogi, Biosorption of hexavalent chromium(VI) by raw and acid treated green alga *Oedogonium hatei* from aqueous solutions, *J. Hazard. Mater.* 163 (2009) 396-402.
- [20] V.K. Gupta, I. Ali, V.K. Saini, adsorption studies on the removal of Vertigo Blue 49 and DNA13 from aqueous solution using carbon slurry developed from a waste material, *J. Colloid. Interf. Sci.* 315 (2007) 87-93.
- [21] A.K. Jain, V.K. Gupta, S. Jain, and Suhas, Removal of chlorophenols using industrial waste, *Environ. Sci. Technol.* 38 (2004) 1195-1200.
- [22] V.K. Gupta, I. Ali, V. K. Saini, Defluoridation of waste using waste carbon slurry, *Water Res.* 41 (2007) 3307-3316.
- [23] V.K. Gupta, I. Ali, Suhas, V.K. Saini, Adsorption of 2, 4-D and carbofuran pesticides using fertilizer and steel industry wastes, *J. Colloid. Interf. Sci.* 299 (2006) 556-563.
- [24] D. Mohan, V. K. Gupta, S.K. Srivastava, S. Chander, Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste, *Colloid. Surf. A; Physiochem. Eng. aspects* 177 (2001) 169-181.
- [25] V.K. Gupta, S.K. Srivastava, D. Mohan, S. Sharma, Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions, *Waste Management* 17 (1997) 517-522.
- [26] N. Daneshvar, D. Salari, S. Aber, Chromium adsorption and Cr (VI) reduction to trivalent chromium in aqueous solutions by soya cake, *J. Hazard. Mater.* B94 (2002) 49-61.

- [27] E.I. El-Shafey, Behavior of reduction-sorption of chromium (VI) from an aqueous solution on a modified sorbent from Rice Husk, *Water air and soil pollution* 163 (2005) 81–102.
- [2822] J.S. Mattson, H. B. Mark, Jr. *Activated Carbon Surface Chemistry and Adsorption from Solution*; Marcel Dekker: New York, 1971.
- [29] F.W. Pontius, *Water Quality and Treatment*, fourth ed., McGraw-Hill, New York, 1990.
- [30] Q.L. Diana, M. Oliveira, L.C.A. Gonçalves, Luiz Oliveria, R.G. Guilherme, Removal of As(V) and Cr(VI) from aqueous solutions using solid waste from leather industry, *J. Hazard. Mater.*, 151 (2008) 280-284.
- [31] G. McKay, M.S. Otterburn, A.G. Sweeny, The removal of colour from effluent using various adsorbents –IV Silica: Equilibria and column studies, *Water Res.* 14 (1980) 21-27.
- [32] A. Bhatnagar, A.K. Jain, A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, *J. Colloid Interface Sci.* 281 (2005) 49–55.
- [33] H. Gao, Y. Liu, G. Zeng, W. Xu, T. Li, W. Xia, Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste - Rice straw, *J. Hazard. Mater.* 150 (2008) 446-452.
- [34] U.K. Garg, M.P. Kaur, V.K. Garg, D. Suda, Removal of hexavalent waste from aqueous solutions by agricultural waste biomass, *J. Hazard. Mater.* 140 (2007) 60-68.

- [35] M. Dakiky, M. Khamis, A. Manassara, M. Mer'eb, Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents, *Adv. Environ. Res.* 6 (2002) 533–540.
- [36] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste, *J. Colloid Interface Sci.* 271 (2004) 321-328.
- [37] V.K.Gupta, M.Gupta, S.Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud- an aluminium industry waste, 35 (2001) 1125-1134.
- [38] C.J. N.loutier, A.Leduy, R.S.Ramalho, Peat adsorption of herbicide 2,4-D from wastewaters, *Can. J. Chem. Eng.*, 63 (1985) 250-257.
- [39] A.H. Mollah, C.W. Robinson, Pentachlorophenol adsorption and desorption characteristics of granular activated carbon – II. Kinetics, *Water Res.*, 30 (1996) 2907-2913.

Table 1.

Langmuir and Freundlich isotherm constants for the adsorption of Cr(VI) on carbon slurry at different temperatures and pH 2.0.

Temp (K)	Langmuir constant			Freundlich constant		
	<i>b</i> (L/mg)	<i>q_e</i> (mg/g)	<i>R</i> ²	<i>n</i>	<i>K_F</i> (mg/g)	<i>R</i> ²
303	0.0024	15.24	0.985	1.534	1.091	0.99
313	0.0051	6.14	0.99	1.453	1.024	0.99
323	0.0054	5.08	0.99	1.518	1.022	0.98

Table2.

Thermodynamic parameters for the adsorption of Cr(VI) on carbon slurry at different temperatures.

Temp (K)	ΔG° (kJ/mol)	ΔS° (kJ/mol K)	ΔH° * (kJ/ mol)
303	-14.183	0.063	
313	-14.534	0.060	-33.244
323	-13.005	0.063	

*Measured between 303 and 323 K.

Table 3.

Adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo-first and second order adsorption for the carbon slurry (pH 2.0).

Initial conc. (mg/L)	First –order model				Second-order model		
	q_e (mg/g)	k_1 ($\times 10^{-3}$ min^{-1})	$q_{ecal.}$ (mg/g)	R^2	k_2 ($\times 10^{-3}$ g/mg/min)	$q_{ecal.}$ (mg/g)	R^2
50	7.8	42.14	6.567	0.979	13.155	8.123	0.997
100	15.2	49.51	11.34	0.959	6.787	16.287	0.998

Table 4.

Comparison of adsorption capacities of Cr(VI) onto carbon slurry with different sorbents.

Adsorbent	Adsorbent capacity (mg/g)	Reference
Rice straw	3.15	[33]
Maize Corn cob	0.28	[34]
Jatropha oil cake	0.82	[34]
Sugarcane bagasse	0.63	[34]
Sawdust	15.84	[35]
Olive cake	33.4	[35]
Pine needles	21.5	[35]
Almond	10.62	[35]
Coal	6.78	[25]
Cactus leaves	7.08	[35]
Bagasse fly ash	4.35	[36]
Red mud	4.36	[37]
Carbon slurry	15.24	This study

FIGURE CAPTIONS:

Fig.1. SEM photographs of carbon slurry at different magnifications (a) 5000X, (b) 3500X, (c) 2000X and (d) 250X

Fig 2. Effect of pH on the adsorption of Cr(VI) on the carbon slurry, pH 1.0–7.0; initial Cr(VI) concentration 50 and 100 mg/L; adsorbent dose 4.0 g/L, temperature 303 K and particle size 100-150 mesh.

Fig.3. Effect of contact time on the adsorption of Cr(VI) on the carbon slurry, at pH 2.0, initial Cr(VI) concentration 50 and 100 mg/L, adsorbent dose 4.0 g/L and particle size 100-150 mesh.

Fig.4. Effect of particle size of the carbon slurry on the adsorption of Cr(VI), at pH 2.0, initial Cr(VI) concentration 100 mg/L, adsorbent dose 4.0 g/L and temperature 303 K.

Fig.5. Effect of adsorbent dosage on the uptake of Cr(VI) on carbon slurry at pH 2.0, 100 mg/L Cr(VI) concentration and temperature 303 K.

Fig: 6. Effect of Cr(VI) concentration on its adsorption on carbon slurry at 303 K, 4.0g/L dose.

Fig. 7 Adsorption isotherms of chromium at different temperatures.

Fig. 8. Second-order kinetic modeling of Cr(VI) ions adsorption on carbon slurry.

Fig. 9. Breakthrough curve of Cr(VI) on activated carbon slurry.

Fig.1. SEM photographs of carbon slurry at different magnifications (a) 5000X, (b) 3500X, (c) 2000X and (d) 250X

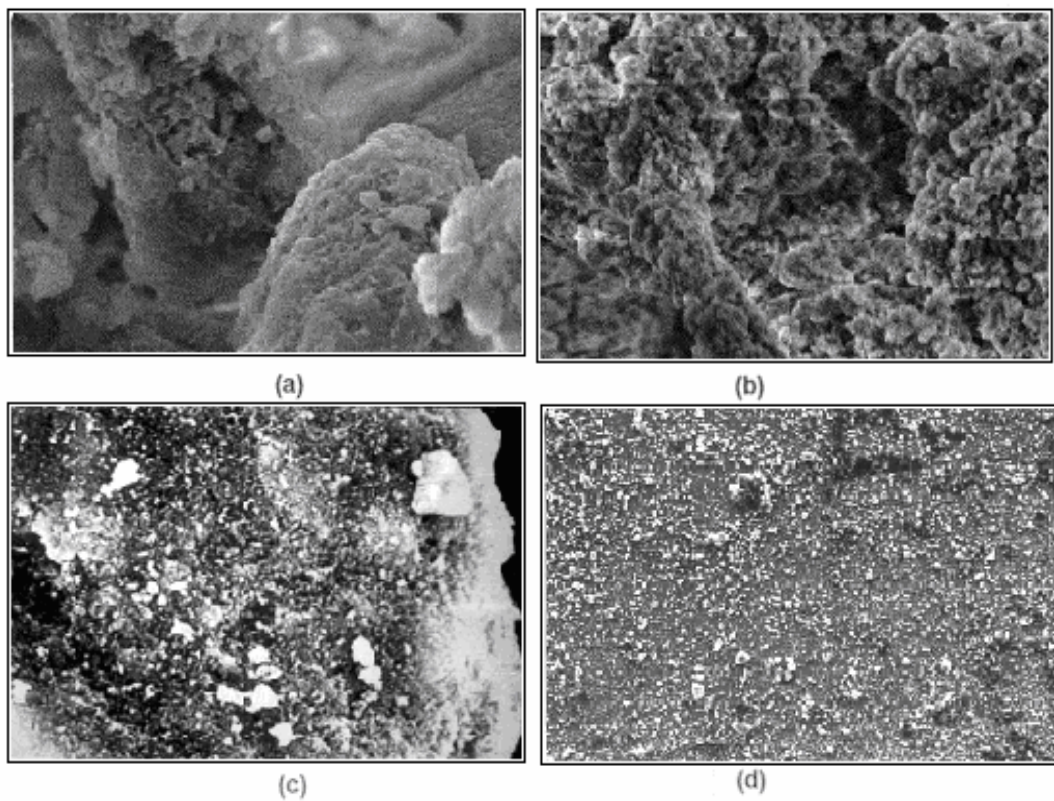


Fig 2. Effect of pH on the adsorption of Cr(VI) on the carbon slurry, pH 1.0–7.0; initial Cr(VI) concentration 50 and 100 mg/L; adsorbent dose 4.0 g/L, temperature 303 K and particle size 100-150 mesh

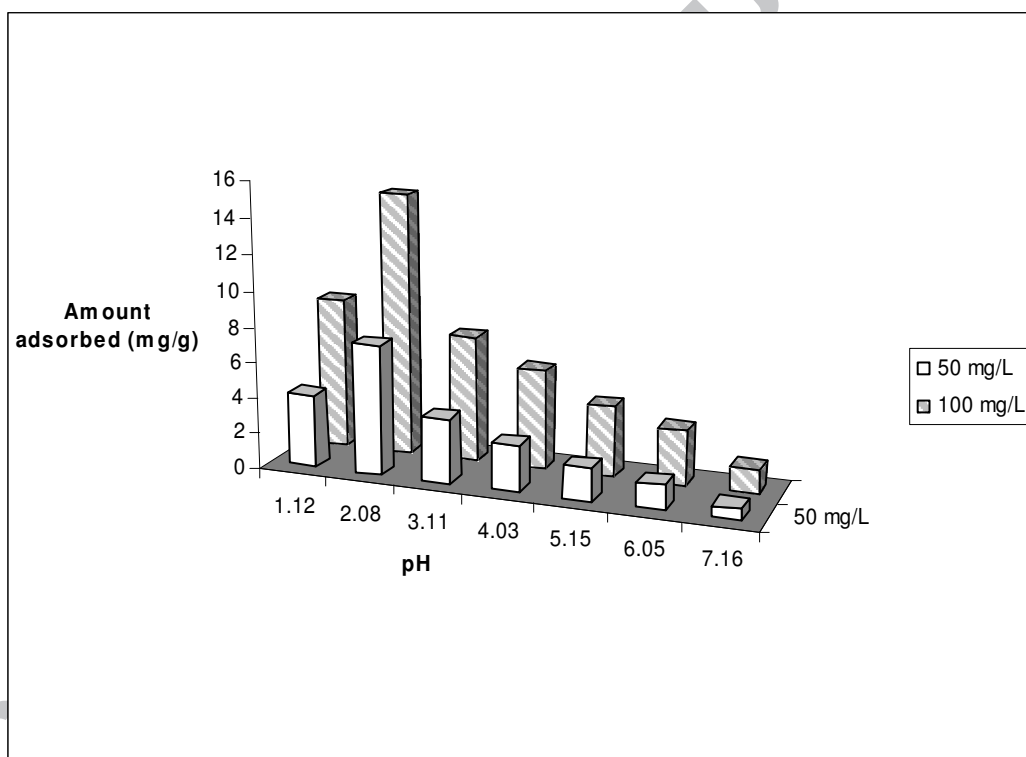


Fig.3. Effect of contact time on the adsorption of Cr(VI) on the carbon slurry, at pH 2.0, initial Cr(VI) concentration 50 and 100 mg/L, adsorbent dose 4.0 g/L and particle size 100-150 mesh.

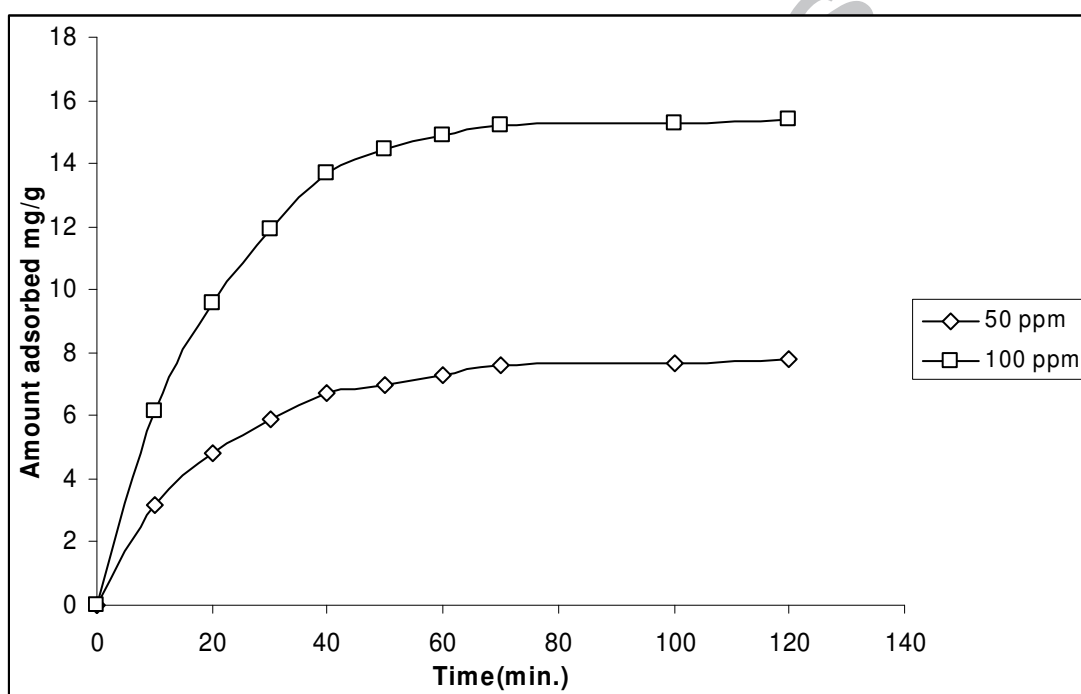


Fig.4. Effect of particle size of the carbon slurry on the adsorption of Cr(VI), at pH 2.0, initial Cr(VI) concentration 100 mg/L, adsorbent dose 4.0 g/L and temperature 303 K.

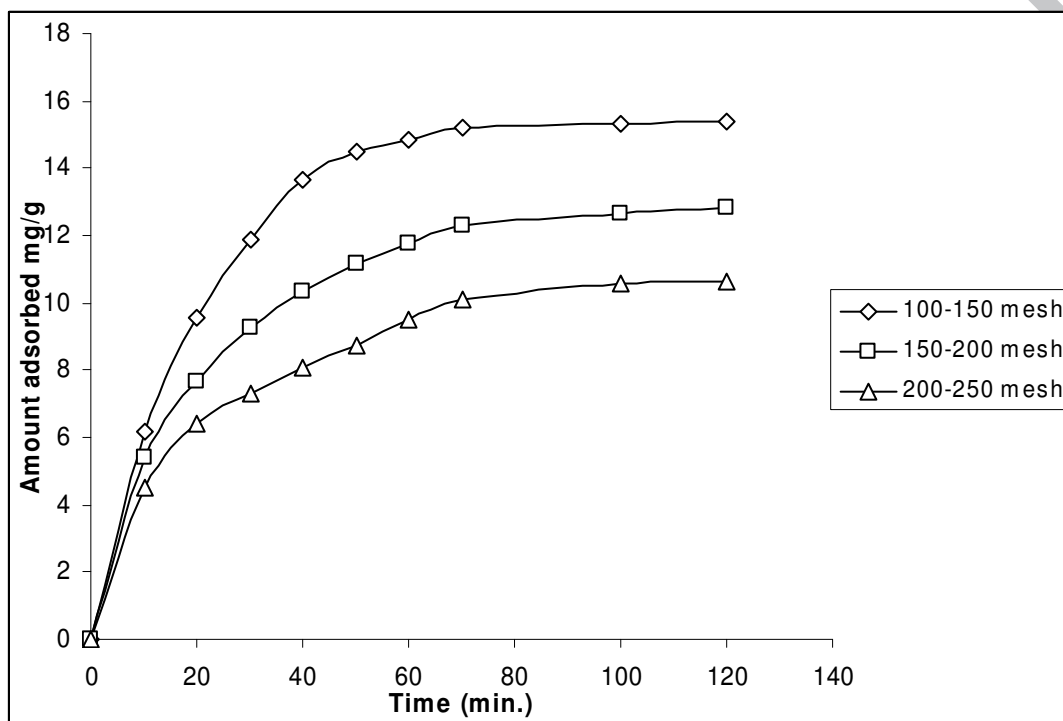


Fig.5. Effect of adsorbent dosage on the uptake of Cr(VI) on carbon slurry at pH 2.0, 100 mg/L Cr(VI) concentration and temperature 303 K.

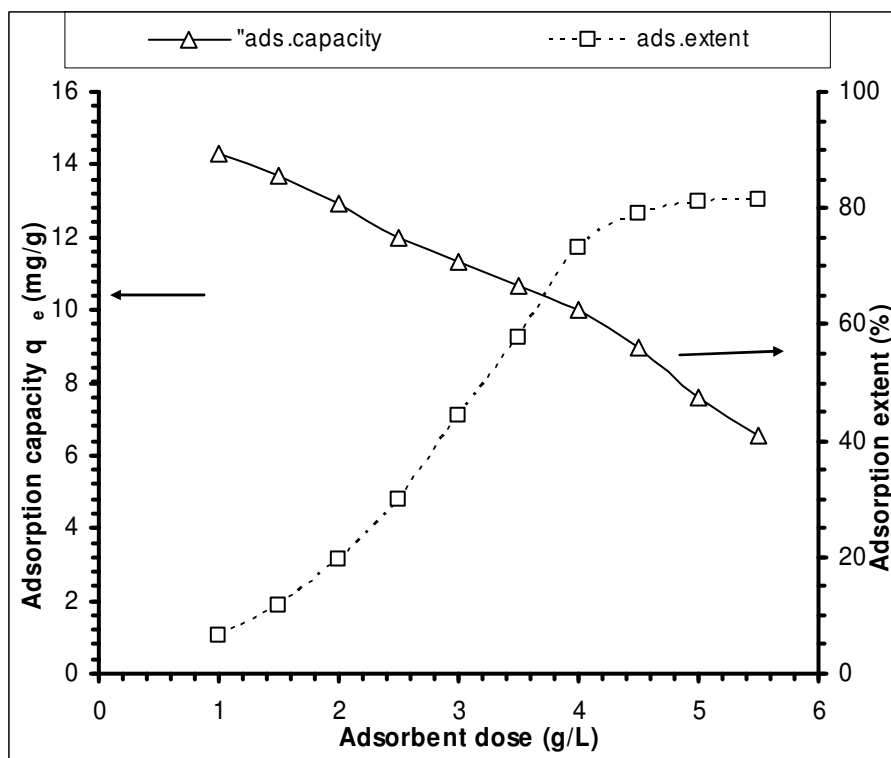


Fig: 6. Effect of Cr(VI) concentration on it's adsorption on carbon slurry at 303 K, 4.0 g/L dose.

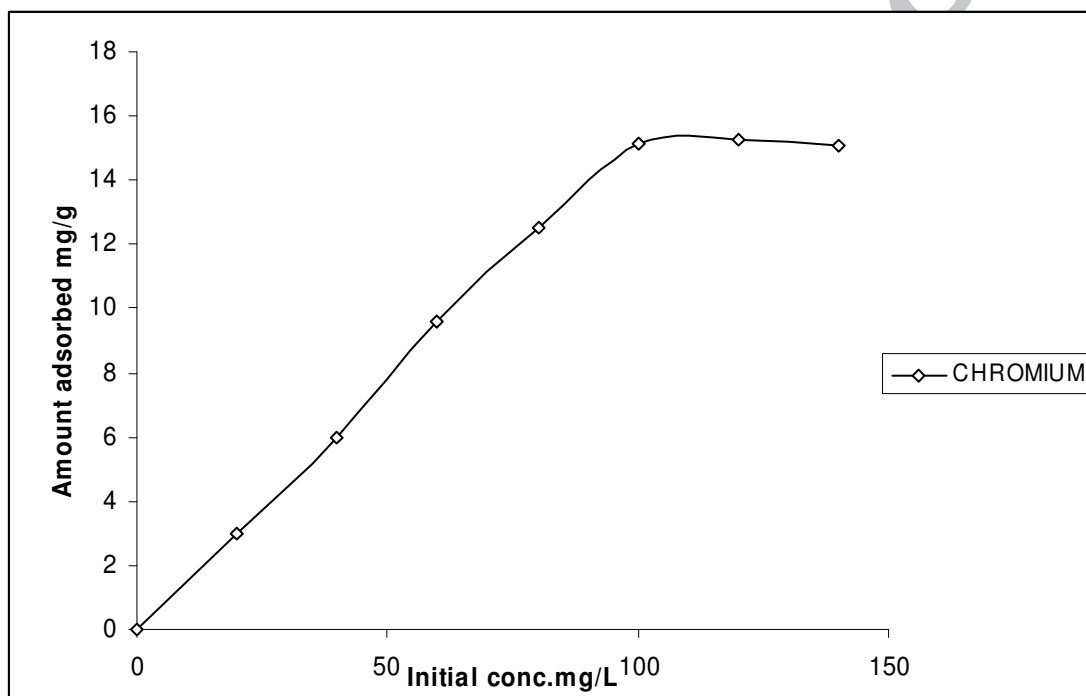


Fig. 7 Adsorption isotherms of chromium at different temperatures.

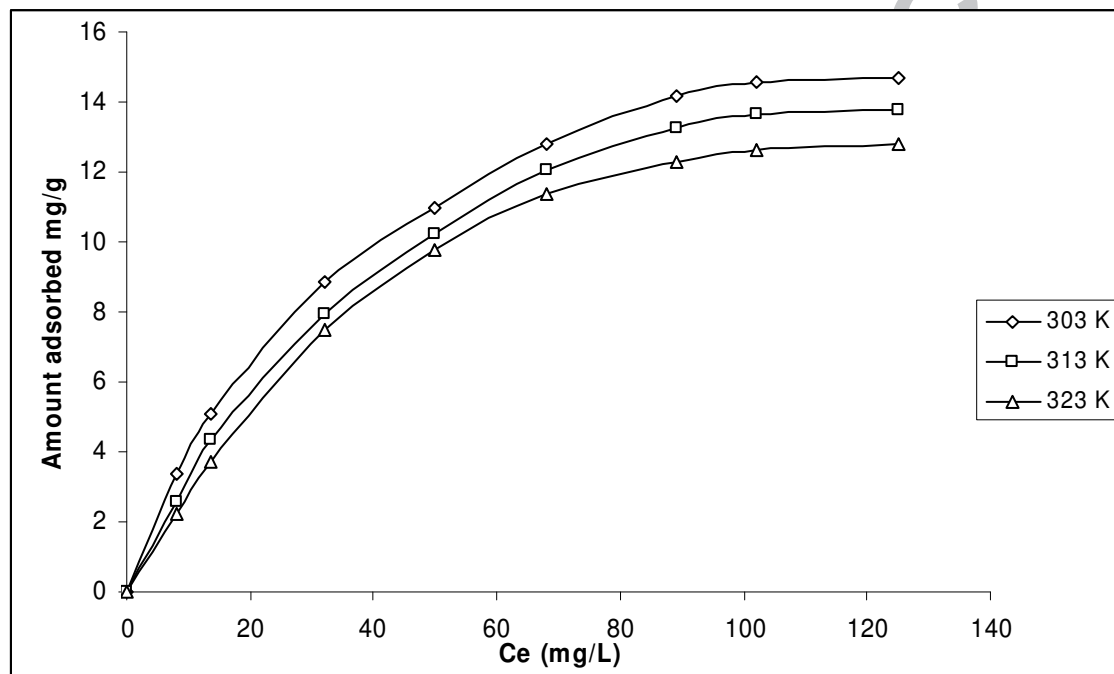


Fig. 8. Second-order kinetic modeling of Cr(VI) ions adsorption on carbon slurry.

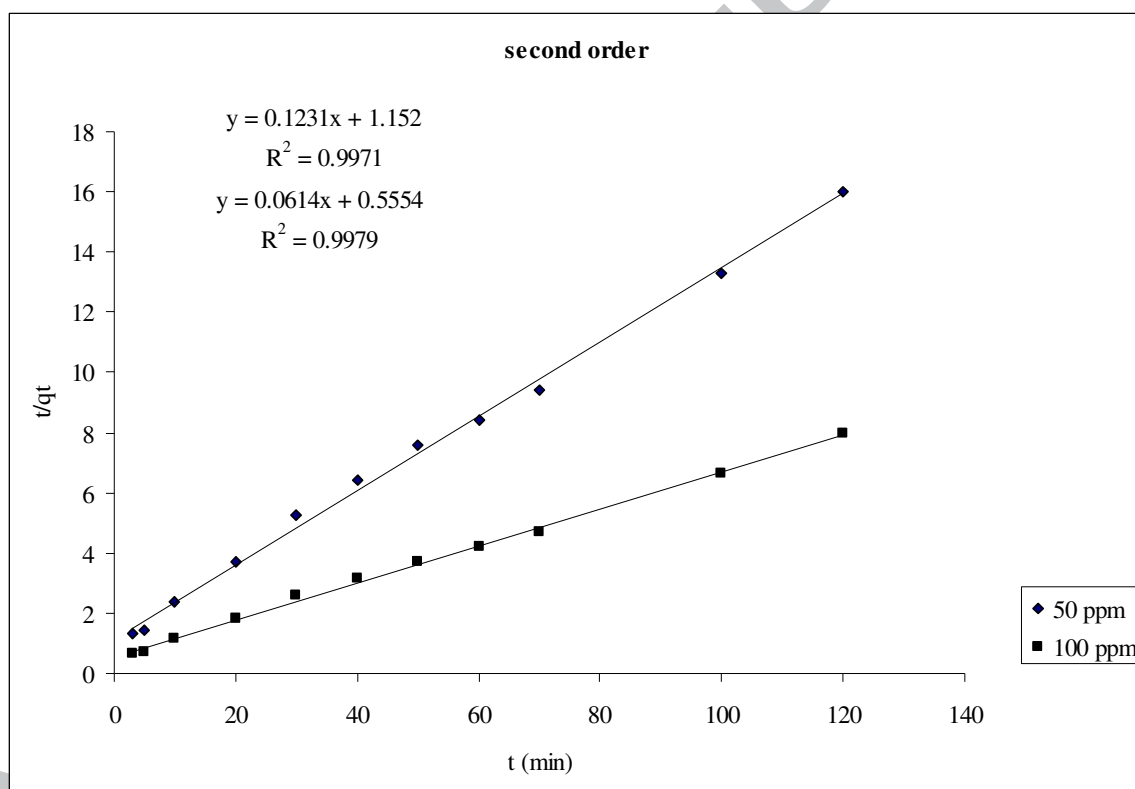
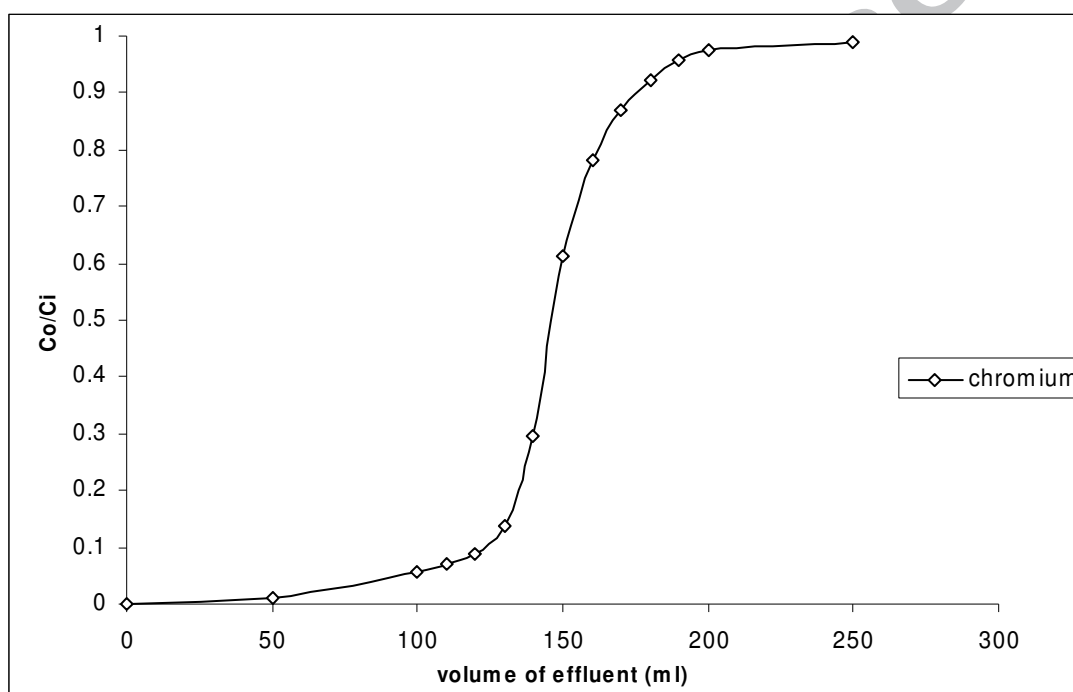
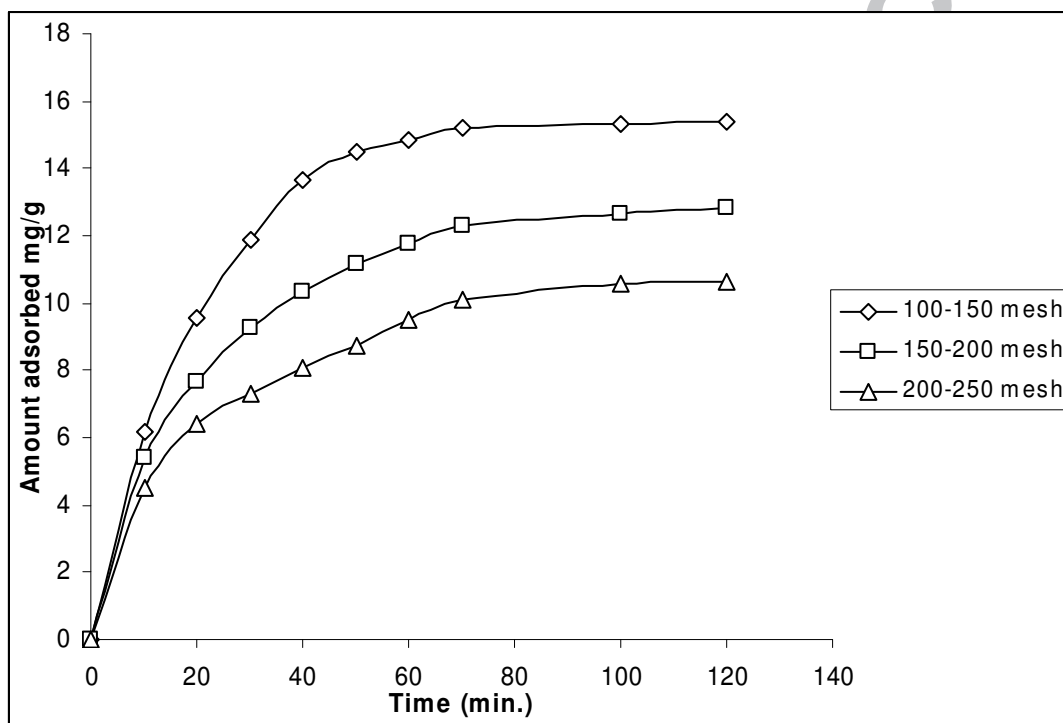


Fig 9. Breakthrough curve of Cr(VI) on activated carbon slurry.



Graphical abstract



Effect of particle size of the carbon slurry on the adsorption of Cr(VI)