

Treatment of Water Containing Chromium (VI) Using Rice Husk Carbon As a New Low Cost Adsorbent

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ABSTRACT: Presence of heavy metals in the aquatic systems has become a serious problem. As a result, there has been a great deal of attention given to new technologies for removal of heavy metal ions from contaminated waters. Adsorption is one of the effective methods for removal of toxic heavy metal such as chromium (VI). In the present study, adsorbent is prepared from rice husk, a low cost by product from a rice mill. The rice husk carbon is activated using H_3PO_4 (40%). The stock solution of Cr (VI) is prepared by dissolving 2.828 gm of potassium dichromate (Central Drug House (CDH), India) in 1 litre of demineralized water. Batch mode experiments are done. The effect of various parameters like adsorbent dose, pH and contact time are studied. The studies demonstrate that the Rice Husk Carbon (RHC) has a significant capacity for adsorption of Cr (VI) from aqueous solution. The RHC characteristics are reported as FTIR and other physical properties are tabulated average. The break through capacity for Cr (VI) (100 mg/l, pH 2) is on average 38.1 mg/g. The adsorption of chromium (VI) was found to be maximum (93-94%) at low values of pH (around 2) for the carbon dosage of 1000mg/L and nearly 100% for carbon dosage of 1200mg/L. RHC exhibits high degree of selectivity for Cr (VI) adsorption. The adsorbent prepared from rice husk carbon is efficient and it is proposed that it can be conveniently employed as a low cost alternative in the treatment of industrial waste water.

Key words: Adsorption Efficiency, Activated Carbon, Spectrum, Aqueous Solution, Carcinogen, Reduction, Electrostatic force

INTRODUCTION

Toxic metals are often discharged by a number of industrial processes and this can in turn lead to the contamination of fresh water and marine environment (Low *et al.*, 2000; Braukmann, 1990; Raji & Anirudhan, 1997; Yu *et al.*, 2011; Kargar *et al.*, 2012; Mzoughi and Chouba, 2012). Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater (Valdman *et al.*, 2001; Ghaderi *et al.*, 2012; Alimohammad Kalhori *et al.*, 2012; Ashraf *et al.*, 2012). Unlike organic pollutants, majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end products, and result in a number of environmental problems (Kalswain & Yu, 2001; Yan & Viraraghavan, 2001; Nasrabadi *et al.*, 2010; Haruna *et al.*, 2011; Serbaji *et al.*, 2012; Ogundiran *et al.*, 2012). Due to their non-biodegradability and persistence, metals can accumulate in the environment elements such as food chain and thus may pose a significant danger to human health (Yeti *et al.*, 1998; Kortenkamp *et al.*, 1996; Bakkaloglu *et al.*, 1998; Okuku and Peter, 2012; Mhadhbi *et al.*, 2012; Divis *et al.*, 2012). Chromium (VI)

compounds known as chromates and dichromates enter waters from many industrial processes such as electroplating, leather tanning, metal finishing, paints and pigments etc (Sharma, 2001; Hu *et al.*, 2003). Chromium (VI) is the most water soluble and easily enters the living cells. As determined by the National Toxicology Programme (NTP), the International Agency for Research on Cancer (IARC), Cr (VI) is a human carcinogen. It also causes skin irritation resulting in ulcer formation. Overexposure to Cr(VI) leads to liver damage, pulmonary congestion and oedema. Research on toxicological effect of chromium on water bodies concluded that high concentration of Cr(VI) in water is lethal to various fishes. Generally Cr (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, concentration, ion exchange, reverse osmosis, electrodialysis, solvent extraction and evaporation etc (Iqbal *et al.*, 2002; Dean *et al.*, 1972; Sengupta & Clifford, 1986; Geselbacht, 1996; Schnoor, 1997; Applegate, 1984). All these methods are very expensive and also not so effective.

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Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatment (Al-Ashesh *et al.*, 2000). Removal of heavy metals by adsorption is an emerging field of research (Sharma & Bhattacharya, 2004; Gupta & Babu, 2006). The process of adsorption has an edge over other methods due to its sludge free clean operation. Adsorption using activated carbon is an effective method for the treatment of wastewater rich in metals like Cr (Ouki *et al.*, 1997), Cd (Ramos *et al.*, 1997), Ni (Shim *et al.*, 2001), Cu (Monser & Adhoum, 2002). It completely removes them even from the dilute solutions (Huang & Wu, 1997). However cost is an important parameter when comparing the sorbent materials (Bailey *et al.*, 1999). Commercial activated carbons are very expensive, therefore various low cost new adsorbents are being studied by researchers which are suitable for water pollution control (Namashivayam *et al.*, 2001; Selvi *et al.*, 2001; Dakiky *et al.*, 2002; Demirkas *et al.*, 2004). The agricultural waste products are much widely being studied for their adsorption efficiency. These products are readily available and low in cost also. Research has been done on many materials like sugarcane bagasse (Homagaia *et al.*, 2010), plant waste (Ngah & Hanafiah, 2008), leaves (Horsfall & Vicente, 2007), pomegranate peel (El-Ashtoukhy *et al.*, 2008), rice hull (Wang and Lin, 2008), saw dust (Bulut & Tez, 2007), cotton seed (Srinivasan and Sathiya, 2009), tea leaves (Lavecchia *et al.*, 2010) etc. Coal and straw are inexpensive but ineffective. Peat moss has been found effective in adsorbing heavy metals. Coconut shell, crop milling waste and biomass also gave good results.

This work reported here deals with the adsorption studies on the activated carbon prepared from rice husk for the removal of chromium (VI) from aqueous solutions. Rice husk carbon is activated by H_3PO_4 and batch experiments are carried out for removal of Cr (VI) using activated adsorbent. The effect of various parameters such as adsorbent dosage, initial metal concentration and pH has been studied.

MATERIALS & METHODS

The adsorption studies required experiments which involve preparation of reagents and rice husk carbon. The stock solution of Cr(VI) was prepared by dissolving 2.828 gm of potassium dichromate (CDH, India) in 1 litre of demineralized water. All other reagents were of analytical grade. Rice husk was locally procured from a rice mill. The husk was washed with hot distilled water to remove water soluble impurities and dried in sun. Then it was impregnated with H_3PO_4 (40%) and carbonized at $450 \pm 20^\circ\text{C}$. For impregnation, the ratio of acid volume to weight of rice husk carbon was used as

2:1. This rice husk carbon was then washed with demineralized water and dried in a hot air at $100 \pm 50^\circ\text{C}$. Finally it was ground and sieved to 170 – 200 mesh before utilizing it as activated rice husk carbon.

Moisture content of the activated carbon was determined by heating a known weight of sample in hot air oven maintained at $105 \pm 5^\circ\text{C}$ for 4 hrs. Heating, cooling and weighing were repeated at 30 min interval until the constant weight was obtained. The difference in weights gave the amount of moisture content. After determining moisture content the same sample was ignited in muffle furnace at 1000°C for about 3 hrs. The process of heating and cooling was repeated until constant weight was obtained. Ash content was calculated by difference between initial and final weights. In order to determine the bulk density a 50 mL graduated cylinder was weighed accurately and filled to 50 mL mark with carbon and weighed again accurately. The difference gave weight of carbon. The density was then calculated by dividing the weight of carbon by 50. Accurately weighed carbon sample (5g) was transferred into 500 mL Pyrex glass beaker. About 100 mL of 4 mol/L HCl was added and heated to boiling temperature with continuous stirring. The material was then allowed to settle and the supernatant liquid was filtered through a Gooch crucible with an asbestos mat. The procedure was repeated thrice with the residue remaining in the beaker using 100 mL of 4 mol/L HCl each time. The combined filtrate was concentrated on a water bath upto about 50 mL volume, transferred to China dish, evaporated to dryness on a water bath and finally dried in hot air over at $105 \pm 5^\circ\text{C}$. This was cooled and weighed. The weight of residue represented the matter soluble in 4 mol/l HCl. The matter soluble in 2 mol/L NaOH was determined with the same procedure. Dried carbon (5g) was added to 100 mL of freshly boiled and cooled water (pH – 7) and heated to boiling. After digestion for 10 min the solution was filtered while hot and then cooled to room temperature. The pH was determined using the pH meter.

The characterization of activated carbon is followed by batch experiments and column studies and lastly process of column regeneration. Batch experiments are carried out in conical flasks with different amount of adsorbent and 100 mL of metal solution with various known concentrations (1-10 mg/100mL) at room temperature by agitating on a shaker with agitation speed of 120 rpm. At pre-defined time intervals the flasks are removed from the shaker, the contents are filtered using Whatman no. 4 filter paper and the filtrate is analyzed for Cr(VI) spectrophotometrically and Cr(III) was determined by subtracting Cr(VI) amount from total chromium estimated. Similar experiments were repeated at various

pH values (1.5-6) and for different amount of adsorbent (20-200mg/100mL) also. The effect of adsorbent dose and pH were studied at room temperature and concentration of Cr(VI) used in solution was 4.33mg/100mL. Adsorption studies have traditionally been used for investigation and fixing the operational parameters but in practice the final technical systems normally use column type operations. A glass column (i.d. 1.25 cm) was filled with 5gm of Rice Husk Carbon on a glass wool support. The weighed carbon was made into slurry with DMW and fed slowly into the column. The column was loaded with Cr(VI) solution (104 mg/L) which percolated downwards under gravity, at flow rate of ~ 5 mL/min. The operation of the column was stopped as Cr(VI) was detected in the effluent (Breakthrough Point). Column Regeneration is recovery of the adsorbate material as well as regeneration of adsorbent and is an important process in wastewater treatment. Chemical regeneration has been tried for the cyclic use of the column. 3 mol/L NH_4OH is used as the desorbing agent and the loss in column efficiency is made up by the treatment of the same with 4 mol/L HNO_3 . Column experiment is also done with chromium plating shop waste water to see the effect of other foreign components present in it.

RESULTS & DISCUSSION

The FTIR spectrum of RHC is given in Fig. 1. This shows characteristic peak of hydrogen bonded OH group ($3600 - 3400 \text{ cm}^{-1}$). The sharp peaks at 3000 and 2980 cm^{-1} represent C-H stretching vibration (aliphatic). The bands attributed to acidic HPO_4^{2-} are found at 2320 , 1105 , 1055 and 990 cm^{-1} . The peak at 690 cm^{-1} corresponds to P=O stretching and the peak at 1405 cm^{-1} may be assigned to the deformation vibration of P=OH .

The physico-chemical characteristics of rice husk carbon are summarized in Table 1. This shows that rice husk carbon is fairly stable in HCl upto 4 mol/L and in NaOH upto 2 mol/L. The experiments were conducted to check reduction of Cr(VI) to Cr (III). The uptake of chromium (VI) at different pH of solution (3, 2, 1.5) was studied and also the effect of different carbon dosage was studied. The results showing these effects are plotted in Fig. 2 and these reveal that the adsorption of Cr (VI) on rice husk carbon increases with the decreased pH of the solution. It is evident from the plots that optimum pH is 2.0. Improved adsorption at low pH may be explained on the basis of assumption that the large number of H^+ ions present in solution at low pH can neutralize the negatively charged rice husk carbon surface or convert the neutral groups to the positively charged groups. Hence high degree of adsorption of Cr(VI) may be attributed due to the electrostatic force of attraction between the adsorbent and adsorbate. The effect of adsorbent dose was that the increase in adsorbent amount results in the increase in percent removal of the metal. This can be explained by the fact that increased amount of adsorbent provided larger surface area for adsorption of the metal. The amount of adsorbent required for complete removal of Cr(VI) at optimum pH is 1200 mg/L. Similar pH effects are reported for other carbon materials (Srivastava *et al.*, 1989). The adsorption of metal also increases with the increasing contact time but the rate of adsorption becomes low with time due to the continuously reducing surface area available for the adsorption. The percentage removal of chromium nearly becomes constant (93-94%) after 3 hours for an initial concentration of 43.3mg/L and adsorbent dose of 1g/L (Fig. 4). The study of varying concentration of metal in solution show that the rate of adsorption increases with the higher concentration of metal but the

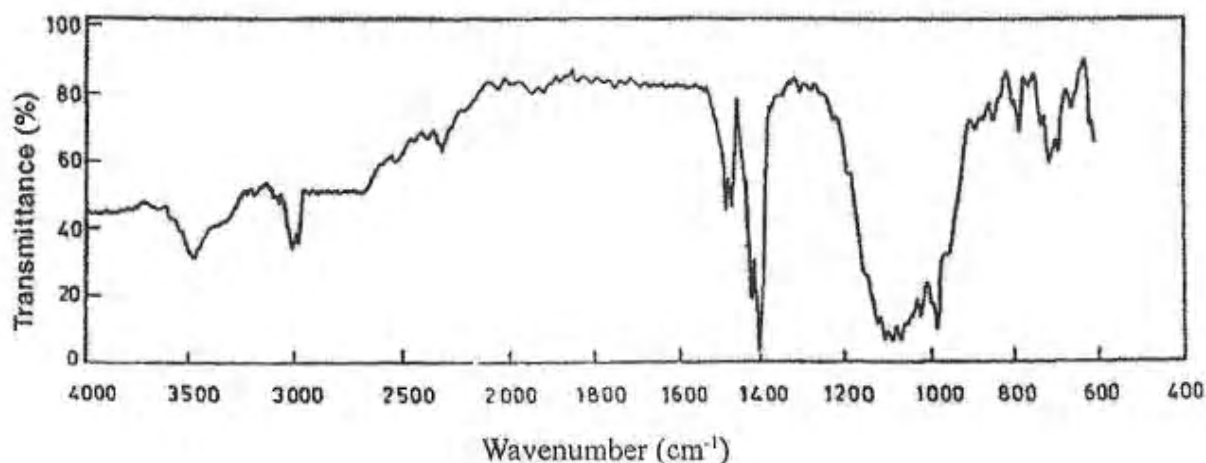
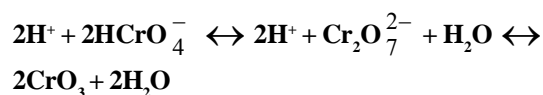


Fig. 1. FTIR Spectrum of RHC Using KBr Disc Method

percentage removed decreased with increasing metal concentration. The experiments revealed that adsorption capacities increased upto 5×10^{-3} mol/L adsorbate concentration and then becomes constant. The amount of reduction of Cr (VI) into Cr (III) when equilibrated over the pH range 1.5 – 3.0 is plotted in Fig. 3 for various carbon dosage. The results show that the conversion into Cr (III) was upto the extent of 12% over the pH range 2.0 – 3.0. At pH less than 2.0, Cr (III) was found to increase steadily while at pH > 3.0, it was negligible. Sigworth and Smith have proposed the possibility of heavy metal precipitation on the carbon surface by nucleation as one of the pathways for heavy metal removal by activated carbon (Sigworth & Smith, 1972).

An equation describing the phenomenon of proton and Cr (VI) interaction with rice husk carbon may be presented as :



Similar reactions have been reported on filtrasorb 400 activated carbon. This may eventually lead to the reduction of chromium as a result of oxidation of carbon by chromic acid. The present investigations are in agreement with low pH conditions. The results of column experiment, performed at pH 2 and 2.5 (Table 2) show that breakthrough capacity of the adsorbent is higher at lower pH (2) and is equal to 39.3 mg/g. Attempts have been made to recover the adsorbed metal as well as to regenerate the adsorbent. 3 mol/L NH_4OH is an important desorbing agent for Cr (VI). The average recovery of Cr(VI) was found 85%. The data of chemical characteristics of chromium plating shop waste effluent are given in Table 3.

Table 1. Physicochemical Characteristics of Rice Husk Carbon

S.No.	Characteristics	Values
1	Bulk Density (g/mL)	0.68
2	Surface Area (m/g)	105.42
3	Pore Volume (mL/g)	0.12
4	Average Particle Size, microns	81
5	Moisture Content (%)	13.82
6	Ash Content	38.02
7	Matter Soluble in water (%)	Nil
8	Matter Soluble in 4 mol/l HCl(%)	Nil
9	Matter Soluble in 2 mol/l NaOH(%)	Nil
10	pH	6.5

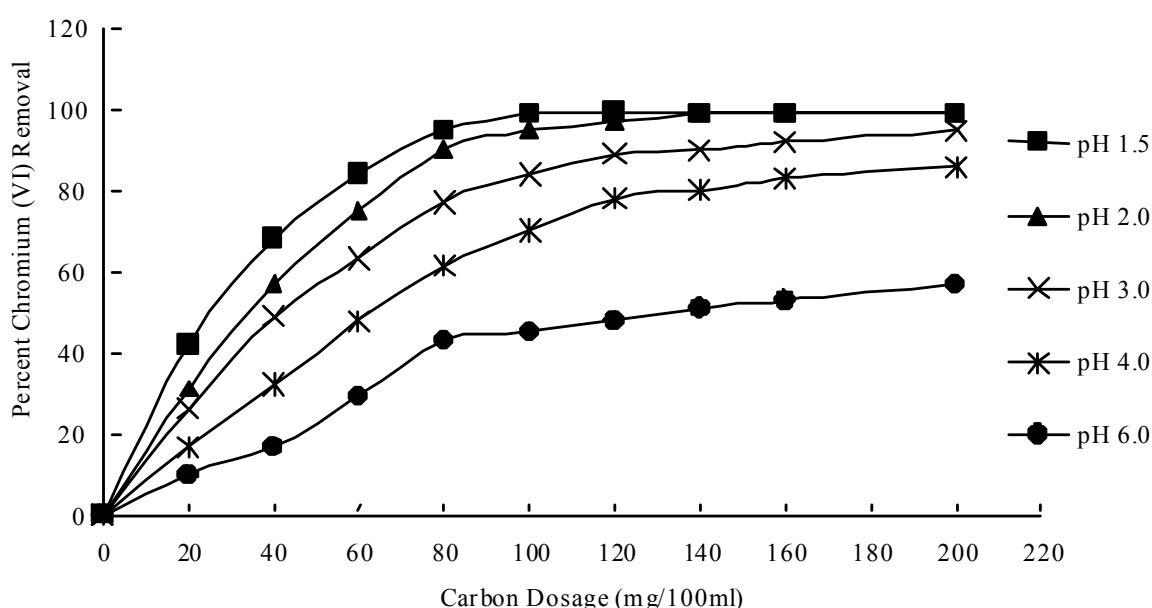


Fig. 2. Chromium (VI) removal as a function of carbon dosage and pH

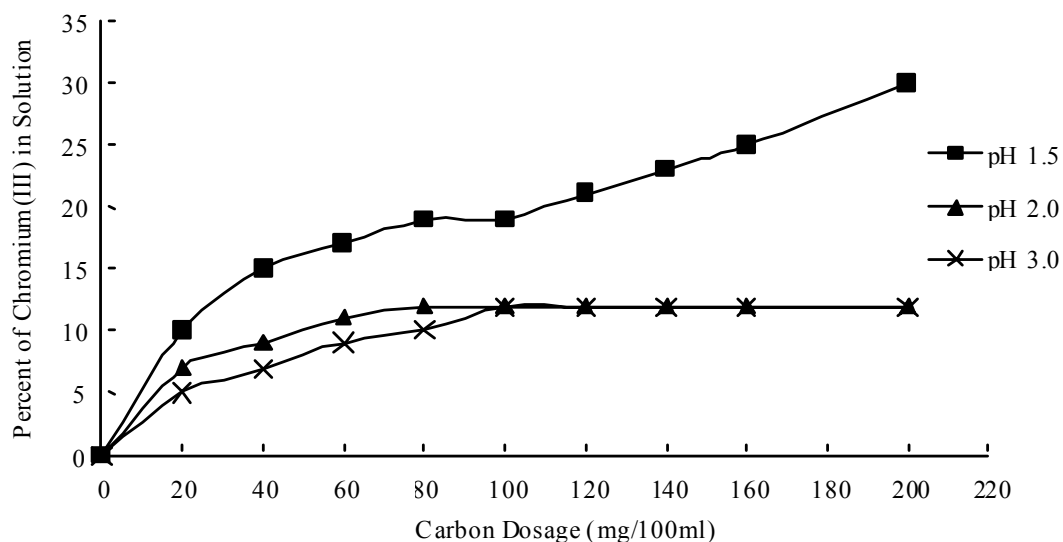


Fig. 3. Chromium (VI) reduction as a function of a pH and carbon dosage

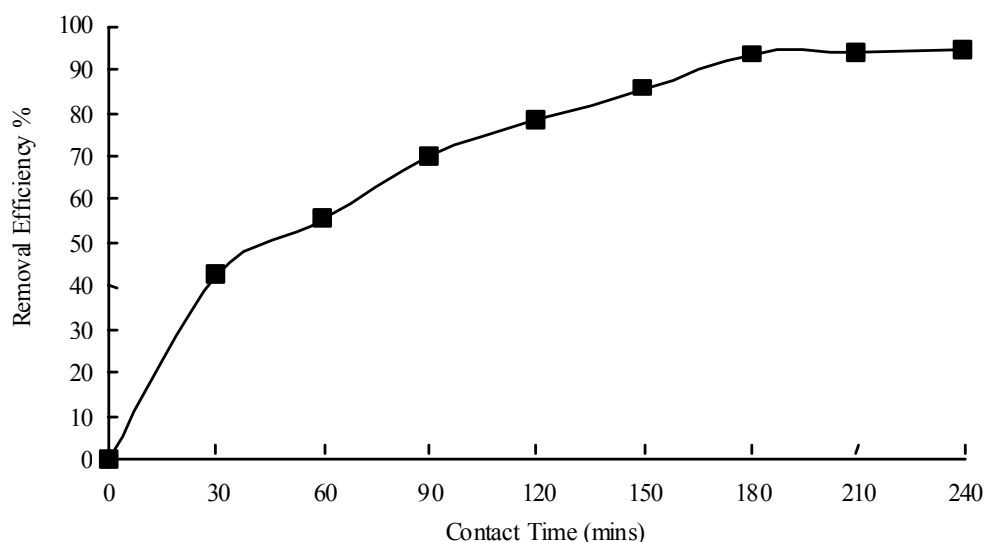


Fig. 4. Effect of contact time on removal of Chromium ions at pH 2.0

Table 2. Chemical Characteristics of Chromium Plating Shop Waste Effluents

S.No.	Characteristics	Values(mg/l)
1	Chromium (VI)	360
2	Chromium (III)	12
3	Iron	6
4	Sulphates	260
5	pH	2.5

Table 3. Break Through Capacity and Recovery of Cr(VI) on RHC Column

S.No.	Sample	Cr(VI) mg/L	pH	BTC mg/g	% Recovery
1	Water	104	2	39.3	85.1
2	Water	104	2.5	38.5	-
3	Chromium plating shop waste effluent	360	2.5	37.2	76.8

The results of break through capacity and recovery of Cr (VI) using rice husk carbon column from water and chromium plating shop waste effluents are presented in Table 3.

The loss in adsorption efficiency of the column is made up by the treatment of the same with 4 mol/L HNO_3 . This stores almost 90% adsorption efficiency of RHC. For synthetic aqueous solutions of Cr (VI) (100 mg/L, pH 2) a column of RHC could be used for five cycles with average breakthrough capacity of 32.1 mg/g. The utilities of the material have been demonstrated by treating this wastewater with composition given in Table 2. The break through capacity observed (Table 3) shows that the presence of sulphate and other foreign ions has negligible effect on the removal efficiency for Cr(VI). This shows the greater selectivity of Cr (VI) at acidic pH. The rice husk by-product of rice mill has been converted into carbonaceous adsorbent material. Cr(VI) ions are treated by both adsorption on RHC and reduction to Cr(III) in the low pH conditions. Reduction does not remove chromium from the aqueous media and only converts it to Cr(III), but by adsorption it is being removed from the solution and that too more effectively as compared to reduction. Hence adsorption is the main treatment process for the waste waters. Some of the Cr(III) ions are also adsorbed by RHC. However Cr(VI) ions are preferentially adsorbed on RHC. RHC exhibits exceptionally high degree of selectivity for Cr(VI) adsorption.

CONCLUSION

This study highlights that the rice husk carbon can be used as a low cost adsorbent alternative for heavy metal removal from waste waters. It shows great capacity for adsorption and is highly efficient. The percentage removal of chromium is high with increasing contact time and the equilibrium time is nearly 3 hours. The percent removal of metal also increases with increased adsorbent dose as evident from the experiments that an adsorbent dose of 1200mg/L completely removes the chromium. As the rice husk is easily available and is also cost effective so it can be used in little greater amounts to obtain complete removal of Cr(VI). Also as RHC reduces Cr(VI) to Cr(III) at lower pH values, so even if Cr(VI) is not completely removed, most of it is converted to Cr(III) which is a non-toxic form of chromium and not so harmful. The adsorption of Cr(VI) is also affected much by the variation in pH of the solution and is found that the maximum adsorption of Cr(VI) occur in pH range 1-2.

The Breakthrough capacity determination shows that the presence of other foreign ions has negligible effect on the adsorption capacity of RHC for the

removal of Cr(VI). This shows the greatest selectivity of Cr(VI) at acidic pH. Thus RHC can be utilized for the treatment of industrial waste effluents containing Cr(VI).

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