

Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: A comparative study

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Abstract

Two low cost adsorbents were prepared by using groundnut husk and were tested for the removal of chromium. All the experiments were carried out in batch process with chromium spiked samples of drinking water. Silver impregnated groundnut husk carbon and groundnut husk carbon were tested for the removal of chromium(VI). Effects of adsorbent quantity, pH, contact time and agitation rate were investigated on removal of chromium. The adsorption data were fitted well by Freundlich adsorption isotherm. Approximately, 97% of hexavalent chromium was removed at pH 3 within 5 h. It was found that adsorbents chemically modified with an oxidizing agent demonstrated better chromium removal capabilities as compared to pure adsorbents in terms of their adsorption rate. On the basis of present studies, it can be concluded that groundnut husk carbon oxidized with silver treatment, has a higher chromium adsorption capacities.

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1. Introduction

At least 20 metals are classified as toxic and half of these emitted into the environment in higher quantities that pose risks to human health [1]. Chromium has both beneficial and detrimental properties. In the environment chromium occurs mainly in the oxidation states (III) and (VI), which have contrasting toxicities, mobilities and bioavailabilities. Whereas Cr(III) is essential in human nutrition (specially in glucose metabolism) as well as for plants and animals at trace concentrations. It is relatively innocuous and immobile a Cr(VI) compounds. Cr(VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [25]. In recent years, due to the extensive use of chromium in industrial processes (such as electroplating, leather tanning, cement preservations, paints and pigments, textile, steel fabrication and canning industries), large quantity of it are discharged into the environment, leading to serious problems and hazardous risks for human health. These industries produce large quantities of

toxic wastewater effluents [26]. The maximum concentration limit for chromium(VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L.

A wide range of physical and chemical processes is available for the removal of Cr(VI) from drinking water, such as electrochemical precipitation, ultrafiltration, ion exchange and reverse osmosis [2,22,33]. A major drawback with precipitation is sludge production. Ion exchange is considered a better alternative technique for such a purpose. However, it is not economically appealing because of high operational cost. There are several adsorbents mentioned which can remove chromium from drinking water [3,4,27,32,5,29,30].

Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly [23]. Groundnut has enormous amount of agricultural waste. Preliminary studies have shown that it is feasible to prepare chars with sufficient densities and high porosity from groundnut husk [6]. The exchange/sorption properties of groundnut husk are due to presence of some functional groups, such as carboxylic, hydroxyl, etc., which have high affinity for metal ions [4]. In recent years, development of surface modified activated carbon has generated a diversity of activated carbon with far suspension adsorption

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capacity. The use of groundnut husk with surface modification by silver impregnation to improve its metal removal performance would add its economic value. It helps to reduce the cost of waste disposal and most importantly would provide a potentially inexpensive alternative to existing commercial activated carbon. Adsorption using commercial activated carbon (CAC) can remove heavy metals from water, such as Cd [28]; Cr [7]; Cu [24]; Ni [8]. However, CAC remains an expensive material for heavy metal removal. Since the carbon derivatives from different material sources are different in nature. The present study was carried out with respect to the inexpensive groundnut husk carbon in the removal of Cr(VI) from drinking water.

2. Material and method

2.1. Carbonization of groundnut husk and silver impregnation

Groundnut husk is a suitable raw material for making high quality activated carbon because of their inherent high densities and carbon contents. Groundnut husk was dried at 105 °C for 24 h to reduce the moisture content. Activated carbon was prepared by treating the groundnut husk with concentrated sulfuric acid in 4:3 ratio [6] and kept in an air oven maintained over the temperature 150–155 °C for a period of 24 h. This carbonized material was well washed several time with distilled water to remove the free acid and dried at 100 °C. After crushing and grinding it was sieved to obtain average particles of 100-mesh size (British Standard Sieve). Fifty grams of groundnut husk carbon was taken in a 250-mL beaker and 0.5 g of silver nitrate added. Slurry was prepared with 2N HCl solution, kept at room temperature for drying and used for Cr removal.

2.2. Scanning electron microscope of the adsorbents

The scanning electron microscope pictures of unimpregnated and silver impregnated groundnut husk carbon are shown in Figs. 1 and 2. In Fig. 2, apart from modified surface area of adsorbent

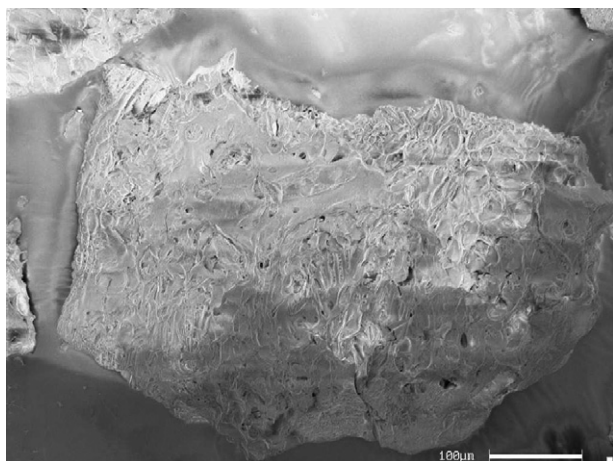


Fig. 1. Scanning electron microscope of GNH.

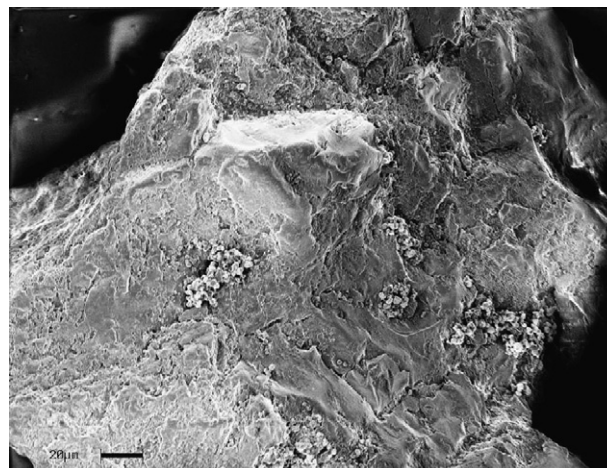


Fig. 2. Scanning electron microscope of SIGNH.

small particles of the precipitate adhering on the surface was seen. Probably these are particles of Ag₂O. These particles are not seen in the unimpregnated groundnut husk carbon (Fig. 1).

2.3. Batch equilibrium experiment

Spiked water sample to be used for the investigation was prepared by dissolving a known amount of potassium dichromate in a known volume of distilled water, in order to avoid the interference with other elements. Ten parts per million of standard chromium solution was prepared from the 1000 ppm stock solution and taken separately in a conical flask. Known quantities of the adsorbents were added to the water. Shaking (at 200 rpm) the contents of the flask at room temperature (30 °C) equilibrated the system, so that adequate contact time between adsorbent and the metal ion was obtained. The suspension was filtered after a regular interval of time through Whatman No. 40 filter paper and the filtrate was analyzed to evaluate the concentration of Cr(VI) metal in the treated water. All the analyses were performed according to standard method [9]. Metal analysis was carried out by using AAS.

2.3.1. Chromium analysis

Batch sorption studies were performed to obtain rate and equilibrium data due to their simplicity. Several operational parameters, such as pH, adsorbent doses, temperature, agitation speed and contact time were investigated.

The results were expressed as the removal efficiency (*E*) of the adsorbent on Cr, which was defined as:

$$E (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where *C*₀ and *C*_e are the initial and equilibrium concentrations (mg/L) of Cr(VI) in solution. The chromium ion concentration was determined by atomic absorption spectrophotometer methods.

2.3.2. Adsorption isotherm

To examine the relationship between sorbed (q_e) and the aqueous concentration C_e at equilibrium sorption isotherm models are widely employed, for fitting the data, of which the Langmuir and Freundlich equations are most widely used. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.

The equilibrium data will be get by varying the initial chromium concentration, while the other parameters are kept constant. Five hours of equilibrium periods for sorption experiments were used to ensure equilibrium condition. The Langmuir model takes the form:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (\text{non-linear form}) \quad (2)$$

where q_e (mg/g) is the amount of metal ions adsorbed onto the unit mass of the adsorbent to form a complete monolayer on the surface, C_e the solution phase metal ion concentration, K_L the Langmuir equilibrium constant which is related to the affinity of binding sites and a_L is the Langmuir constant [10]. The constants a_L and K_L are the characteristics of the Langmuir equation. The linearized form of the Langmuir equation can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (\text{linear form}) \quad (3)$$

Therefore, plot of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$. The constant a_L/K_L is the monolayer adsorption capacity. On the other hand, the Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm equation, which is based on adsorption on a heterogeneous surface. The equation can be written as:

$$q_e = a C_e^b \quad (\text{non-linear form}) \quad (4)$$

where q_e is the adsorption density (mg adsorbate/g adsorbent), C_e the concentration of adsorbate in solution (mg/L) and a and b are the empirical constants. This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\ln q_e = b \ln C_e + \ln a \quad (\text{linear form}) \quad (5)$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ enables the constant a and exponent b to be determined. The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Cr by each adsorbent over the entire concentration range studied. The plot of C_e/q_e versus C_e showed that the experimental data reasonably well fitted the linearized equation of the Langmuir isotherm over the whole concentration range studied. Linear plots of $\ln q_e$ versus $\ln C_e$ showed that the Freundlich isotherm was also representative for the Cr adsorption by both types of adsorbent tested.

3. Results and discussion

3.1. Effect of adsorbent doses on removal efficiency

Keeping other parameters (pH, agitation rate and contact time) constant, the dependence of Cr removal was studied by

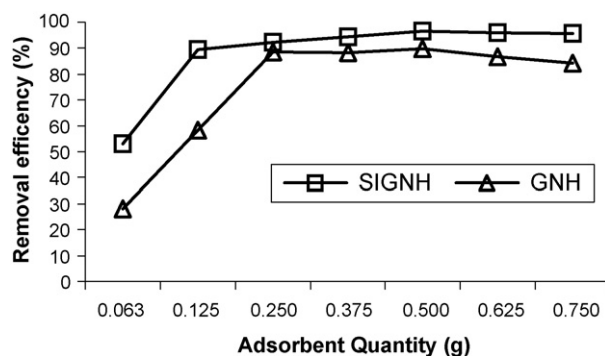


Fig. 3. Effect of adsorbent quantity on removal efficiency.

varying the amount of adsorbents from 0.0625 to 0.75 g/100 mL. Fig. 3 presents the removal efficiency of both the two types of adsorbents used. It can be observed that removal efficiency of the adsorbents generally increased with increasing the quantity. It is due to the fact that the availability of exchangeable sites for the ions. Both of them showed no further increase in adsorption after a certain amount of adsorbent was added (0.0625–0.5 g/100 mL). At 10 ppm concentration of Cr(VI), the maximum removal was about 96.6% for SIGNH, while for GNH it was 89.7% at doses of 0.5 g/100 mL. It is interesting to note that the saturated values of Cr(VI) removal efficiency of the two types of adsorbents are different from one another due to extent of surface modification. Hexavalent chromium and some other metals, such as arsenic, depending upon the pH, are known to exist as anions.

3.2. Effect of pH on removal efficiency

The pH value of the solution is an important factor that controls the sorption of Cr(VI). Fig. 4 shows the extent of removal of Cr(VI) as a function of pH, and it shows that at lower pH, the Cr(VI) removal efficiency was higher and at higher pH the removal reduced considerably. With increase in pH the amount of Cr(VI) removal increased with the optimum achieved at pH 3 and thereafter a plateau was seen. One of the reason for the better adsorption capacity observed at low pH values may be attributed to the large number of H^+ ions present at these pH values, which in turn neutralize the negatively charged hydroxyl groups ($-OH$) ions causing increasing hindrance to diffusion of positively charged dichromate ions. The adsorption of Cr(VI)

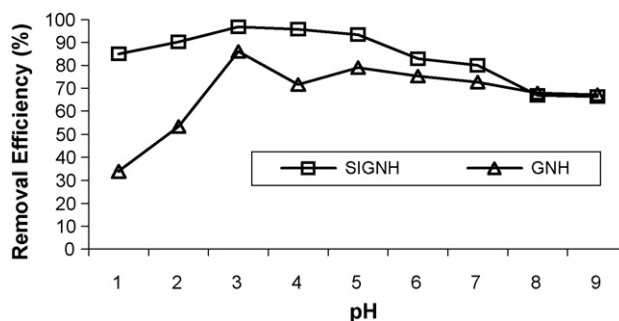


Fig. 4. Effect of pH on removal efficiency.

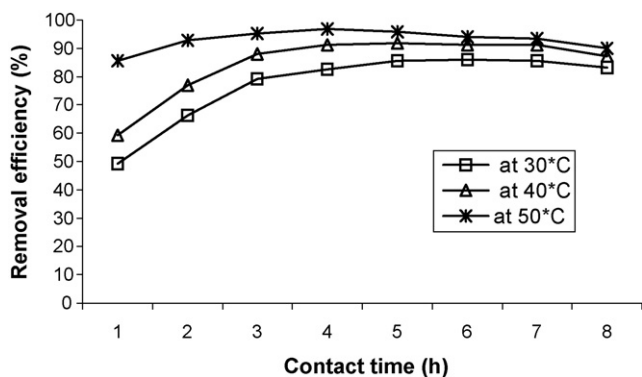
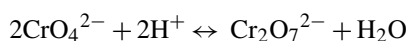


Fig. 5. Effect of contact time and temperature on removal efficiency for SIGNH.

on carbonaceous material developed from the wastes generated in a fertilizer plant was found to be greatest at pH values 1–3 as observed in the present study. Above pH 8, only CrO_4^{2-} is stable, and as the pH decreases into the pH region 3–5 the equilibrium shifts to dichromate according to the overall equilibrium.



At still lower pH values $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ species are formed. In summary, decreasing of the pH results in the formation of more polymerized chromium oxide species. At the pH of highest sorption efficiency, the dominant species were HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$.

3.3. Effect of contact time on removal efficiency

Results (Figs. 5 and 6) indicate that removal efficiency increased with an increase in contact time before equilibrium is reached. Other parameters such as quantity of adsorbent, pH of solution and agitation speed was kept constant, while at different temperature, there was an increase in removal efficiency, hence the reaction is endothermic in nature. It can be seen that Cr(VI) removal efficiency of SIGNH increased from 50 to 90% when contact time was increased from 1 to 5 h. For both SIGNH and GNH the contact time of 5 h was needed to establish the equilibrium.

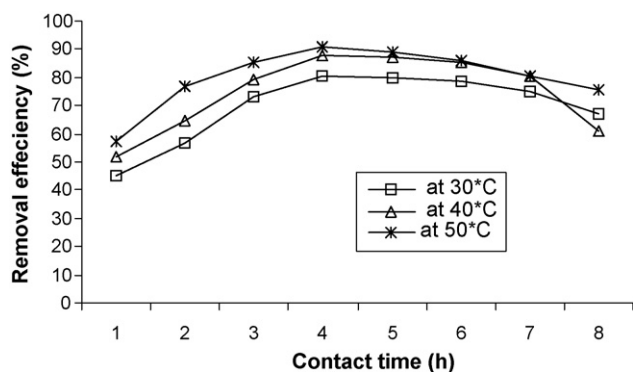


Fig. 6. Effect of contact time and temperature on removal efficiency for GNH.

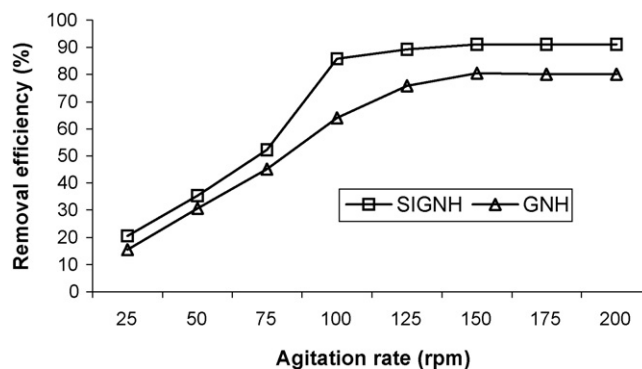


Fig. 7. Effect of agitation speed on removal efficiency.

3.4. Effect of agitation rate on removal efficiency

Agitation rate is varied from 25 to 200 rpm while keeping other parameters constant. Results (Fig. 7) indicate that removal efficiency generally increased with increasing agitation rate. The Cr(VI) removal efficiency of SIGNH adsorbent increased from 20 to 90% when agitation rate increased from 25 to 150 rpm and the removal efficiency remained constant for agitation rate greater than 150 rpm. It is due to the fact that the increase of the agitation rate, improves the diffusion of the chromium ions towards the surface of the adsorbents and a shaking speed in the range of 100–200 rpm is sufficient to assure the surface binding for chromium uptake.

3.5. Effect of concentration on removal efficiency

The adsorption isotherm data will be get by varying the initial chromium concentration, while the other parameters are kept constant. In this study, however, Freundlich isotherm has a better fitting model than the Langmuir as the former have higher correlation regression coefficient than the latter (Table 1), thus indicating to the applicability of a heterogeneous coverage of the Cr on the surface of adsorbent.

Using Langmuir isotherm, the equilibrium data yielded the ultimate adsorption capacity value for the silver impregnated groundnut husk carbon is 11.4 mg/g. This adsorption capacity is considerably higher compared to values obtained with groundnut husk carbon 7.0 mg/g.

3.6. Comparison of the present study with other adsorbents

Our study showed that both silver impregnated groundnut husk carbon and groundnut husk carbon demonstrated better removal capacities for Cr(VI) (11.4 and 7.0 mg/g), respectively, as compared to the reports of other adsorbents (Table 2).

Table 1

Isotherm model constants and correlation coefficients for adsorption of chromium ions

Type of adsorbent	Langmuir			Freundlich		
	a_L/K_L	K_L	R^2	a	b	R^2
Silver impregnated GNH	11.4	0.71	0.91	0.70	0.69	0.99
GNH	7.01	0.33	0.64	3.60	0.83	0.96

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