Adsorption of Cr (Vi) from Aqueous Solution using Black Gram Husk Modified Nanoparticle

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Abstract

The presence of hexavalent chromium in wastewater is a potential hazard to aquatic flora, fauna and humans. Thus, for its removal a novel magnetic nano-adsorbent (MNPBGH) was successfully developed by co-precipitating Fe_3O_4 nanoparticles with an agricultural waste-black gram husk. Modification of Fe_3O_4 surface did not result in phase change but result only in increased diameter. The porous nature of magnetic nanoparticle modified with black gram husk (MNPBGH) exhibited high surface area to volume ratio because of the presence of plentiful interparticle spaces or pores as evident from its SEM analysis. The MNPBGH nano-adsorbent was tested for the treatment of synthetic aqueous solution contaminated with Cr(VI) ions. Batch studies results revealed pH dependency of the adsorption process and the adsorption capacity increased with increase in contact time and with that of initial concentration of Cr(VI) ions while decreased at higher MNPBGH dosage. It was found that the Cr(VI) adsorption increases by increasing temperature from 298 to 308 K and the process is endothermic in nature. The adsorption data followed Langmuir isotherm equation and the maximum adsorption capacity was found to be 215.27 mg g^{-1}. Also fixed-bed column studies were carried out by MNPBGH and influence of various operating parameters like bed depth, feed flow rate and inlet Cr(VI) concentration were tested. The column results revealed increased exhaustion time with increase of bed depth, decrease of flow rate and influent Cr(VI) ion concentrations. The used adsorbent bed in the column had been regenerated and reused consecutively, and the results demonstrated that the developed MNPBGH was suitable for Cr(VI) removal from aqueous solution using batch as well as fixed bed adsorption system.

Keywords: *Magnetic nanoadsorbent, Adsorption, Endothermic, Langmuir, Column*

Water is a limited natural resource and fundamental for the survival of all the life form and also for the good health. With the growth of industrialization and urbanization, the world is reaching to new horizons at the cost of our environment. Definitely the cost which is being paid or will be paid in the near future is surely going to be too high. The most serious drawback of this non-rational growth and development is in the form of environmental disorder with a big pollution problem that has been translated to a critical aspect [1]. Different types of compounds in the form of pollutants get accumulated in the water during its use and become wastewater. The frequently found pollutants are heavy metals (chromium, copper, cadmium, nickel, lead, etc.), organic compounds

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(hydrocarbons, dye, solvents, fertilizers, pesticides, etc.) and chemical products (chemical industries effluents) and these pollutants get mixed in the water body without proper treatment and removal. Among all these pollutants, chromium, a highly reactive metal, is widely used in electroplating, leather tanning, metal finishing and textile industries [2]. Usually, industrial effluents contains both hexavalent and trivalent forms of chromium, however, Cr(VI) is more hazardous to biological activities. Cr(VI) compounds are carcinogenic and corrosive on tissue and long-term exposure causes nausea, skin sensitization, ulceration and kidney damage [3]. Therefore, wastewater contaminated with chromium is unfit for the health. Hence, water pollution with these toxic compounds is one of the major concerns for human health as well as for the environmental quality. Chromium pollution can have an immediate (acute) or a chronic (long term toxicity) impact on the environment. Various techniques have been employed for the removal of chromium from wastewater, which usually include reduction, microfiltration, reverse osmosis, evaporation, ion exchange, precipitation, membrane separation, electrochemical processes, floatation etc. However, these techniques are expensive, not environment friendly, produce residual metal sludge with disposal problem and usually dependent on the concentration of the waste in the water. Therefore, the search for efficient, eco-friendly and cost-effective remedies for wastewater treatment has been initiated. These days, employing environmentally-friendly methods for treatment of wastewater is emphasized much more. Application of some waste products that could help in this regard, in addition to reuse of these waste materials can be an advantage. Several low-cost adsorbents such as bark remnants of Eucalyptus and *Cassia fistula* [4], coconut shell derived activated carbon [5], rice straw [6], saw dust [7], *Lagerstroemia speciosa* bark [8], *Phaseolus vulgaris* husk [9], banana peel [10], orange peel waste [11], etc. have been used previously for the removal of Cr(VI) from aqueous solutions and industrial wastes

at solid-solution interfaces. Also researchers pay attention on the synthesis and utilization of nanoadsorbent for the treatment of Cr(VI) contaminated wastewater. The aim of the present research is to explore the feasibility of utilizing black gram husk waste as a single use and low cost filter for Cr(VI) removal from the aqueous solution. The study is undertaken for the better application and management of such a low cost and valuable agriculture biomass for useful purpose. Literature review shows that any research on black gram husk modified magnetic nanoparticle have not been reported before. The present paper reports preparation of synthesis of black gram husk modified magnetic nanoparticles as low cost active adsorbent and its effectiveness in removing Cr(VI) ions from aqueous solution at various conditions of batch process. The performance of developed adsorbents in fixed bed column process is also studied.
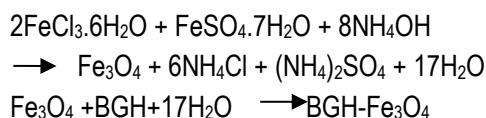
Materials and methods

2.1. Reagents
All the chemicals including potassium dichromate ($K_2Cr_2O_7$), diphenylcarbazide (DPC), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH), ferric chloride ($FeCl_3.6H_2O$), ferrous sulphate ($FeSO_4.7H_2O$), and ammonium hydroxide (NH_4OH) were purchased from SDFCL, India and used without further purification. $K_2Cr_2O_7$ stock solution was prepared by dissolving appropriate quantity of chemical in double distilled water (DDW). All working solutions were prepared by diluting the stock solution with DDW as per requirement in the adsorption process.

2.2. Preparation of adsorbent
The black gram husk (BGH) was washed firstly with tap water and then after DDW for to remove all the dust particles adhered on the surface of the BGH. The washed material was dried in an air oven at 100 °C for 24 h. the dried materials were crushed into powdered form with very fine particle. MNPBGH was

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synthesized chemical precipitation technique with homogeneous composition and narrow size distribution [12]. This technique is probably the most efficient and common method for the synthesis of magnetic nanoparticles. A complete precipitation of Fe_3O_4 was achieved under alkaline condition, while maintaining a molar ratio of Fe^{2+} to Fe^{3+}, 1:2 at 80 °C, under inert atmosphere. After ensuring the complete growth of the nanoparticle crystals, the black colored solution was then added to 10 g of BGH and reaction was carried out for 30 min while maintaining 80 °C temperature under constant stirring. After completion of reaction, the resultant suspension was cooled down to room temperature and then repeatedly washed with DDW till the solution pH becomes neutral. The reactions that occur during production of MNPBGH are as follows:

$2FeCl_3.6H_2O + FeSO_4.7H_2O + 8NH_4OH$

$\longrightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 17H_2O$

$Fe_3O_4 + BGH + 17H_2O \longrightarrow BGH\text{-}Fe_3O_4$

2.3. Detection of hexavalent chromium ion in the aqueous medium

The Cr(VI) ion concentration in the aqueous medium was measured by colorimetric method. A freshly prepared solution of 1,5 diphenylcarbazide in acidic condition produces pink colored complex, which can be analyzed spectrophotometrically at 540 nm (Elico SL210 Vis spectrophotometer).

2.4. Batch studies

All the glassware's used for the adsorption study was washed in 10% (v/v) nitric acid and subsequently rinsed with DDW to remove and avoid any possible interference by other metals. In all sets of experiments a fixed volume of Cr(VI) solution was thoroughly mixed with the desired biosorbent dose (0.05, 0.1, 0.2, 0.3, 0.4, 0.5 (mg/100mL), pH (1, 2, 3, 4, 5, 6, 7, 8, 9), initial metal ion concentration (50, 100, 150, 200, 250, 300, 350, 400 and 500 mg/L), temperature (20-45 °C), and time (0-180 min). Standard acid of 0.1 M HCl and 0.1 M NaOH

solutions were used for the adjustment of solution pH. All the samples were taken in 50 mL stopper conical flask and placed in water bath shaker for desired time period at a constant shaking speed of 250 rpm. At the end of each experiment, the flasks were removed from the shaker and the solutions were separated from the biosorbent by filtering through filter paper (Whatman No. 40, ashless). All the adsorption experiments were carried out in triplicates and the average value was reported in the result.

The amount Cr(VI) ion adsorbed was calculated from the concentrations in the solution before and after biosorption. The percentage Cr(VI) ion biosorption was calculated with the help of following equation 1:

$$\text{Biosorption } (\%) = \frac{C_i - C_e}{C_e} \times 100 \qquad (1)$$

The amount of Cr(VI) adsorbed per unit mass of biosorbent was obtained by using equation 2:

$$\text{Biosorption capacity } (q_e) = \frac{(C_i - C_e)V}{m} \qquad (2)$$

Where Ci and Ce is the initial and equilibrium Cr(VI) ion concentration (mg/L), respectively, qe is the Cr(VI) biosorption capacity (mg/g), m biosorbent mass (mg), and V is the volume of Cr(VI) solution (L).

2.5. Column experiment

Column experiments were carried out with a glass column (length 30 cm and internal diameter 2.54 cm) filled with 10 mg of MNPBGH. The adsorbent is packed in between two supportive layers of glass wool and on upper side with a uniform layer of glass beads which ensures uniform distribution of the Cr(VI) solution. The Cr(VI) was fed into the glass column with the help of peristaltic pump at a controlled flow rate. The column study was performed in the flow rate range (2-10 mL/min), initial Cr(VI) ion concentration (50-200 mg/L) and adsorbent mass (5-15 mg).

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Result and discussion

3.1. Scanning electron microscopy analysis of MNPBGH

Scanning electron microscope images are useful in determining the surface and adsorption details of the adsorbents before and after adsorbate treatment. As shown in Fig.1, the SEM analysis of MNPBGH before Cr(VI) treatment shows irregular rough porous surface with high pore volumes and surface area and after Cr(VI) adsorption it was changed into smooth and more shiner form.
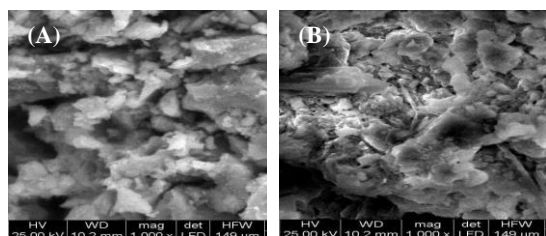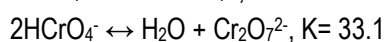

Fig.1: SEM image of MNPBGH (A) before adsorption (B) after Cr (VI) ion adsorption

3.2. Effect of operating conditions on the Cr(VI) adsorption

The adsorption capacity of MNPBGH was significantly affected by the change in the operating condition during batch study. In present study, we analyze the effect of pH, adsorbent dose, temperature initial Cr(VI) concentration and time on the adsorption process.

3.2.1. Effect of pH

The influence of pH on the Cr(VI) ion adsorption is attributed to interactions between ions in solution and complexes formed at the biosorbent surface. The literature studies very well reports the existence of different forms of Cr(VI) in the aqueous solution at various pH values. The species of Cr(VI) present in aqueous solutions are depicted by the equilibrium reactions described below [13]:

$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^-$, $K= 1.6 \times 10^{-1}$

$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-}$, $K= 3.2 \times 10^{-7}$

$2HCrO_4^- \leftrightarrow H_2O + Cr_2O_7^{2-}$, $K= 33.1$

The hexavalent chromium can exist in several stable forms as CrO_4^{2-}, $HCrO_4^-$, $Cr_2O_7^{2-}$, and the ratio of these different Cr(VI) ions forms in aqueous medium depends on the solution pH and chromium ion concentration in the solution. During adsorption of Cr(VI) ions by MNPBGH, with increase in pH from 1 to 9, the removal percentage decreased from 99.26 to 10.79 % and the reason behind this decreased removal efficiency is the presence of oxyanions of Cr(VI) in acidic condition. Similar results were observed [14].

3.2.2. Effect of biosorbent dose

The Cr(VI) removal percentage increased with increasing dose of biosorbent upto a certain extent and then remained constant. 0.5 g/L biosorbent dose show 99.03 % Cr(VI) adsorption and with further increased in dose there is almost constant removal efficiency was observed. Increase in percentage removal with increased biosorbent dose might be due to availability of more active site for Cr(VI) ion binding and after a certain dose most of the adsorbate gets attached with the adsorbent so the removal efficiency becomes almost constant [15].

3.2.3. Effect of temperature

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. The adsorption study shows an increasing trend of Cr(VI) removal with the rise in temperature from 20-45°C. With increase in temperature the mobility of the adsorbate increases there by resulting in decrease of adsorption because of desorption. The trend indicates the exothermic nature of the adsorption process.

3.2.4. Effect of initial concentration

The effect of change in initial Cr(VI) ion concentration on MNPBGH adsorption shows a decreasing trend with increased concentration. The reason for this trend might be because of limited number of active sites on the biosorbent surface. At higher

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concentration more ions are left un-adsorbed in the solution due to active site saturation [11].

3.2.5. Effect of contact time

The removal of Cr(VI) on MNPBGH has been investigated as a function of contact time in the range of 5-180 min with 100 mg/L as initial Cr(VI) ion concentration at room temperature.

The adsorption of Cr(VI) on the MNPBGH was a rapid process as within the first 20 min more than 50 % of the metal ion gets adsorbed. The maximum amount of Cr(VI) uptake was observed after 120 min. Increase in contact time from 120 to 180 min did not result in corresponding increase in adsorption. Initially all the active sites were vacant so the rate of Cr(VI) binding with the adsorbent molecules was very high but reduction in active sites results in reduced uptake rate by the MNPBGH [9].

3.3. Adsorption isotherm, kinetics and thermodynamics

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. In order to quantify the affinity of MNPBGH for Cr(VI) adsorption, widely used Langmuir and Freundlich isotherm models were used for the analysis of the equilibrium data.

The Langmuir model assumes that the process of adsorption occurs at the specific homogeneous sites on the adsorbents and is successfully implemented in many monolayer adsorption processes. The model can be represented as equation 3:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_0C_e} \qquad (3)$$

Where q_e (mg/g), C_e (mg/L), Q_0 and b are the adsorption capacity, equilibrium adsorbate concentration, Langmuir constant related to the adsorption capacity and energy of adsorption, respectively. The Freundlich model can be applied for non-ideal adsorption in heterogeneous surfaces

and multilayer adsorption. The model in its linear equation form can be as follows (equation 4):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (4)$$

Where K_f and n are the Freundlich constants, related to the adsorption capacity and the intensity of adsorbate adsorption on the adsorbent, respectively. In present study, the equilibrium data follow Langmuir model with high correlation coefficient as compared to the Freundlich model confirming the monolayer adsorption of Cr(VI) onto the MNPBGH surface [8].

Similar to the equilibrium isotherm study, the kinetic modeling of the adsorption data is very important as the kinetics of adsorption process provide strong information about the rate law and rate determining step of metal adsorption. The kinetics of Cr(VI) adsorption was investigated using pseudo-first order and pseudo-second order kinetic model and the equation of these two models can be represented as given below:

Pseudo-first order (equation 5)-

$$\log(q_e - q_t) = \log q_e - \frac{K_{1ads}\, t}{2.303} \qquad (5)$$

Pseudo-second order (equation 6)-

$$\frac{t}{q_t} = \frac{1}{k_{2ads}q_e^2} + \frac{1}{q_e}t \qquad (6)$$

Where q_t (mg/g), K_{1ads} and K_{2ads} are the adsorption capacity at any time t, rate constant of first-order and second-order kinetics, respectively. The correlation coefficient of for the linear plot of pseudo-second order was superior compared to the pseudo-first order kinetic model, confirming its applicability during Cr(VI) adsorption [16].

The temperature effect on the adsorption process was better understood on the basis of thermodynamic study. Three basic thermodynamic parameters were studied: the Gibb's free energy

change (ΔG°), the enthalpy (ΔH°) and entropy change (ΔS°). The ΔG°, ΔH° and ΔS° of the Cr(VI) adsorption on the MNPBGH adsorption related to the equilibrium constant (K_c) is calculated from the equations (7-9):

$$\Delta G^0 = -RTlnK_c \qquad (7)$$

$$K_c = \frac{C_{Ae}}{C_e} \qquad (8)$$

$$lnK_c = \left(\frac{\Delta S^0}{R}\right) - \left(\frac{\Delta H^0}{RT}\right) \qquad (9)$$

Where R is the universal gas constant (8.314 J/mol K), T is the reaction temperature in K, K_c is the equilibrium constant, C_{Ae} is the solid-phase concentration at equilibrium (mg/L), C_e is the equilibrium metal concentration in solution. The value of ΔH° and ΔS° was calculated from the plot of lnK_c vs. 1/T. As shown in Table 1, the negative value of ΔG° imply spontaneous adsorption of Cr(VI) onto MNPBGH. Also the magnitude of ΔG° decreased with increase in temperature indicating that the adsorption was more favorable at lower temperature. The value of ΔH° also concludes the

same finding with the negative value, indicating the exothermic nature of adsorption process. An increase in the degrees of freedom of the solid-liquid interface during adsorption of Cr(VI) onto MNPBGH was shown by the positive ΔS° [17]. The value of all isotherms, kinetic and thermodynamic parameters is represented in Table 1.

3.4. Adsorption dynamic column studies

3.4.1. Effect of flow rate

During biosorption process, particularly for continuous treatment of wastewater on large scale, it is important to evaluate the effect of flow rate on column performance. Therefore, the influence of flow rate on biosorption of Cr(VI) by MNPBGH was studied by varying the flow rate from 2 to 10 mL/min and keeping all other parameters constant. From the fig. 2(A), it was observed that breakthrough generally occurred faster with higher flow rate. The reason is that as the flow rate increased, the rate of mass transfer also gets increased, hence the amount of Cr(VI) adsorbed onto the unit bed height also known as mass transfer zone increased [18].

Table 1: The isotherm, kinetics and thermodynamics constant for Cr(VI) adsorption onto MNPBGH.

Isotherm parameters			
Langmuir isotherm	Q_0 (mg/g)	b (L/mg)	R^2
	333.3333	1.1112	0.9427
Freundlich isotherm	K_f (mg/g)	n	R^2
	147.1423	0.2003	0.8729
Kinetic parameters			
Pseudo first order	K_{1ads} (/min)	q_e (mg/g)	R^2
	0.0403	234.6389	0.9279
Pseudo second order	K_{2ads} (mg/g min)	q_e (mg/g)	R^2
	0.0001	256.4103	0.991
Thermodynamic parameters			
Temperature (K)	ΔG° (kJ. mol^{-1})	ΔH° (kJ. mol^{-1})	ΔS° (kJ. mol^{-1} K^{-1})
293	-11.2830	-149.635	0.471
298	-10.5885		
303	-5.9814		
308	-3.6621		
313	-1.4109		
318	-0.8382		

3.4.2. Effect of bed height

The accumulation and adsorption of metal ions during fixed bed column process is governed by the amount of adsorbent packed. 0.5, 1.0 and 1.5 g of MNPBGH which correspond to 0.25, 0.50 and 0.75 cm of the adsorbent height in the column, respectively was selected for the study.

From Fig. 2(B), the breakthrough time increased with increasing the bed height. As the bed height increased, the Cr(VI) ions gets more time to contact and also more surface area with large number of binding sites MNPBGH that resulted in higher removal of adsorbate in the column. Also the higher bed height results in decreased adsorbate concentration in the effluent. The slope of breakthrough curve was slightly decreased with increasing bed height, which resulted in a broadened mass transfer zone [19].

3.4.3. Effect of initial Cr(VI) ion concentration

The effect of influent Cr(VI) concentration on the breakthrough curves is shown in Fig. 2(C). It is illustrated that the process of adsorption reached rapid saturation and the breakthrough time decreased with increasing influent concentration of Cr(VI) ions. A delay breakthrough was achieved with decrease in Cr(VI) concentrations, and the treated volume was the highest at the lowest influent concentration. The reason may be that high Cr(VI) concentration leads to quick saturation of the adsorbent, which in turn leads to the earlier breakthrough and exhaustion time [19]

Conclusion

In this study, adsorption of Cr(VI) in batch and fixed bed column system from its aqueous solution on a laboratory developed magnetic nanoparticle modified with black gram husk (MNPBGH) were investigated. The result of batch study has shown that the uptake of Cr(VI) increases with an increase in adsorbent dose, contact time while opposite trend was observed in case of pH, temperature and initial Cr(VI) concentration. The Langmuir and pseudo-first order kinetic model was found to be applicable during isotherm and kinetic study, respectively. The adsorption capacity calculated from Langmuir model was found to be 333.33 mg/g. Also fixed bed column experiment were conducted and breakthrough time was found to be directly proportional to the bed height while inversely proportional to the influent Cr(VI) ion concentration and flow rate.
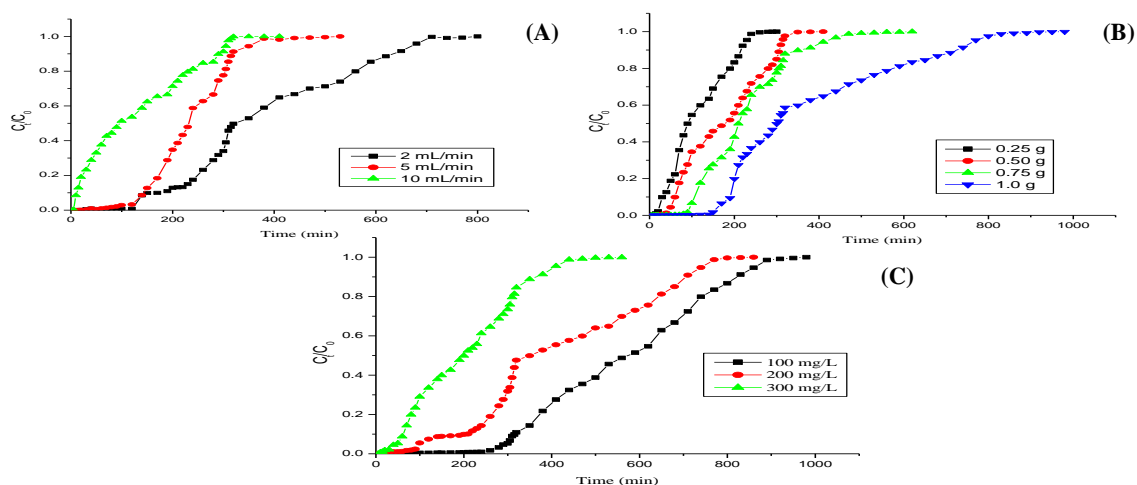

Fig. 2: Effect of (A) flow rate, (B) adsorbent mass, and (C) initial Cr(VI) concentration on the breakthrough curve .

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