

Removal of Cr(VI) from water using GO/PVA as adsorbent

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ABSTRACT

Cr (VI) is a known toxic heavy metal and has been considered as a priority pollutant in water. The effluent of various industries including electroplating, anodizing baths, leather tanning, steel industry and chromium based catalyst are the major source of Cr (VI) contamination in the aquatic environment. Cr (VI) show high mobility in the environment and can easily penetrate cell membrane of the living tissues to exert noxious effects. The Cr (VI) contamination in drinking water causes various hazardous health effects to the human health such as cancer, skin and stomach irritation or ulceration, dermatitis, damage to liver, kidney circulation and nerve tissue damage. Herein we attempt to develop an efficient adsorbent for the removal of Cr (VI) from water. In connection to this polyvinyle alcohol functionalized graphene oxide (GO/PVA) composite was prepared. Thus obtained GO/PVA was characterized through FTIR and SEM. The prepared GO/PVA composite was utilized for the removal Cr (VI) in batch mode experiment. The process variables such as contact time, Initial Cr (VI) concentration, pH, and temperature were optimized. The maximum 99.8 % removal of Cr (VI) was achieved at initial Cr (VI) concentration 60 mg/L, pH 3, temperature 40 °C and equilibrium was achieved within 50 min. The two widely used isotherm models viz. Langmuir and Freundlich were analyzed using linear correlation coefficient (R^2) and it was found that Langmuir model gives best fit with high value of R^2 for the data of present adsorption system which indicate the monolayer adsorption of Cr (VI) on the GO/PVA. Kinetic studies were also conducted using pseudo-first order and pseudo-second order models and it was observed that chemisorptive pseudo-second order model described the kinetics of current adsorption system in better way with high value of correlation coefficient. Thermodynamic studies were conducted and results showed that the adsorption was spontaneous and endothermic in nature

Keywords GO/PVA, Removal, Kinetics, Isotherm, Thermodynamics

1. INTRODUCTION

Hexavalent chromium [Cr(VI)] is a toxic heavy metal therefore its contamination in water is a matter of considerable concern because of its carcinogenic, mutagenic and teratogenic nature which affects human health and environment. The effluent discharge of various

industries such as electroplating, dye, lather tanning, steel and pulp release Cr(VI) in large amount to water bodies[1,2] The maximum permissible limit of Cr(VI) for the discharge to inland surface water is 0.1 mg/L whereas World Health Organization has set 0.05 mg/L maximum allowable concentration in drinking water[3,4]. There are several conventional methods for Cr(VI) removal such as reduction followed by chemical precipitation, ion exchange, reduction electrochemical precipitation, solvent extraction, adsorption, membrane separation, reverse osmosis, evaporation, foam separation, freeze separation, and biosorption[5,6]. But the process of adsorption has significant advantages such as simplicity, economical viability, efficiency and flexibility of metal recovery. These advantages make the process much attractive and scientifically exploratory. Numerous biosorbents have been investigated for the excellent adsorption potential for the heavy metal ions[7-9].

In spite of having various natural and synthetic adsorbent, the design of an efficient adsorbent with exceptionally high potential adsorbent is still needed to be explored[10]. Currently, the adsorption technology has been employed to remove the various environmental toxic pollutants using a graphene oxide composite which is a simple and highly efficient[11]. Till now, the adsorptive removal of pollutant from water has been performed using graphene oxide based adsorbents[12]. In the present study Graphene Oxide/Poly Vinyl Alcohol (GO/PVA) composite was prepared for the removal of Cr(VI) ion from the water. The adsorption studies were conducted in the batch mode method and adsorption parameters were optimized. The kinetic, isotherm and thermodynamic studies for the removal of Cr (VI) have also conducted.

2 MATERIALS AND METHOD

2.1 Materials

Graphite powder, Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4), Phosphoric acid (H_3PO_4), Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and Polyvinyle Alcohol (PVA) were purchase from Sigma Aldrich. Hydrogen peroxide (H_2O_2), Hydrochloric acid (HCl), Sodium hydroxide (NaOH) and Nitric acid (HNO_3) were procured from Qualigens Fine Chemicals Pvt. All chemicals were used as received without further purifications. The deionized double distilled (DW) was used for making the standards and other solutions throughout the experiment.

2.2 Preparation of GO/PVA composite

The GO was prepared through modified Hummer's Method. Briefly 3 g graphite powder and 15 g KMnO_4 were added into the 9:1 mixture of H_2SO_4 and H_3PO_4 . This obtained mixture was stirred for 12 h. at 50°C . The mixture was allowed to cool at room temperature and poured into 1 L distilled water. Then 10 mL 30% H_2O_2 was added to neutralize the residual KMnO_4 and stirred for additional 1 h. Then mixture was centrifuged at 10000 rpm for 10 min. and solid material was collected and washed with distilled water until the pH became 7. Thus obtained black mass was GO which was used for the preparation of the GO/PVA composite. For this purpose 0.05 g GO was suspended in the 50 mL DMSO by the sonication for 2h. Then 0.2 g PVA and 0.05 g DCC were added and the reaction mixture was refluxed at 80°C for 12h. After that reaction mixture was cooled at room temperature and the solvent was removed using rotary evaporator. Then a black mass was collected which was washed through acetone and distilled water many times. The finally obtained black mass was GO/PVA composite which was characterized and used for the removal of Cr(VI) from water.

2.3 Batch Adsorption studies for the removal of Cr(VI)
 The batch mode removal experiment was conducted in the 100 mL Erlenmeyer flasks with the 10 mL working solution of desired concentration of Cr(VI). The calculated amount of GO/PVA composite was added in the Erlenmeyer flasks containing Cr(VI) solution and then flasks were well sealed. The flasks were shaken with the orbital shaker for preselected time. After that the adsorbent GO/PVA was separated by centrifugation at 5000 rpm for 10 min. The supernatant was collected for the analysis of unadsorbed Cr(VI). The concentration of Cr(VI) was conducted Atomic Absorption Spectrophotometer (AAS), Shimadzu AA-6300. The instrument was operated at lamp current of 25 mA, wavelength 359.4 nm, slit width of 0.7 nm and air to fuel ratio of 2:2.

3 RESULTS AND DISCUSSION

3.1 Characterization of GO/PVA

The interaction between GO and PVA was investigated by FT-IR spectra which was conducted using Spectrum 100,

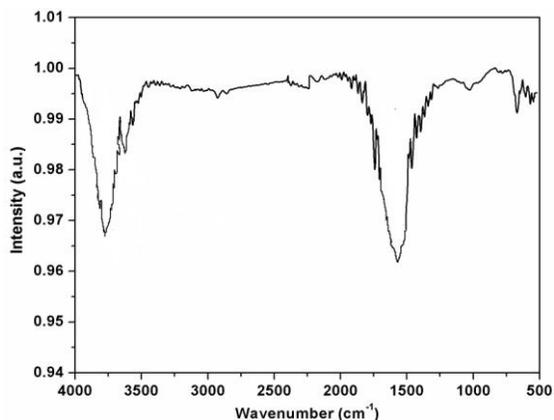


Figure 1 FT-IR spectrum of the GO/PVA composite

PerkinElmer spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ with KBr pellets. Figure 1 shows the FT-IR spectrum of the GO/PVA composite having the peak at 1544 cm^{-1} suggesting the presence of ester bond which was formed due to reaction between hydroxyl group of the PVA and carboxylic functional group of the GO. The FT-IR spectrum has shown another broad peak at 3755 cm^{-1} due to the hydroxyl group of the PVA chain. The morphology of

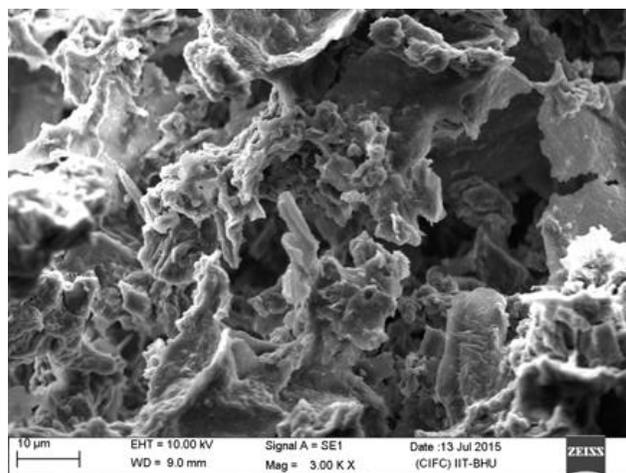


Figure 2 . SEM micrograph of GO/PVA

GO/PVA composite was conducted using Quanta 200 F Scanning Electron Microscopy (SEM). Figure 2 represents the SEM micrograph of GO/PVA composite which shows the interconnected GO sheets leaving the pores. This rough surface and porous structure of the GO/PVA composite make it an excellent adsorbent for the removal of Cr(VI).

3.2 Effect of contact time on the removal of Cr(VI)

The effect of contact time on the removal of Cr(VI) was investigated by varying the contact time from

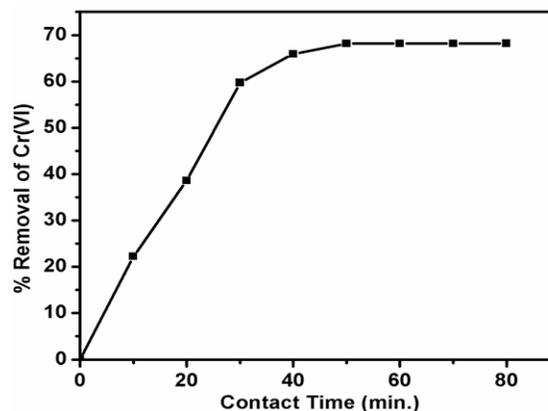


Figure 3. Effect of Contact time on the removal of Cr(VI)

10 to 80 min and keeping initial Cr(VI) concentration 60 mg/L, solution pH 7, GO/PVA dose 0.8 g/L and temperature 30°C . Figure 3 represents the effect of contact time on the removal of Cr(VI) which clearly shows that initially the removal was rapid due to the easy availability

of free binding sites and high concentration gradient. But as time passed the rate of removal was decreased due to the less extent of free binding sites and low concentration gradient. Finally the equilibrium was established at 50 min after that no more significant removal was observed therefore 50 min was considered as optimum time for the removal of Cr(VI).

3.3 Effect of pH on the removal of Cr(VI)

The effect of the pH on the removal of Cr(VI) was investigated in the pH range from 2 to 12 keeping initial Cr(VI) concentration, contact time 50 min, temperature 30° C and GO/PVA dose 0.5 g/L. Figure 4 represents the effect of pH on the removal of Cr(VI) which shows that the % removal was increase with the increase in the pH from 2 and maximum 74.64 % removal was obtained at pH 3.

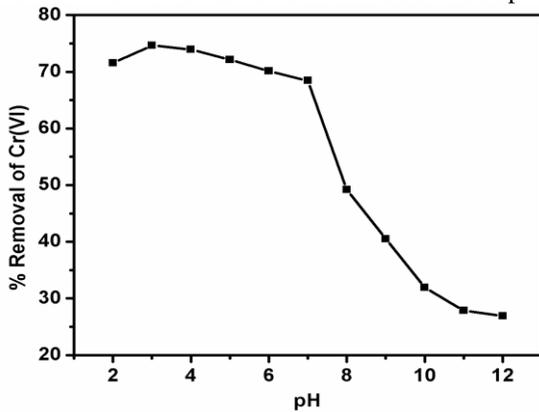


Figure 4. Effect of pH on the removal of Cr(VI)

After that the removal was continuously decreased on further increase in the pH from 3 to 12. Therefore, the pH 3 is optimum ph for the removal of Cr(VI) from water using GO/PVA as adsorbent.

3.4 Effect of GO/PVA dose on the removal of Cr(VI)

The effect of GO/PVA dose was investigated by varying the dose from 0.1 to 1 g/L and keeping the initial Cr(VI)

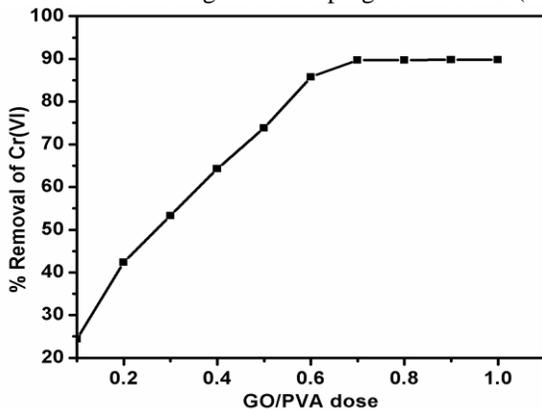


Figure 5. Effect of GO/PVA dose on the removal of Cr(VI)

concentration 60 mg/L, contact time 50 min, pH 3 and temperature 30° c. The effect of on the removal of Cr(VI) is represented in the figure 5 which showed that the removal of Cr(VI) was increased with increase in GO/PVA dose

from 0.1 to 0.7 g/L. This was due to increase in binding sites per unit volume of Cr(VI) solution. The increase in GO/PVA dose above 0.7 g/L did not lead significant increase in % removal therefore 0.7 g/L GO/PVA is selected as optimum for the removal of Cr(VI).

3.5 Effect of temperature on the removal of Cr(VI)

The effect of temperature in the removals of Cr(VI) was investigated. The experiment was conducted by varying the temperature from 10 to 50° C and keeping the Cr(VI) concentration 60 g/L, contact time 50 min, pH 3 and GO/PVA dose 0.7 g/L. The result is represented in the figure 6 which shows that the increase in temperature favored the removal of Cr(VI). The maximum 99.8 % removal of Cr(VI) was achieved at 40° C. Therefore the removal of Cr(V) is endothermic process and 40° C is optimum temperature for the removal of Cr(V).

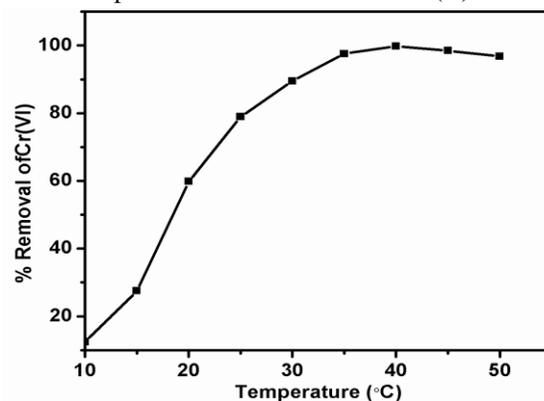


Figure 6. Effect of Temperature on removal of Cr(VI)

3.8 Kinetic Studies

The residence time of adsorbate at the solution-adsorbent interface is determined by adsorption kinetics which control the removal rate of the adsorbate. Therefore, to design a continuous system for adsorption, the kinetic studies are essential. The kinetic experiments were carried out at optimum condition as well as to evaluate the

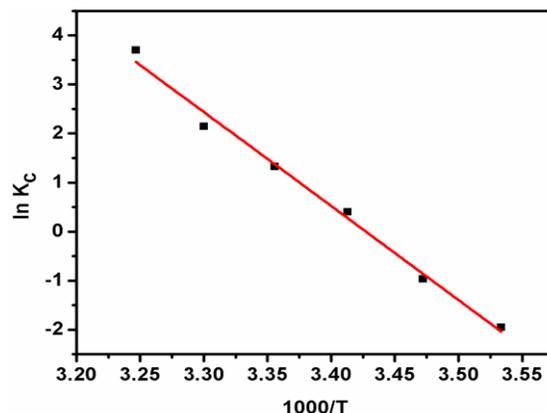


Figure 7. Pseudo-second-order kinetic plot

adsorption as a function of time the concentration of Cr (VI) was analyzed at regular time interval. To define the

kinetic behavior of this adsorption system, pseudo-first order and pseudo-second order model were employed and evaluated. It was observed that pseudo-second order kinetics model showed better fitness for Cr(VI) removal over GO/PVA in terms of high correlation coefficients 0.98 (Fig. 7) as compare to correlation coefficients 0.87 of pseudo-second order kinetics. The fitness of pseudo-second order model with the empirical data indicates that chemisorptive valence force was the rate limiting step in the current adsorption system[13].

3.9 Isotherm Studies

The equilibrium, adsorption pattern and distribution sorbate at liquid-surface interface at a given temperature are generally represented by adsorption isotherm.

The adsorption pattern of Cr(VI) by varying initial Cr(VI) concentration in the range of 20 to 100 mg/L was analysed by Langmuir isotherms and Freundlich isotherm. It was observed that the Langmuir isotherm better expressed the current adsorption system because of higher correlation coefficients 0.99 as compare to correlation coefficients 0.91 of Freundlich isotherm model which indicated the monolayer adsorption on the homogeneously distributed binding sites on the GO/PVA surface.

3.10 Thermodynamic studies

To perform the thermodynamic study in the range from 10 °C to 50 °C all the parameters were kept constant at

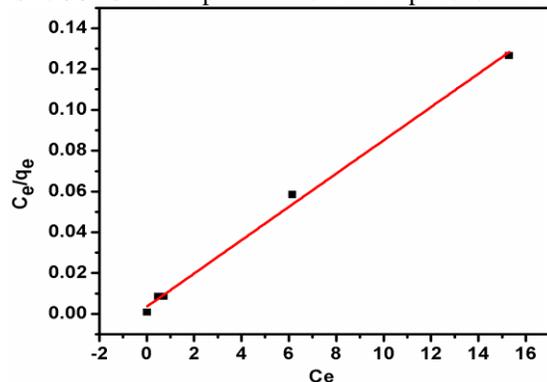


Figure 8. Van't Hoff plot their optimal values.

The thermodynamic parameters were calculated using slope and intercept of Van't Hoff plot ($\ln K_c$ vs. $1/T$, Fig. 8). It was found that the process was endothermic in nature which was confirmed by the positive value of enthalpy change (ΔH) whereas the spontaneity of adsorption process was confirmed by the negative magnitudes of ΔG for all the investigated temperatures. In addition to this, the positive value of change in entropy (ΔS) represented the increase in degree of randomness which might be due to the disorderliness at solid-liquid interface.

4. Conclusions

GO/PVA composite was successfully prepared and utilized for the removal of Cr(VI) from water. Almost complete removal i.e. 99.8 % was achieved at initial Cr(VI) concentration 60 mg/L, GO/PVA dose 0.7 g/L, pH 3 and

temperature 40° C. The removal of Cr(VI) take place in monolayer pattern following pseudo-second-order kinetic model and the process is endothermic nature.

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