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A novel amine impregnated graphene oxide adsorbent for the removal of hexavalent chromium

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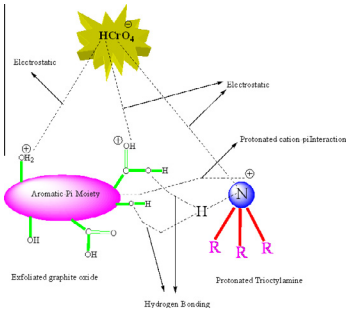
HIGHLIGHTS

- Trioctylamine impregnated exfoliated graphene oxide was prepared as novel adsorbent.
- The sorbent has an adsorption capacity of 232.55 mg g^{-1} for chromium(VI).
- Mechanism involves electrostatic interaction and hydrogen bonding.
- Method applied to wastewater sample.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile and novel method for the removal of toxic chromium based on the appealing interaction between exfoliated graphene oxide (EGO), trioctylamine (TOA) and Cr(VI) is reported in this paper. Trioctylamine in acetone medium was impregnated onto EGO and Cr(VI) was adsorbed on the surface of the TOA–EGO adsorbent at pH 2.5 through cation-π, lone pair-π and electrostatic interactions. Characterization of the adsorbent was done using FT-IR, SEM, EDAX and XRD studies. Various isotherm models were studied and an adsorption capacity of 232.55 mg g^{-1} could be realized by fitting the experimental data with the Langmuir model. Second order kinetics and exothermic nature of the adsorption process validated the experimental data. Regeneration of the adsorbent was accomplished using ammonium hydroxide and the potential of this novel adsorbent material has been utilized in chromium remediation from tannery wastewater.

1. Introduction

The ground water contamination due to the chromium compounds used in electroplating and tannery industries [1] requires the development of sustainable remediation technologies. With the Environmental Protection Agency (EPA) setting a limit of 0.1 mg L^{-1} for total chromium [2,3] in water, newer adsorbents having high performance efficiency are required for the removal of hexavalent chromium [4]. Amongst the low cost carbon based adsorbents, sawdust [5], agricultural bio-waste [6] and activated carbon [7] have good adsorption capacity for chromium. An electrochemical method for the removal of chromium from aqueous solutions using electrodes of stainless steel nets coated with single walled carbon nanotubes [8] has been reported. Novel adsorbents belonging to carbon family have proved to be more effective towards heavy metal adsorption. Graphene is one such material having a two dimensional layer structure and is known for its potential in diverse applications [9–12]. Graphene oxide (a graphene derivative) is more useful for adsorption due to the presence of several functional groups on its surface [13,14]. The efficacy of graphene oxide has been demonstrated in the removal of organic dyes [15,16]. However, metal ion removal using graphene oxide has not been fully explored as compared to the other carbon adsorbents. Nevertheless, there have been quite a few recent reports for metal adsorption using modified graphene oxide. Chandra

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and Kim [17] have reported Hg(II) removal from aqueous solutions using polypyrrole-reduced graphene oxide (PPy-RGO) composite wherein graphene acts as an electron buffer. Reduced graphene oxide–iron oxide hybrid materials are known for their versatile application in the removal of organic and inorganic pollutants [18]. Preconcentration of U(VI) using graphene oxide nanosheets [19], and a comparative study of GO against activated carbon [20] for Cu(II) removal has been recently reported. Graphene oxide/ferric hydroxide composites have been explored for efficient arsenate removal from drinking water [21]. Magnetic graphene prepared using graphene oxide -ferrocene [22] is known to adsorb chromium with an adsorption capacity of 4.86 mg g^{-1}. Calcined graphene/MgAl-layered double hydroxides and nanoparticle decorated graphene are reported for Cr(VI) adsorption [23,24]. Reduction of hexavalent chromium using EDTA reduced graphene oxide has been reported [25]. A recent work reports the interaction of an ionic liquid, Aliquat-336 with graphene oxide and its utility towards chromium remediation in effluent samples [26]. A novel super adsorbent for Cr(VI) using polyaniline nanorods dotted on graphene oxide nanosheets has been reported [27]. Amine functionalized Fe_3O_4 hollow microspheres–graphene oxide composite [28] shows a maximum adsorption capacity of 32.33 mg g^{-1} for Cr(VI). Poly (amidoamine) modified graphene oxide [29], polypyrrole/GO composite nanosheets [30] have been well studied for the effective adsorption of hexavalent chromium. Literature review reveals that long chain amines have not been explored in conjunction with exfoliated graphene oxide (EGO) for chromium adsorption. The utility of TOA in the modification of a synthetic resin for the adsorption of chromium has been reported [31]. Nevertheless, till date there are no reports on the study of interaction of EGO–TOA for chromium adsorption. TOA is a long chain tertiary amine that could interact with EGO through lone pair-π interaction as well as hydrogen bonding. In acidic medium, the protonated amine shows considerable affinity towards the hydrochromate anion in the form of electrostatic interaction. Since, chromium is a hard acid it shows good affinity towards nitrogen which acts as a hard base. Hence, this novel adsorbent merits considerable investigation in understanding the interaction with hexavalent chromium.

2. Experimental section

2.1. Materials and characterization

The starting material, graphite used in the preparation of graphene oxide was procured from Sigma Aldrich. A stock solution of 1000 mg L^{-1} Cr(VI) was prepared using A. R. grade potassium dichromate and a working solution of 100 mg L^{-1} for batch adsorption was prepared by appropriate dilution with Milli Q water. A working solution of 20 mg L^{-1} Cr(III) was prepared using $CrCl_3$ obtained from Qualikems Fine Chemicals, India. Trioctylamine was obtained from Spectrochem India. The other required reagents were procured from Merck and S. D. Fine Chemicals, India respectively. Spectrophotometric determination of chromium and the FT-IR spectra of the adsorbent were recorded using Jasco model V 650 and 4200 instruments respectively. The FT-IR spectra of TOA–EGO adsorbent were recorded in the range 500–4000 cm^{-1} by mixing 0.01 g of the material with 0.1 g KBr (spectroscopy grade). An Li 127 (Elico, India) model pH meter was used for pH measurements. PANalytical X'pert PRO diffractometer (Philips) using Cu Kα radiation (λ = 1.54 Å) operating at 40 kV, 30 mA and step size of 0.05° was used for recording the XRD pattern of the solid adsorbent. The powder samples for XRD were mounted on a glass plate sample holder and the scan was performed in the 2θ range 10–80° respectively. The SEM images and the EDAX spectra were obtained using a JEOL JSM-6390 analyzer.

2.2. Adsorbent preparation and batch study

The exfoliated graphite was prepared as reported previously and the obtained material was subjected to $KMnO_4$ oxidation by the well-known Hummer's method in order to obtain the exfoliated graphene oxide [32–34]. The EGO obtained was dried in a vacuum oven (Biotechnics, India) and a 17.5 mL volume of 0.04 mole TOA in acetone was added with stirring (for 8 h) to 1 g EGO taken in a 50 mL round bottom flask. The TOA–EGO adsorbent obtained in this process was washed and dried in a vacuum oven (Biotechnics India), and utilized for batch studies. Comprehensive characterization of the adsorbent was done using various physicochemical techniques to confirm the presence of TOA and EGO in the adsorbent. Batch adsorption studies were carried out with 100 mg L^{-1} hexavalent chromium containing 0.2 g of the TOA–EGO adsorbent. With an aqueous phase volume of 50 mL at pH 2.5, the amount of chromium adsorbed (q_e) was obtained by equilibration at various time intervals using the expression

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e indicates the initial and equilibrium Cr (VI) concentrations, V and W specifies the volume of sample solution (L) the weight (g) of the TOA–EGO adsorbent respectively. Diphenylcarbazide gives a distinct violet color complex with hexavalent chromium at 540 nm and this reaction was utilized for the spectrophotometric determination of chromium in the solution phase after adsorption [35]. Equilibrium is attained in 60 min with quantitative adsorption (99.4 ± 0.042%) of hexavalent chromium.

3. Results and discussion

3.1. Adsorption mechanism

The presence of various functional groups in EGO is an added advantage with regard to its interaction with TOA. Trioctylamine is a long chain amine that would interact with EGO through lone pair-π interaction as well as hydrogen bonding [36–38]. The pH of the aqueous medium plays an important role in the interaction of hexavalent chromium with trioctylamine and graphene oxide. It has been well established [26] that in pH range 2.5–4, Cr(VI) exists as $HCrO_4^-$ (hydrochromate anion) and at higher pH the equilibrium favors CrO_4^{2-} (tetraoxochromate) oxyanion. In strongly acidic medium (pH less than 2), the dichromate ion, $Cr_2O_7^{2-}$ predominates in solution. The optimum pH for adsorption of hexavalent chromium onto TOA–EGO adsorbent was observed in the range 2.5–4.0. It is quite probable to visualize a cation-π interaction between the protonated amine and the aromatic moiety in EGO. The N–H···O hydrogen bonding coupled with the electrostatic interaction [39] of $HCrO_4^-$ with the protonated tertiary amine favors the facile adsorption of chromium(VI) onto the surface of EGO. The scheme depicting the interaction between the amine, graphene oxide and Cr(VI) is given in Fig. 1. At higher pH, the competition from hydroxyl anion for the active sites of the TOA–EGO adsorbent would affect the adsorption. Hence, at higher pH, the surface charge on the EGO becomes negative [26] and hence the affinity between the hydrochromate anion and the TOA–EGO adsorbent decreases leading to a reduction in the percentage adsorption.

3.2. Column adsorption

The sample breakthrough volume was ascertained from column study and with 10 mg L^{-1} Cr(VI) (flow rate 10 mL min^{-1}) a sample volume of 900 mL (Fig. 2) could be quantitatively adsorbed onto a glass column (2 cm packing height, 30 cm length, 4.0 g TOA–EGO