



High-performance towards removal of toxic hexavalent chromium from aqueous solution using graphene oxide-alpha cyclodextrin-polypyrrole nanocomposites



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ABSTRACT

Graphene oxide (GO) was functionalized with alpha cyclodextrin (α CD) through a covalent bond to form GO- α CD nanocomposites (NC). GO- α CD NC was further modified with polypyrrole (PPY) to afford an advanced GO- α CD-PPY NC for the removal of highly toxic Cr(VI) from water. The prepared GO- α CD-PPY NCs were successfully characterised with AT-FTIR, FE-SEM, HR-TEM, BET and XRD techniques. Adsorption experiments were performed in batch mode to determine optimum conditions that include temperature, pH, concentration of Cr(VI) and contact time. It was deduced from the experiments that the adsorption of Cr(VI) by the GO- α CD-PPY NC is pH and temperature dependent, where optimum adsorption was achieved at pH 2 and it increased with increasing temperature. The adsorption kinetics followed the pseudo-second-order model and the adsorption isotherms fitted well to the Langmuir isotherm model with maximum adsorption capacities ranging from 606.06 to 666.67 mg/g. Effect of co-existing ions studies revealed that cations and anions had no significant effect on the adsorption of Cr(VI). Desorption studies also illustrated that the NC can be re-used up to 3 cycles.

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1. Introduction

Water resources have been subjected to severe exploitation and damage over several decades by human activities such as mining, manufacturing, chemical and goods production, electricity production, agriculture, and improper sanitation [1]. The main sources of pollution are effluents and solid discharge from industries which include heavy metals from smelting and mining, and nonpoint sources such as soluble salts (natural and artificial), use of insecticides/pesticides, disposal of industrial and municipal wastes, and excessive use of fertilizers [1]. Of particular concern are heavy metals which are becoming one of the most serious environmental problems. Heavy metals are commonly used in leather tanning, metal, nuclear power plants, and metal salt production [2]. Unlike organic contaminants, heavy metals are not biodegradable and have a propensity to accumulate in living organisms [3]. The consequences of heavy metals ingestion and exposure are adverse; they include damage to the central nervous system, skin dermatitis, to mention but few [4].

Several methods including chemical precipitation [5], ion-exchange, membrane filtration [6], and electrochemical methods have been

proposed, and are currently used [7] for heavy metals. However, these methods have several drawbacks such as fouling of membranes by metal hydroxides and carbonates, low effectiveness in low concentrations of heavy metals, and high costs [7]. Adsorption is renowned as a highly effective wastewater treatment technology, in terms of cost and removal efficiency. It is simple, offers flexibility in design and operation and produces high-quality treated effluent. Moreover, because adsorption is reversible, adsorbents can be re-generated by appropriate desorption processes [7]. In adsorption, choosing and designing smart adsorbents is critical and necessary. Some of the traditional adsorbents that have been used for the removal of heavy metals and Cr(VI) in particular include activated carbon [8], bio adsorbents and low cost adsorbents such as fly ash, clay, and lignin by-products [7]. The drawbacks associated with some of these adsorbents are relatively low adsorption capacities, weak mechanical strength, separation after treatment and low surface areas [9].

Graphene is a monomer source of some carbon allotropes such as fullerenes and carbon nanotubes [10]. Owing to its extraordinary properties that include mechanical strength and flexibility [10], graphene has become the wunderkind in material science and technology since its discovery in 2004 [10]. Graphene, however, has a major drawback of aggregation due to the strong van der Waals interactions and π - π stacking of the graphene sheets [10]. This reduces dispersibility in water and therefore limits applications. Aggregation can be minimized or eliminated by introducing functional groups on the graphene sheets

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through chemical oxidation to afford graphene oxide (GO) [10]. In recent years, there has been growing research interest regarding modification of single graphene/GO sheets with various host molecules such as cyclodextrin, metal nanoparticles and polymers to form nanocomposites which show increased surface area and superior properties, compared to the native graphite material. The superior properties are caused by the synergistic effect between the host molecule and graphene nanosheets. Several heavy metals such as arsenate [11], Zn^{2+} , Cd^{2+} and Pb^{2+} [12] have been removed by graphene based adsorbents.

Cyclodextrins (CDs), which are significant hosts in supramolecular chemistry [13], are cyclic oligosaccharides composed of six, seven or eight glucose units, which are conical in shape with a hydrophobic inner cavity and a hydrophilic exterior. CDs have the ability to specifically bind to various organic and inorganic pollutants to form inclusion complexes. For this reason, attaching α CDs and polypyrrole (PPY) to GO to afford GO- α CD-PPY nanocomposites (GO- α CD-PPY NC) would be ideal for the removal of heavy metals, in particular, Cr(VI). The GO- α CD-PPY NC would also possess increased surface area, good mechanical properties, strong acid resistance and increased adsorption capability. Fan and co-workers [9] demonstrated the fast and efficient removal of Cr(VI) using magnetic α CD-graphene oxide nanocomposites (MCGN), where their adsorption capacity was more than 120 mg/g compared to nanomaterials [14].

The aim of this work is to synthesise GO- α CD NC for the removal of Cr(VI). This nanocomposite will further be modified with PPY to form GO- α CD-PPY NC. Polypyrrole has remarkable properties which are relevant in the removal of heavy metals, which include high chemical stability, ion exchange ability, ease of preparation, and low cost [15]. To the best of our knowledge, there are no reports on the removal of Cr(VI) using GO- α CD-PPY NC, thus we report the synthesis, characterisation and application of the GO- α CD-PPY NC in the removal of Cr(VI) at optimized conditions.

2. Experimental

2.1. Synthesis of GO- α CD and GO- α CD-PPY NC

Graphene oxide (GO) was synthesised using a modified Hummers method [16] through oxidation of graphite flakes (GFs) (Sigma Aldrich, South Africa). The synthesis of GO- α CD was carried as reported in literature [9] with some changes. GO (0.02 g) was dispersed in water through sonication for ~45 min and α CD (0.2 g) (Sigma Aldrich, South Africa) was added to the GO dispersion. The pH of the solution was adjusted between 9 and 10 using different concentrations of NaOH (0.1–7 M) (Sigma Aldrich, South Africa) to find the optimum synthesis conditions, where 5 M gave the highest yield of 1.23 g. To obtain the GO- α CD, the suspension was stirred overnight, centrifuged and dried at 60 °C. The GO- α CD-PPY NC were prepared via in situ polymerization of pyrrole (PY) monomer in the presence of $FeCl_3$ (Sigma Aldrich). GO- α CD NC (0.2 g) was sonicated thoroughly and stirred for 24 h. PY monomer (0.8 mL) (Sigma Aldrich, South Africa) was syringed into the reaction flask and stirred for 1 h. $FeCl_3$ (6 g) was then added, and the reaction was carried out for 3 h. After this, acetone was added to stop the polymerization reaction, followed by filtration of GO- α CD-PPY NCs. The NCs were washed with distilled water until the filtrate became colourless and finally the NCs were washed with acetone to remove oligomers [17].

2.2. Batch adsorption experiment

Adsorption studies were carried out in batch mode. Cr(VI) solutions were prepared by diluting the stock solution of 1000 mg/L. These were then placed in a thermostatic shaker (at a speed of 200 rpm) at different temperatures for 24 h. To determine the concentration of the remaining Cr(VI) after adsorption, standard UV-vis spectroscopic method by

Gilcreas and co-workers [18] was used. Cr(VI) removal efficiency was determined using Eq. (1).

$$\%Cr(VI) \text{ removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

where C_o and C_e are initial and equilibrium concentration (mg/L) of Cr(VI), respectively. In order to determine the optimum pH for Cr(VI) removal, pH studies were carried out from 2 to 11. The pH of the Cr(VI) solutions was adjusted by using HCl (1.0 M) and NaOH (1.0 M) solutions.

Batch adsorption isotherm experiments were carried out at different temperatures, whereby isotherm results were generated by using a mass of 0.025 g of NC in 50 mL Cr(VI) solutions with concentrations ranging between 100 and 700 mg/L at pH 2.0 for all temperatures. The kinetics studies were conducted in a beaker, where a fixed mass of the adsorbent was used at different concentrations of Cr(VI) that was stirred at 200 rpm and operated at -25 °C using 0.5 g/L dose.

The equilibrium sorption capacity and time-dependent capacity were determined using Eqs. (2) and (3):

$$q_e = \left(\frac{C_o - C_e}{m} \right) V \quad (2)$$

$$q_t = \left(\frac{C_o - C_t}{m} \right) V \quad (3)$$

where q_e and q_t are the equilibrium amount and the time-dependent amount of Cr(VI) adsorbed per unit mass (m) of adsorbent (mg/g), respectively, and C_t (mg/L) is the bulk-phase Cr(VI) concentration (mg/L) at any time 't' and V is the sample volume (L).

2.3. Characterisation of the adsorbent

FTIR analyses were performed on a Perkin-Elmer Spectrum 100 spectrometer, equipped with an FTIR microscopy accessory and a diamond crystal. The surface morphology of the samples was investigated by an Auriga Field Emission Scanning Electron Microscope (FE-SEM; Carl Zeiss, Germany) and a JEOL JEM-2100 High Resolution Transmission Electron Microscope (HR-TEM; JEOL, Japan). A JEOL JEM-2100 HR-TEM instrument with a LaB6 filament operated at 200 kV was used to obtain TEM images. For the X-ray measurements, a Pan Analytical instrument and X'pert data Collector software was used. The surface area of the nanocomposites was determined by a Micromeritics Tristar II 3020 Surface Area and Porosity BET analyser using nitrogen adsorption.

3. Results and discussion

3.1. Synthesis of GO- α CD and GO- α CD-PPY nanocomposites

The FTIR spectra of α CD(a), GO(b), GO- α CD(c), and GO- α CD-PPY NC(d) are presented in Fig. 1. For α CD and GO- α CD, the FTIR spectra show a broad peak at ~ 3375 cm^{-1} which is typically assigned to the O-H groups present in α CD and GO sheets. The absorption band at ~ 1720 cm^{-1} present in pure GO, due to the carboxyl group which is disappeared after the conjugation of GO with α CD (Fig. 1(c)). This is indicative of the formation of GO- α CD via nucleophile reaction. The somewhat broad vibration peak at 1179 cm^{-1} in pure GO assigned to the epoxy groups which is also disappeared during the formation of GO- α CD NC. These features indicated that the cyclodextrin molecules could be attached to the GO sheets by nucleophilic reaction between deprotonated hydroxyl groups on the secondary face of the α CD in alkaline solution and the epoxy groups/carboxylic groups on GO [11,19]. Upon polymerizing PY in between the GO- α CD sheets, Fig. 1(d), the O-H, C=O and C-O absorption bands disappeared, whereas, peaks at

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