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Removal of Cd (II), Pb (II) and Cu (II) ions from aqueous solution by polyamidoamine dendrimer grafted magnetic graphene oxide nanosheets

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ABSTRACT

In this study, the as-synthesized magnetic graphene oxide (mGO) nanocomposite was grafted with amine groups, namely the first and second generation of polyamidoamine dendrimer (mGO1st- and mGO2nd-PAMAM) with different oxidation levels and shown to be effective in removing Cd (II), Pb (II) and Cu (II) ions from aqueous solution in batch system. Raman spectroscopy, atomic force microscopy (AFM), Fourier-transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to identify the structural characteristics of amine functionalized nanocomposites. The pH_{ZPC} value of the sorbent was estimated to be 7.2 by titration methods. The different amine functionalization of the mGO stage of the two adsorbents and the differences in the behavior of the three metal ions under magnetic strength were found to be important in order to consider the performance of the adsorption systems. The adsorption capacities of metal ions were 435.85, 326.729 and 353.59 mg g^{-1} for Cd (II), Pb (II) and Cu (II), respectively. The obtained data were successfully fitted with the pseudo-second-order kinetic model. The adsorption capacity was dependent on the temperature and increased with the increase of temperature. Also, the equilibrium data were evaluated using the Freundlich, Langmuir, and Redlich–Peterson (R–P) isotherm models, suggesting the obtained data were fitted to the Freundlich isotherm model and the adsorption mechanism is heterogeneous. According to thermodynamic analysis, the adsorption process was found to be endothermic and spontaneous in nature. Moreover, the adsorbent was regenerated after a five time adsorption–desorption cycle without significant loss in adsorption capacity. The results from this study support that the as-synthesized adsorbent proves excellent removal ability of the metal ion from water and wastewater.

1. Introduction

Toxic metals are one of the most persistent pollutants as a result of different industrial mining, and agriculture wastewater that have adverse effects on ecological environment and human health due to their toxicity, bioaccumulation, persistence and non-biodegradable when discharged into water bodies [1]. Therefore, the removal of metals ions from wastewater before being discharged into aquatic systems is necessary. Several studies have been conducted to prevent the entry of metals into the aquatic environments. Nowadays, several technologies especially in large scale and industrial application including membranes, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, chemical precipitation, flocculation, settling and discharge have been used to reduce the toxic metal ions from water and wastewater [2] Although these methods are effective but in many cases, requiring a large quantity of chemicals and high energy input. For example, sulfide or hydroxide precipitation needs adjustment of the pH within the neutral to slightly alkaline range and also produces large volume of sludge [3]. Also, these methods have applied limitations to remove metal ions from solutions at low amounts of concentration, which might fail to achieve treatment limits [4]. Consequently, promising wastewater treatment methods will require developments and innovations to ensure reliability, safety and security, quality of life and system operations. Among treatment processes, one of the impressive methods for metal ions removal is the use of adsorbents. The adsorption process seems to be a suitable method according to the simplicity of operation, low generation volume of waste, less space required for installation, cost-effectiveness and finally regeneration and reusable adsorbent for water and wastewater treatment [2]. Therefore, they have received considerable attention for use in environmental treatments.

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Some adsorbent including activated carbon [5], multi-walled carbon nanotubes [6], zeolites [7], chitosan [8], metal oxide [9] and polymer adsorbents [10] were used for toxic metal ions removal from water and wastewater.

Nowadays, graphene is an ideal material for removing heavy metals from aqueous solution due to its exceptional physicochemical properties including high surface area (a huge specific surface area over 2600 m^2 g^{-1}) [11] and flexibility, good chemical stability, chemical ineffectiveness, high electrical conductivity, optical transmission [12] and ion adsorption capacity in the Nano-scale [13]. Also, graphene can be easily modified due to the presence of oxygen groups on its surface with the oxidation process. The oxidation of graphite powder using the Hummers method introduces many functional groups on the surface of graphene oxide (GO) nanosheets including carboxyl, hydroxyl, and epoxy [14], which is suitable for further functionalization process. However, the separation of GO from aqueous solution due to its small particle size is very difficult. Therefore, the synthesis of magnetic-GO (mGO) is the appropriate adsorbent, which makes the separation easier and faster from aqueous solution (without filtering) at the end of the adsorption process [4,15]. Also, in many studies, it has proven to be a good adsorbent for metals ion removal after functionalization [16–18]. Therefore, in the present study, the GO was synthesized from the oxidation of graphite powder with the Hummers method. The mGO nanosheets were prepared via the solvothermal method. Then, the mGO was functionalized with NH_2, ethylenediamine (EDA) and tris(2-aminoethyl) amine (TAEA) branches in a different level of oxidation in order to form NH_2 terminated polyamidoamine dendrimer for the removal of Cd (II), Pb (II) and Cu (II) from the aqueous solutions.

In the present study, graphene oxide (GO) was prepared by a modified Hummer's method and magnetic Fe_3O_4–GO nanocomposite (mGO) was synthesized by hydrothermal method. The amine functionalization of mGO was carried out with the first and second generation of poly (amidoamine) dendrimer groups and its application for the adsorption of Cd (II), Pb (II) and Cu (II) from aqueous solution was studied in a batch system. The effects of the different solution pH, the dose of adsorbent, the contact time, Cd (II), Pb (II) and Cu (II) ions ion concentration, and the temperature from aqueous solution using the as-synthesized amine functionalized mGO nanocomposite were investigated. The thermodynamic properties, including enthalpy, entropy and Gibbs free energy, of the adsorption were determined. Also, the obtained data were fitted with the Freundlich, Langmuir and Redlich Peterson isotherm models. Finally, adsorption–desorption cycles were also studied for the subsequent recycling.

2. Materials and methods

2.1. Materials and reagents

For the synthesis and preparation of GO, the following substrates were used: purified graphite powder, sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), sodium nitrate, hydrochloric acid (HCl) purchased from Merck (Germany) and potassium permanganate ($KMnO_4$) was prepared from Scharlau. Also, for the magnification of GO, subsequent materials were purchased: ethylene glycol (EG) and ferric chloride ($FeCl_3 \cdot 6H_2O$) from Merck and sodium acetate (NaAc) from Merck, Germany. Finally, ethylenediamine (EDA), N,N'-Dicyclohexylcarbodiimide (DCC), methyl acrylate (MA) and methanol (Merck) and tris(2-aminoethyl) amine (TAEA) (Sigma Aldrich, USA), were used for amidation and branches of mGO. Additionally, molecular sieve 3 Å powder (Merck chemical, Germany) was used for drying the methanol. Deionized water ($EC < 0.05$ μS m^{-1}), was used throughout the experiments.

2.2. Synthesis process

2.2.1. Preparation of GO

The GO was synthesized using a modified Hummers method by the oxidation of graphite powder [14,19]. Firstly, 100 ml H_2SO_4 (95%) was added into a 500 ml flask and then cooled by immersion in an ice bath followed by stirring. Subsequently, 3 g graphite powder and 2 g sodium nitrate were added under vigorous stirring to avoid agglomeration. After the graphite powder was well dispersed (about 0.5 h), 15 g $KMnO_4$ was added gradually and the temperature of the mixture was kept below 10 °C by cooling. Then the mixture was stirred at room temperature overnight. Secondary, 120 ml of deionized water was slowly added to the paste (about 0.5 h). The diluted suspension was stirred at 90 °C for 12 h. Then the temperature was reduced to 60 °C. After that, the solution was diluted further with 100 ml deionized water and 35 ml of 30% H_2O_2. Finally, the mixture was filtered and washed with 5% and 10% HCl aqueous solution to remove metal ions followed by deionized water until the pH was 7 and then dried in a freeze dryer overnight.

2.2.2. Preparation of mGO

The mGO nanosheet was fabricated with solvothermal synthesis according to the literature [20]. The as-prepared GO (500 mg) was exfoliated and dispersed under ultrasonication (200 W, 40 kHz) in 60 mL of EG for more than 3 h. Then, 0.9 g $FeCl_3 \bullet 6H_2O$ and 2 g NaAc were added to the exfoliated GO-EG solution under vigorous stirring. After agitation and stirring for about 30 min in ambient temperature and degassed by nitrogen purging, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 10 h followed by cooling to room temperature naturally. The black precipitate was centrifuged, rinsed with deionized water and ethanol several times, and finally dried at 60 °C in a vacuum oven for 48 °C to remove residual solvent.

2.2.3. Preparation of mGO-NH_2

For preparation of amino modified mGO, 500 mg of mGO was placed in a 100 ml flask. Then, 20 ml EDA and 0.7 g DCC were added at 100 rpm under argon atmosphere with mechanical stirring. The mixture was then refluxed for 48 h at 70 °C. After that, the resulting NH_2 grafted-mGO was isolated from the solution using an external magnetic field, washed five times with ethanol and dried in a vacuum oven at 70 °C. Then, obtained adsorbent was stored in glass a container [21].

2.2.4. Growth of 1st- and 2nd-PAMAM dendrimer on mGO-NH2

The growth of the amidoamine branches process of mGO-NH2 was achieved in two steps: (1): Michael addition of MA to amine groups; (2) amidation of the resulting esters with TAEA and EDA in succession. Firstly, 500 mg of mGO-NH2 was sonicated (200 W, 40 kHz) in 20 ml of dry methanol for 1 h. The mixture was degassed by argon purging to remove the oxygen. Simultaneously, 20 ml of MA and 60 ml of dry methanol were cooled in a round-bottomed ice-water bath and stirred for 60 min. Then, the suspension of mGO-NH2 was added dropwise into the prepared solution within 30 min. The magnetic mixture was stirred for 60 min in an ice-water bath. For the completion of this stage, the reaction was operated for 24 h at room temperature, followed by another 10 h at 50 °C. After the reaction, the prepared sample was collected by using a magnet and washed with dry methanol five times and was vacuum dried at 60 °C for 24 h [22]. TAEA (4 ml) and dry methanol (40 ml) were stirred in a round-bottomed flask and cooled in an ice–water bath for 30 min. Afterwards, the mGO-NH2–MA obtained from the previous stage was sonicated in 20 ml of dry methanol for 30 min. Then, TAEA solution was

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