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Carbon gel-supported Fe-graphene disks: Synthesis, adsorption of aqueous Cr(VI) and Pb(II) and the removal mechanism

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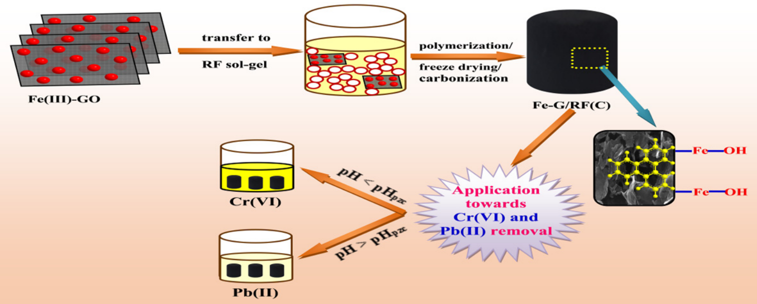
HIGHLIGHTS

- Mechanically strong, porous carbon disk-supported Fe-graphene was synthesized.
- *In situ* doped Fe served as crosslinker and adsorption sites for Cr(VI) and Pb (II).
- Fe-G/RF(C) showed large surface area (~537 m^2/g) with 94% microporosity.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon gel-supported Fe-graphene (Fe-G) disks were synthesized via sol-gel polymerization of resorcinol-formaldehyde (RF), followed by carbonization of the polymeric mass. Fe(III)-graphene oxide were *in situ* doped in the gel at the incipience of polymerization. The Fe(III) served as a crosslinker between graphene oxide and RF matrix as well as the polymerization catalyst. The prepared Fe-G/RF(C) disks were used as an efficient adsorbent for aqueous Cr(VI) and Pb(II). Various analytical techniques were used to characterize the physico-chemical properties of the prepared materials, including surface morphology, surface area and point of zero charge. The compressive strength of the Fe-G/RF(C) disks was measured to be significantly high (0.12 MPa). The maximum adsorption capacities of Fe-G/RF(C) for Cr(VI) and Pb(II) were determined to be 108 and 172 mg/g at the optimized solution pH. Significant adsorption of the metals was attributed to the large surface area (~537 m^2/g) and microporosity (94%) in the material, high chemical reactivity of graphene, and amenability of the material surface to protonation by pH-adjustment. The synthesized amorphous carbon gel-supported Fe-graphene disks can be effectively used as packed bed materials for the adsorptive removal of toxic metal ions present in industrial aqueous effluents under flow or dynamic conditions.

1. Introduction

Recently, graphene-based materials have attracted a great deal of interest as an adsorbent for environmental remediation applications, primarily because of its chemical reactivity, large surface area, and stability in aqueous medium over a wide pH range [1,2]. The graphene-based adsorbents have also been used for the removal of toxic metal ions from wastewater.

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Adsorption capacity of graphene/graphene oxide (GO) has been determined to be extremely high (70–120 mg/g) for several metals, attributed to the ion exchange and electrostatic attraction [3–5]. Graphene has been functionalized with iron (Fe) nanoparticles (NPs) to increase its adsorption capacity for aqueous metals via strong binding affinity of the protonated/deprotonated Fe-oxide surface for metal ions [6,7]. Graphene has also been chemically functionalized with various reagents such as pyrrole and amines with a view to augmenting its adsorption capacity for metals [2,8,9]. Nano/micron size of the material, however, critically impedes its practical applications under flow conditions. Therefore, there is a need to provide a suitable support to graphene for its practical use as an adsorbent for wastewater treatment.

A literature review shows that hydrogel/aerogel-supported graphene or graphene oxide (GO) has been synthesized in various shapes including bead, sponge, disk and rod for the removal of aqueous metals. For example, biodegradable and biocompatible alginate- [10] and chitosan [11] beads encapsulating GO have been synthesized for the adsorption of Cu(II) ions. Vu et al. encapsulated magnetic GO in the alginate beads so that the spent materials can be magnetically separated from water [12]. Polymeric materials such as cellulose, chitosan and siloxane-supported graphene/GO materials have been synthesized in the sponge [13] and disk [14,15] forms for the removal of metal ions from water. A major drawback of such substrates, however, is that these are highly pH sensitive. Therefore, chemical stability is a concern in using polymeric materials in water. Chitosan dissolves at acidic pH, whereas alginate dissolves at high or basic pH [16]. Also, alginate shrinks at acidic pH. In some hydrogels or aerogels, stacking of graphene layers has been shown to block the active adsorption sites [11]. Moreover, the supported graphene materials exhibit significantly lower adsorption capacity than the un-supported graphenes. Carbon-supported graphenes is a potential alternative to polymer-supported graphenes.

Carbonaceous materials are environmentally benign, chemically stable and highly porous. Surprisingly, only a very few carbon-supported graphenes have been synthesized for wastewater remediation applications [17,18]. Specifically, Bogatyrov et al. used the polymerization-pyrolysis method to synthesize the spheres of carbon-graphene composite for the removal of explosives, namely, nitramines, nitrate esters and nitroaromatics from water by adsorption [17]. Wei et al. were the first to prepare a metal-carbon-graphene composite by doping RF gel with a Ni metal. The composite material was used for the removal of oil and a few organic solvents from water [18]. In this composite, Ni served as a catalyst as well as a crosslinker, and helped to sustain the porous structure of the adsorbent material during pyrolysis. The metal itself, however, did not play any role in adsorption, and the organic compounds were removed via π-π interactions between the surface functional groups of carbon and organic molecules. It follows that choice of a metal to be doped in the carbon-supported graphene is critical. (1) It should maintain the structure/shape of the RF gel, post-carbonization or pyrolysis. (2) The metal should increase the mechanical strength of the composite to be used as packed bed materials, and (3) the doped metal should serve as an adsorbent site for aqueous metals to be removed from water. The metal should also possibly act as the catalyst for the RF gel polymerization.

The present study describes the synthesis of the chemically stable and mechanically strong carbon gel-supported Fe-graphene disks for the removal of aqueous Cr(VI) and Pb(II). These metals, used as the model solutes in the study, are commonly found in aqueous effluents of acid battery manufacturing plants and electroplating and tannery industries, and are considered to be highly toxic posing serious problem to human health and ecosystems [19–21]. The following section describes the preparation of the adsorbent materials. The subsequent sections describe the physico-chemical properties and adsorption behaviour of the materials. The multiple roles of the *in situ* doped Fe in the carbon-graphene composite are elucidated. A plausible reaction mechanism for the adsorption of Cr(VI) and Pb(II) metals in water is proposed.

2. Materials and methods

2.1. Chemicals

All reagents used in this study were of analytical grade. Resorcinol, formaldehyde, iron nitrate, sodium nitrate, sulphuric acid, potassium permanganate ($KMnO_4$), hydrogen peroxide and hydrogen chloride (HCl) were purchased from Merck, Germany. The graphite rods, used as the precursor for synthesizing GO, were purchased from Sigma-Aldrich (Germany). Nitrogen (N_2) gas having 99.999% purity was purchased from Sigma Gases (India). All samples were prepared using Milli-Q water.

2.2. Synthesis of GO

Graphite rods (750 mm long × 12 mm diameter) were crushed into small pieces using 1.0 lb-hammer and milled for 9 h in a ball mill (Retsch, Germany) to produce the graphite powder. The GO was synthesized by the oxidation of graphite powder using the Hummers method. Briefly, graphite powder (2 g), sodium nitrate (1.5 g) and H_2SO_4 (75 ml) were mixed in a glass beaker, using a magnetic stirrer (speed = 100 rpm). An ice bath was used to prevent the temperature of the mixture from increasing because of oxidation. Approximately 9g of $KMnO_4$ was slowly mixed into the reaction mixture. After approximately 2 h, the ice bath was removed and the mixture was kept for 7 days at room temperature (~30 °C). Stirring was continued. The colour of the mixture changed from dark green to brownish grey during oxidation. Next, 100 mL-volume of 5% H_2SO_4 was mixed into the reaction mixture. The reaction mixture was continuously stirred for 1 h. Approximately 4–5 ml of 30% H_2O_2 was mixed dropwise into the mixture until the colour changed from brownish grey to brilliant yellow. The produced GO-containing suspension was washed to remove SO_4^{2-} from the suspension. The SO_4^{2-} ions were removed from the GO suspension by mixing it with 1 M HCl solution. The mixture was centrifuged at 8000 rpm for 40 min. The supernatant was discarded and the residual was re-washed. The step was repeated five times. The removal of SO_4^{2-} from the suspension was confirmed using ion chromatography. Next, chloride ions were removed from the suspension using the same procedure as above, i.e., washing with Milli Q water, until the mixture became muddy [22]. The mixture was dried at 60 °C for 24 h. Next, GO was dispersed in Milli Q water and ultra-sonicated to produce a suspension of exfoliated GO.

2.3. Synthesis of carbon gel-supported Fe-graphene

Resorcinol-formaldehyde (RF)-based hydrogel was synthesized via sol gel polymerization technique. Scheme 1 illustrates the synthesis steps for Fe-G/RF(C). Approximately 25 g of $Fe(NO_3)_3{\cdot}9H_2O$ used as a precursor for Fe(III) was mixed into the exfoliated GO suspension (25 mg/25 mL). Next, resorcinol (0.674 g) and formaldehyde (1.020 g) were mixed into the Fe-GO suspension under gentle stirring conditions to prepare a homogeneous mixture. The Fe-GO/RF mixture was transferred into a cylindrical Teflon container and ultra-sonicated at 60 °C. The mixed Fe(III) in the reaction mixture served as the polymerization catalyst. A brown colour gel was produced after approximately 2 h. The gel