Journal of Industrial and Engineering Chemistry 30 (2015) 14–19

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Short communication

Removal of heavy metal ions from pharma-effluents using graphene-oxide nanosorbents and study of their adsorption kinetics

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ARTICLE INFO

Article history:
Received 12 March 2015
Received in revised form 4 June 2015
Accepted 6 June 2015
Available online 14 June 2015

Keywords:
Graphene-oxide
Pharma-effluent
Atomic absorption spectroscopy
Industrial waste water

ABSTRACT

Nanomaterials open up enormous opportunities in the areas of industrial waste water treatment and their application. Effective removal of toxic heavy metal ions like Pb(II), Ni(II) and Cr(VI) from pharmacy waste-effluent using graphene-oxide(GO) nanosorbents is reported here. Cr and Pb ions are completely removed by GO, however Ni ion trace was gradually decreased when GO concentration was increased. The concentration of GO at 70 mg removes all heavy metal ions effectively with the permissible pH of 8.00 and very low conductivity of 0.027 dS/m in 100 mL effluent, studied using atomic absorption spectroscopy. Also the adsorption isotherm models and adsorption kinetics are discussed.

Introduction

Nanomaterials utilization for industrial applications has been increasing rapidly in the recent years. Heavy metals are considered with great concern because of their extreme toxicity even at their low concentration, tendency of accumulation in organisms or food chain and its pollution. The indiscriminate disposal of wastewater is a worldwide environmental concern as it has many negative impacts on human health. Wastewaters from many industries such as metallurgical, mining, chemical manufacturing and battery manufacturing industries contain many kinds of toxic heavy metal ions [1]. Due to the discharge of large amounts of metal-contaminated wastewater, heavy metals such as *Cr*, *Ni*, *As*, *Pb* and *Cd* are the most hazardous among the chemical-intensive industries [2]. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. Traditional techniques for the elimination of heavy metal ions include precipitation, membrane filtration, ion exchange, flotation and electrochemical deposition. These processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge [2]. Recently, a large interest and particular focus are given to innovative physico-chemical removal process such as adsorption. Recently, few studies reported on the removal of heavy metal ions by using mesoporous carbons, polydopamine-mediated surface functionalized graphene, porous magnetic silica composite, nanocomposite hydrogels and electrocoagulation [3–10].

In recent years, adsorption has become one of the alternative treatments for cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of treated effluent [11]. Adsorption techniques have become an attractive way to remove heavy metals from wastewater considering their low cost and high efficiency [12]. Treatment techniques should be not only suitable, appropriate and applicable to local conditions, but also able to meet the maximum contaminant level (MCL) standards established as given in Table 1 [13]. Many sorbent materials have been studied extensively to remove heavy metal ions that suffer from either low-sorption capacities or efficiencies [14–22]. Although many techniques can be employed for the treatment of waste-water laden with heavy metals, it is important to note that the selection of the most suitable treatment for metal-contaminated wastewater depends on some basic parameters such as pH, initial metal concentration, the overall treatment performance compared to

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http://dx.doi.org/10.1016/j.jiec.2015.06.005
1226-086X/

Table 1
MCL standards of most hazardous heavy metals.

Heavy metals	Toxicity	MCL (mg/mL)
Arsenic (As)	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen	0.01
Chromium (Cr)	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper (Cu)	Liver damage, Wilson disease, insomnia	0.25
Nickel (Ni)	Dermatitis, nausea, chronic asthma, coughing, carcinogen	0.20
Zinc (Zn)	Depression, lethargy, neurological signs and increased thirst	0.80
Lead (Pb)	Damage of fetal brain, diseases of kidneys, circulatory & nervous system	0.006
Mercury (Hg)	Rheumatoid arthritis, diseases of kidneys, circulatory and nervous	0.00003

other technologies, environmental impact as well as economics parameter.

Nanomaterials have gradually developed important roles to resolve this problem because of their high surface area, enhanced active sites, and abundant functional groups on the surfaces [23]. Graphene is an atomically thin two-dimensional carbon based nanomaterial that is composed of sp^2 hybridized carbon atoms as found in graphite. Most forms of graphene used in different applications are pristine graphene, graphene oxide (GO) [24], and reduced graphene-oxide. Unlike carbon nanotubes, graphene requires special oxidation processes to introduce hydrophilic groups to improve metal ion-sorption. The preparation of GO nanosheets from graphite using modified Hummer's method introduces many oxygen-containing functional groups such as –COOH, –C=O, and –OH, on the surfaces of GO nanosheets. These functional groups are essential for the high-sorption of heavy metal ions. Considering the oxygen-containing functional groups on the GO surfaces and high surface area (theoretical value of 2620 m^2/g), the GO nanosheets should have high-sorption capacity in the pre-concentration of heavy metal ions from large volumes of aqueous solutions [23].

In this paper, we report the synthesis of GO by using modified Hummer's method and their application for the removal of heavy metal ions such as Pb(II), Ni(II) and Cr(VI) from pharma effluents (collected from *Ukkadam* area, Coimbatore, Tamil Nadu, India). The novelty of this work includes the complete removal of heavy metal ions from pharma-effluent with low adsorbent dosage of GO nanosheets. The equilibrium adsorption isotherm models such as *Langmuir* and *Freundlich* models are discussed in detail in order to understand adsorption kinetics. Materials and methods section describes about the materials and methods in which a detailed methodology for synthesis of GO nanosheets is given. In the Results and discussion section, we present the results and discussion in which a quantitative and qualitative analysis of GO nanosheets including Raman, X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscopy (SEM), batch experiments, effect of solution pH on adsorbent dosage, effect of electrical conductivity (EC) on adsorbent dosage, and effect of heavy metal ion concentration on adsorbent dosage by atomic absorption spectroscopy (AAS) against the concentration of adsorbent dosage are discussed in detail. To the best of our knowledge, this is the first work reporting on removal of heavy metal ions from pharma effluents using GO as nanosorbent materials on real time basis.

Materials and methods

Materials

The expandable graphite powder (acid washed), potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), hydrogen peroxide (H_2O_2), and hydrochloric acid (HCl) were purchased from Sigma Aldrich. All the chemicals used in this experiment were research grade. Deionized water was used throughout the experiment.

Synthesis of graphene-oxide nanoparticles

The GO nanoparticles were synthesized by modified Hummers method in which expandable graphite powder was used as the starting material. The process flow chart from graphite to GO is given in Fig. 1. The structure and properties of GO depend on the proper synthesis procedures and degree of oxidation. Briefly, the graphite powder (2 g) and sodium nitrate (2 g) were stirred together in 95% H_2SO_4 (90 mL) for 4 hrs. $KMnO_4$ (12 g) was gradually added into this solution while keeping the temperature less than 10 °C. The mixture was then stirred for 1 h and the same was diluted with slow addition of water (184 mL). This mixture was then stirred at 35–40 °C for 2 h until it becomes pasty brown.

Further, this solution was kept in a reflux system at 50 °C for 10 min and to 30 °C for next 10 min. The same solution was kept at 25 °C for 2 h under stirring. The reaction was terminated by addition of 200 mL of distilled water and 48% of H_2O_2 solution (40 mL). The mixture was washed by repeated centrifugation with 10% HCl aqueous solution followed by deionized water until the pH of the solution becomes neutral and the same was then sonicated. The precipitate obtained is dried at 60 °C for 24 h to get GO nanoparticles as shown in Fig. 2(a).

Results and discussion

Characterization techniques

The UV–vis spectroscopy analysis for GO nanoparticles was performed using spectrophotometer (Hewlett Packard HP-8453). X-ray diffraction characterization was performed on X-ray diffractometer system (Shimadzu model, XRD 6000) with Cu-*K*α radiation in the range of 20–70° (λ = 1.5418 Å). FT-IR spectroscopy measurement was conducted in FT-IR spectrometer (Model: Bruker IFS 66/S). The molecular morphology of carbon and its ordered carbon bonding was characterized using Raman spectroscopy. The surface morphology of the prepared GO was analyzed using field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). The alkalinity of the GO treated effluent was measured using pH instrument. The

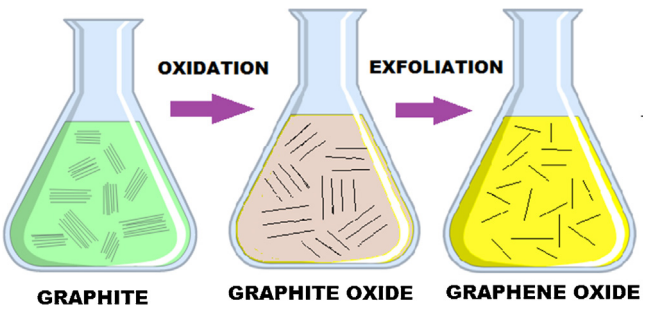

Fig. 1. Process flow from graphite to graphene-oxide.