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Chitosan coated magnetic nanoparticles as nano-adsorbent for efficient removal of mercury contents from industrial aqueous and oily samples

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ABSTRACT

Chitosan coated magnetic nanoparticles have been synthesized and developed as highly efficient nano-adsorbent for the removal of Hg^{2+} ions from industrial aqueous and oily samples. TEM, DLS, UV–vis, FTIR spectroscopy, VSM and zeta-potential techniques were applied for characterization of nanoparticles. The results confirmed formation of narrow dispersed nanoparticles with mean diameter about 10 nm. The effects of experimental conditions such as, pH, temperature, nano-adsorbent dosage and the concentration of chitosan on the removal ability were investigated. In order to regenerate of adsorbent, some eluents were used for desorption of mercury ions and the best results were achieved using EDTA and H_2SO_4.

Introduction

The spread of a wide range of contaminants in surface water and groundwater has become a critical issue worldwide, due to the population growth, rapid development of industrialization and long-term droughts [1]. Heavy metal ions such as Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, and Cu^{2+} are very harmful environmental pollutants because they are highly toxic at low concentrations and can accumulate in living organisms, causing several disorders and diseases [2,3].

Among these ions, Hg^{2+} is considered to be one of the most dangerous since it can be accumulated in the human body and causes a wide variety of symptoms, such as headache, edema and anema, even at quite low concentrations. It is also, especially severe for children's growth. Main contamination sources of mercury include chloro-alkali plants, waste battery, oil refinery, paint production, pharmaceutical, paper/pulp, gold mining, solid waste incineration, fossil fuel combustion, and chemical manufacturing [3–5].

Also, crude oil and liquid condensate produced around the world can contain small quantities of mercury. The mercury contents in the condensate range from nil to over 10 ppm. In processing the condensate, the mercury deposits in the processing unit to cause concerns in corrosion, operation safety and health safety of personnel. The mercury deactivates can shorten the life of hydrogenation catalysts in the processing, part of the mercury can also end up in the wastewater, causing contamination of the refinery site and, particularly, the wastewater treating facilities including the settling pond [6–8]. Also, the mercury in the oil and condensate can be emitted in air upon combustion, causing concerns in air pollution. To protect the equipment and the environment, it is desirable to remove the mercury from the condensates and the crude oils or reduce it to levels that are as low as possible as soon as they arrive at the refinery. In the submitted US EPA Mercury Report to Congress [9], combusted hydrocarbons are identified as major anthropogenic sources of mercury emissions to the atmosphere in the US. Water discharges from refineries and petrochemical plants have been identified as sources of aquatic mercury contamination.

So, according to the development of industrialization in twenty-first century, the removal of mercury in water and wastewater is crucial. The main techniques that have been used on metal content reduction from industrial waste are chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, solvent extraction, and adsorption. However, these methods are limited by high operational cost and/or may also

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be inefficient in the removal of some toxic metal ions, mainly at trace level concentrations [2]. Among all above methods adsorption was known as a highly effective and economical technique [10,11].

To date, many novel adsorbents, such as nanomaterials, ion imprinted material, mesoporous materials, carbon nanotubes and magnetic nanoparticles have been employed. Nanometer-sized materials are the just kind of new adsorbents and have gained much attention. Because of their distinct chemical, physical and biological properties and due to their high surface to volume ratio, they are able to adsorb metal ions with high adsorption capacity [12,13].

The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years. Magnetic adsorbents can be used to adsorb contaminants from aqueous or gaseous effluents [14,15]. After the adsorption is carried out, the adsorbent can be separated from the medium by a simple magnetic process. These adsorbents have a variety of surface functional groups which can be tailored for use in specific applications [1,2,8,9]. The recent successful synthesis of monodispersed magnetic nanoparticles, particularly iron oxide nanoparticles, provides a convenient tool for exploring magnetic separation techniques. Because they have the capability to treat large amounts of wastewater within a short time and can be conveniently separated from wastewater. Moreover, they could be tailored by using functionalized polymers, novel molecules, or inorganic materials to impart surface reactivity [16]. It is believed that magnetic nanoparticles (MNPs) exhibit the finite size effect or high ratio of surface-to-volume, resulting in a higher adsorption capacity for metal sorption. Furthermore, there are no diffusion limitations, since the available surface is totally external as the MNPs are nonporous. Thus, an efficient, economic, scalable and non-toxic synthesis of Fe_3O_4 nanoparticles is highly preferred for potential applications and fundamental researches. However, bare magnetic particles are prone to form aggregates and their magnetic properties can be altered in complex environmental and biological systems [17]. In order to improve the stability and biocompatibility, the superparamagnetic iron oxide nanoparticles are often modified with some surfactants or polymers. The superparamagnetic Fe_3O_4 nanoparticles coated with polymers are usually composed of the magnetic cores to ensure a strong magnetic response and a polymeric shell to provide favorable functional groups and features [18]. Numerous types of magnetic nanoparticles for heavy metals removal could be tailored by using functionalized natural or synthetic polymers to impart surface reactivity [19]. Recently, removal of mercury from water samples has been carried out by solid phase extraction (SPE) techniques using different adsorbents [20–30], and also magnetic adsorbent [4,31–35].

The application of biopolymers such as chitin and chitosan is one of the emerging adsorption methods for the removal of dyes and heavy metal ions, even at low concentrations [36]. chitosan is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin. chitosan is known as an ideal natural support with many useful features such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. The preparations of chitosan coated iron oxide nanoparticles by a coprecipitation method, crosslinking method, and covalent binding method using coupling agents have been reported [37–39].

In the present work, chitosan-coated iron oxide nanoparticles were prepared and characterized using different techniques such as transmission electron microscopy (TEM), dynamic light scattering (DLS), Fourier transform infrared (FT-IR), UV–visible spectroscopy, vibration sample magnetometer (VSM), and Zeta-potential analyzer. The removal ability of as-prepared nanoparticles was investigated by determining the mercury contents of the synthetic and industrial samples using inductively coupled plasma (ICP) method. The results obtained at optimum conditions of pH, temperature and adsorbent dosage show that this nano-adsorbent can be used efficiently and economically for the removal of mercury from industrial samples. The results showed that these nano-adsorbents could remove mercury ions during less than 5 min with high adsorption loading capacities, which is more efficient than the other reported works.

To the best of our knowledge, mercury removal from industrial wastes by using this kind of nano-adsorbent is new. Also, we could not find any other reports on the removal of mercury from oil samples using this kind of nano-adsorbent. In addition, this nano-adsorbent was found to be stable and have good reusability with no appreciable loss in activity over several cycles. Therefore, the problem of phase separation associated with conventional separation techniques can be solved. Compared to the traditional micron-sized supports used in separation process, nano-sized adsorbents possess quite good performance due to high specific surface area and the absence of internal diffusion resistance.

Since, chitosan can be extracted from chitin exist in some hard shell animals' skins like shrimp, this nano-adsorbent can be scale up economically.

Experimental

Materials

Chitosan, ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), Ammonium hydroxide (NH_4OH), monochloroaceticacid (CH_2ClCO_2H) and mercury nitrate ($Hg(NO_3)_2$) were purchased from Merck and Carbodiimides (cyanamide, CH_2N_2) were purchased from Aldrich. All chemicals were the guaranteed or analytic grade reagents commercially available and used without further purification.

Apparatus

The magnetite nanoparticles were characterized by transmission electron microscopy (TEM-Philips, CM10), Fourier transform infrared spectroscope (FT-IR-Perkin-Elmer, RX1), dynamic light scattering (DLS-HORIBA L-550), vibration sample magnetometer (VSM-Meghnatis Daghighe Kavir(MDK)), UV–vis spectrophotometer (Shimadzu UV-1800), zeta-potential analyzer (ZEN 3600, Malvern)and inductively coupled plasma (ICP-Varian, vista-pro).

Preparation of chitosan-bound Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared by co-precipitation of the $Fe^{3+}$and Fe^{2+}ions by ammonia solution and treating under hydrothermal conditions [40]. Chemical precipitation was achieved at 25 °C under vigorous stirring by adding NH_4OH solution. The precipitates were heated at 80 °C for 30 min, washed several times with water and ethanol, and then finally dried in a vacuum oven at 70 °C.

Since chitosan has no suitable functional groups to bind directly onto iron oxide nanoparticles, it was first carboxymethylated and then covalently bound onto iron oxide nanoparticles via carbodiimide activation. Chitosan was carboxymethylated according to the following method [41]. First, 3 g chitosan and 15 g sodium hydroxide were added into 100 ml of isopropanol/water (80/20) mixture at 60 °C to swell and alkalize for 1 h. Then, 20 ml of monochloroacetic acid solution (0.75 g ml^{-1} in isopropanol) was added into the reaction mixture in drops in 30 min. After reaction for 4 h at the same temperature, 200 ml of ethyl alcohol was added to stop the reaction. Finally, the solid was filtered, rinsed with ethyl alcohol to desalt and dewater, and dried in an oven at 50 °C.