

Simple, Rapid, And Efficient Water Purification By Chitosan Coated Magnetite Nanoparticles

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Abstract

Chitosan coated magnetite nanoparticles were prepared and used as adsorbent or chelating agent to remove organic contaminants, and heavy metals. The method is simple and rapid. The obtained results are promising, where the prepared particles are able to remove more than 90% and 60% from organic and inorganic contaminants respectively.

Keywords: chitosan, heavy metals removing, magnetic nanoparticles, organic contaminants

Introduction

Recent human life causes continuous accumulation of organic, inorganic, and biological contaminants in the environment. Purification of water has attracted the greater interest mainly due to the restricted quantities of water that can be safely used directly and the high cost of purification installations [1]. Many efforts have been reported in the literatures to clean wastewater either by chemical or biological methods [2-5].

Chitosan is a polysaccharide comprising copolymers of glucosamine that can be prepared by partial deacetylation of chitin [6]. Chitosan is known as an ideal natural support for enzyme immobilization due to its hydrophilicity, biocompatibility, biodegradability, non-toxicity and good adsorption properties [7]. In water treatment, chitosan has been used as an adsorbent to remove organic pollutants, heavy metals, and oils. Also chitosan has shown an antimicrobial activity [8-13].

Chitosan coated magnetite nanoparticles (CMNP) is a type of nanoparticles that contain a core of a magnetic material, usually a mixture of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) coated with thin chitosan layer [14]. The binding of chitosan onto Fe_3O_4 nanoparticles affords novel magnetic nano-adsorbent for the efficient

water purification. Where the nano-scale particles allow the highest surface area for adsorption and the magnetic core allows the easy separation of contaminated particles by applying outer magnetic field. This study introduces the using of CMNP as an efficient technique in water purification from different chemical and biological pollutants.

Materials and methods

Materials

Chitosan (low molecular weight, 85% degree of deacetylation) was purchased from Sigma–Aldrich (USA). FeCl₃, FeCl₂ copper sulphate, lead acetate and crystal violet were purchased from Merck (Germany). Crude petroleum oil was obtained from local sources.

Preparation of Fe₃O₄ nanoparticles

The magnetite (Fe₃O₄) nanoparticles were prepared by a chemical co-precipitation of Fe (III) and Fe (II) ions. An equal volumes of (0.2 mol/L) FeCl₂ and (0.3 mol/L) of FeCl₃ aqueous solution were mixed under the presence of N₂ gas. The solution was heated up to 60° C, then NH₄OH (25% w/v) was dropped into the mixture with vigorous stirring. The black precipitate that formed was collected by magnetic separation, washed several times with deionized water and finally dried at room temperature.

Preparation of chitosan coated Fe₃O₄ nanoparticles

0.5 g Chitosan solution was dissolved in 50 ml 2% (v/v) acetic acid. 10 ml of this solution was used to suspend 30 mg of MNPs. The mixture was vigorously stirred for 30 minutes then 2.5 ml NaOH (1N) was added drop wisely to precipitate the coated MNPs. The particles were magnetically separated, washed several times by deionized water and dried at room temperature under nitrogen stream.

Characterization

Structure and size of crystals were determined by XRD on a Rigaku MINIFLEX II X-ray diffractometer using Cu K α radiation ($\lambda = 1.540562$). TEM observation was performed on a microscope (JEOL JAM-2100-HR-EM).

Removing of oil spills

0.1 g crude petroleum oil was mixed with 10 ml water and different weight of CMNP (0.1 –1 g). The mixture was vigorously stirred for 60 minutes and allowed to stand for another few minutes. The contaminated CMNP was separated magnetically while the oil residue was extracted by hexane. The amount of remaining oil was determined by weighing the residual oil after hexane evaporation.

Removing of dyes

Dyes removal experiments were carried out in a 250mL flask while using crystal violet and methyl orange. 50 mL of solution pH 4, CMNP (0.1–1g), and pollutant concentration (0.05 g), were agitating at 100 rpm for 60 minutes. Aliquots were carefully withdrawn from the solution at various time intervals to determine the concentration of remaining dyes by measuring the absorbance at 590 nm for crystal violet, and 480 nm for methyl orange.

Removing of heavy metals

50mL of an aqueous solution of known metal concentration (0.1mmol/L) and (0.1 -1 g) of CMNP were incubated at room temperature under constant agitation rate 100 rpm and pH 4. Every 20 minutes, a small sample was taken from the flask to determine the metal concentration by flame Atomic Absorption Spectrophotometry (Buck scientific VGP 210). The amount of metal removed was calculated as per cent of initial concentration.

Results And Discussion

Synthesis and characterization of chitosan coated magnetite nanoparticles

From X-ray diffraction analysis and TEM Imaging (fig. 1), it is clear that we obtained Fe_3O_4 (magnetite) as a single mineral phase in nano average size 10-20 nm.

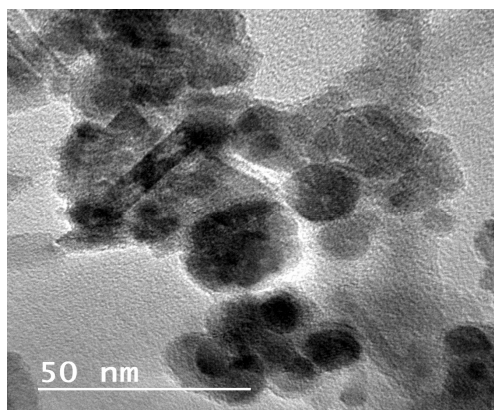


Figure 1: TEM images of magnetic nanoparticles

Removing of organic contaminants and heavy metals:

The presence of amino groups in chitosan structure leads to the binding of metal cations by formation of complexes or chelation. The protonation of these groups in acidic media causes high affinity for anionic compounds (metal anions, organic compounds, dyes)[7]. The acidic pH has been reported as the best condition for using chitosan as adsorbent [7-13]. So pH 4 was selected as an optimum pH for all experiments.

Effect of CMNP concentration

As shown in fig. 2, the adsorption capacities of the different contaminants considerably increased with CMNP concentration. The highest affinity was found with petroleum, where 1g of CMNP removed about 98% from it, while the lowest capacity was recorded by heavy metals that showed semi equal removing percentage.

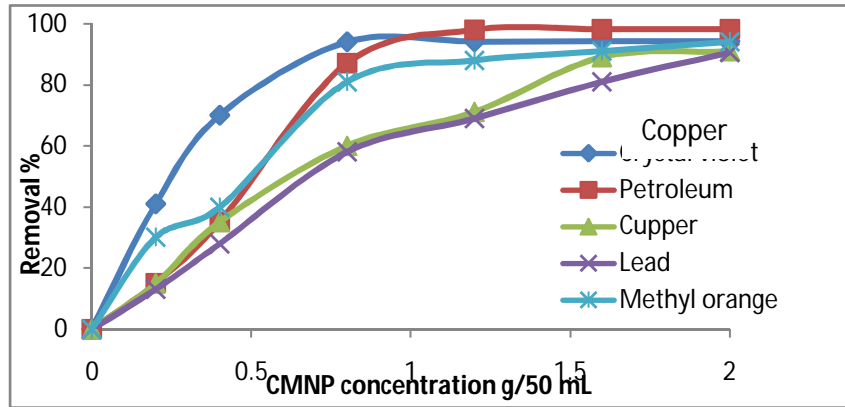


Figure 2: the relation between CMNP concentration and the removal % of different contaminants.

Contact time

The adsorption capacity showed a significant increase during the first 20 minutes and then gradual increase in% sorption by increasing shaking time till 40 minutes (fig 3). On the basis of this observation, a 40 minutes shaking time were found suitable for the maximum sorption.

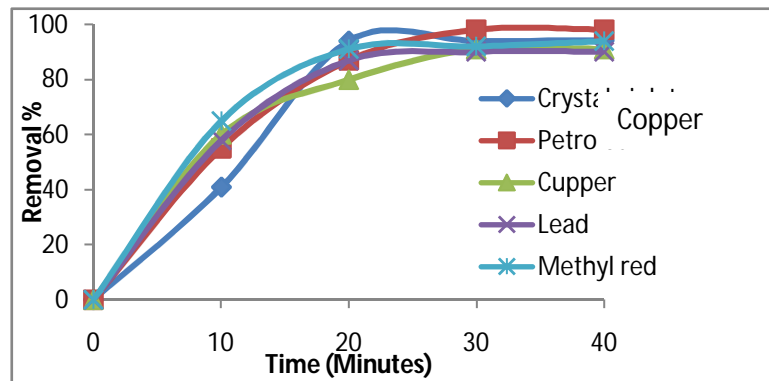


Figure 3: the relation between contact time and the removal % of different contaminants

Conclusion

Chitosan coated magnetite nanoparticles were synthesized and successfully used to remove different contaminants from water. The high capacity of the synthesized

particles, the process simplicity and material availability make CMNP an excellent tool for water purification. We recommend the investigation of using CMNP in treatment of wastewater from different source such as industrial and agriculture sources.

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