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# Performance study on sequestration of copper ions from contaminated water using newly synthesized high effective chitosan coated magnetic nanoparticles

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ABSTRACT

Chitosan coated magnetic nanoparticles (CMNP), a novel adsorbent active under a robust range of environmental conditions of pH and temperature have been employed as an effective adsorbent for the removal of copper ions from the wastewater and later which can be easily separated from the aqueous solution via magnetic separation. The novelty of the present research is the incorporation of the growing field of nanotechnology in wastewater treatment by adsorption as well as use of magnetic particles as a carrier for the adsorbent for more effective separation of the adsorbent from wastewater, by the mere application of an external magnetic field. The CMNP particles have been characterized by Fourier Transform Infrared Spectroscopy (FTIR), Energy dispersive X-Ray analysis (EDAX), and vibrating sample magnetometer (VSM) analyses. The adsorption experimental data were analyzed by Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan, Sips, Toth, Temkin and Dubinin–Radushkevich isotherms. Thermodynamic parameters were also evaluated and the sorption process was found to be energetically feasible, spontaneous and exothermic in nature, suggesting that the adsorption of Cu(II) ions onto CMNP was presumably physisorption. The spent adsorbent can be easily regenerated by treating it with 0.1 N HCl/NaOH solution followed by vigorous agitation.



## 1. Introduction

Untreated effluents and wastewater from industries and households are often attributed to environmental pollution and land degradation, exerting a large amount of strain on the environment, frequently detrimental to the ecosystem [1]. Wastewater containing heavy metals are of great concern due to their possibility to trigger metal toxicity in various life forms, including plants and lower microorganisms. Toxic metals can bio-accumulate in the body and in the food chain [2]. For example, when untreated effluents containing heavy metals are released into the environment, the metals can get incorporated into plants or marine animals. Animals including livestock and humans get affected by heavy metal toxicity when the level of accumulation becomes abnormally high. Not all heavy metals are toxic, some, such as iron is essential in appropriate levels for normal metabolism [3]. Also, a general feature of heavy metals is the persistent nature of their toxicity.

Copper is one such heavy metal and has widespread industrial applications such as wire and cable, integrated circuit and printed circuit boards, dyes, paints, motors and rotors, antimicrobial and biostatic and as a wood additive [4]. The divalent cation of copper [Cu(II)] ions is highly soluble in water and causes copperiedus, the consequences of copper toxicity which include acute symptoms of vomiting, hypotension, hematemesis and jaundice [5]. The chronic symptoms of copper toxicity are coma, liver cirrhosis and kidney failure. Safety guidelines dictate that the copper levels in drinking water be less than 0.05 mg/L as set by the Bureau of Indian Standards (BIS) [6]. Thus the removal of copper from water/wastewater and the treatment of industrial effluents have been of paramount importance.

Various techniques have been employed at both laboratory and industrial scale, such as, treatment with activated carbon [7], ion exchange [8], chemical precipitation [9] and membrane separation technology [10]. However such methods have been found to be ineffective and expensive when metal ions are present in low concentration. Also, industrial scale operations of such methods involve high energy requirement, equipment and skilled manpower. Such processes also contribute to generation of secondary wastes that are further difficult to process and treat.

Adsorption can be employed successfully to decontaminate wastewater which contains heavy metals [11]. Various inexpensive materials can be used to sequester heavy metals by the process of adsorption, which has various advantages over conventional treatment methods

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which include, the process being very cheap, environment friendly, absence of a chemical sludge and no requirement for skilled labor. The binding mechanism will vary based on the adsorbent, chemical nature of the adsorbate, pH, temperature and the ionic strength of the solution. However, adsorption processes have certain conditions such as, separation of adsorbate–adsorbent complex from the solution and regeneration of the adsorbent. This makes conventional adsorption using activated carbon [12] expensive, partly due to the need for regeneration of the adsorbate covered carbon particles and high efficiency filtration required to separate the minute particles from the solution. Thus, a number of non-conventional adsorbents are being worked upon that facilitate cost effectiveness and ease in separation. A number of low cost adsorbents such as wood [13], bagasse [14], pith [15], peanut hull [16], sawdust [17], fly ash [18], dehydrated wheat bran [19], seeds of *Capsicum annuum* [20], chitosan [21] coated with α-ketoglutaric acid particles [22] and fungal biomass [23]. Combining magnetic nanotechnology with biosorption provides a viable solution to the problem of separation of the adsorbent from the solution, as it can be easily separated by the application of an external magnetic field [24]. Some of the perks offered by such a robust adsorbent are easy separation of metal enzyme–adsorbent complex from the solution (Fig. 1), making its industrial application more cost effective with less fouling.

Chitosan, a biopolymer produced by deacetylation of the polysaccharide chitin, obtained from crustacean shells has proved to have a reasonably high metal sequestering capacity in solutions [25]. To facilitate ease in separation from the solution, chitosan is coated over magnetic nanoparticles (MNPs). Chitosan coated magnetic nanoparticles can be easily separated from the solution by the application of an external magnetic field, which attracts and immobilizes the chitosan entrapped magnetic particles in solution [24,26–27], following which the solution can be filtered using normal filtration technique. This paper primarily deals with the synthesis of magnetite nanoparticles followed by the surface modification of the synthesized MNPs with chitosan. The prepared chitosan magnetic nanoparticles (CMNPs) were employed to study the biosorption of Cu(II) ions from wastewater. The effects of various operating parameters such as adsorbent dosage, contact time, pH, temperature and initial metal ion concentration were studied for the removal of Cu(II) ions from the wastewater. The equilibrium isotherms, thermodynamics and kinetics of the biosorption process were also studied. Such a broad experimentation with the high adsorption efficiency of metal ions from the wastewater using CMNP has not been studied before, to the best of our knowledge.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals required for the synthesis of chitosan coated magnetic nanoparticles were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL) — Mumbai, India, which were of analytical grade. $CuSO_4 \cdot 5H_2O$ purchased from Merck, India was used to prepare the Cu(II) ion stock solution. Extra pure chitosan (medium molecular weight, 75–85% deactylated, molecular weight 400,000 Da) was used for the present studies. Neodymium magnets were purchased from Magna Tronix, Chennai, India. W.S Tyler Test sieve (45 μm, ASTM E11 specification) was purchased from Tyler sieves, Ohio, USA.

### 2.2. Synthesis of chitosan coated magnetite microparticles

Synthesis of chitosan coated magnetite nanoparticles (CMNP) was previously developed by our research groups [26]. The CMNP were dried at 70 °C in a hot air oven until it was completely dry, ground finely and sieved using 45 μm sieves. After sieving the particles were stored in an air tight container.

### 2.3. Characterization

The surface active functional groups present in chitosan, MNP and CMNP were determined using FTIR (Agilent Technologies Cary 660 FTIR spectrometer, USA). The elemental composition of the chitosan, MNP and CMNP particles to determine the ferrous content was done using energy dispersive X-Ray spectroscopy (EDX, FEI Quanta 200 FEG, USA). The extent of magnetization of the magnetite nanoparticles and chitosan coated MNP were determined using vibrating sample magnetometer (VSM, Lakeshore, USA, Model 7407). The concentration of Cu(II) in the experimental solutions was determined using atomic absorption spectroscopy (ELICO SL-176 Double beam AAS, India).

### 2.4. Adsorption experiments

Adsorption experiments were conducted in varying the operating conditions of solution pH, temperature, initial metal ion concentration, adsorbent dosage concentration and contact time with the aim of performing thermodynamic studies, estimating adsorption isotherm parameters and determining adsorption kinetics. The copper ion solution of 100 mL was taken in a series of 250 mL Erlenmeyer conical flasks. The pH of the test solutions were maintained at the fixed value by 0.1 N


**Fig. 1.** Real time representation of magnetic separation of CMNP in solution.

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