



Magnetic-epichlorohydrin crosslinked chitosan schiff's base (m-ECCSB) as a novel adsorbent for the removal of Cu(II) ions from aqueous environment



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ABSTRACT

Metal ions cause a serious public health problem. It is a great challenge to find an effective and efficient adsorbent to remove heavy metals from wastewater. Chitosan-based adsorbents are potential and effective for heavy metal ion removal. Hence a novel m-ECCSB was synthesized, characterized and utilized as an adsorbent for the removal of Cu(II) ions from aqueous solution. Various factors affecting the uptake behavior such as pH, adsorbent dosage, contact time, initial concentration of Cu(II) and temperature effect were investigated. Maximum adsorption capability (123.10 mg/g) was obtained at pH = 6, adsorbent dose of = 250 mg, rotational speed = 200 rpm, contact time = 60 min, and temperature of 323 K. The result of the kinetic study shows that the adsorption of Cu(II) could be described by the pseudo-second-order equation. Equilibrium data were analysed with the Langmuir, Freundlich and Dubinin-Radushkevich isotherms and Langmuir model was found to provide the best fit of the experimental data. The thermodynamic parameters showed that the adsorption of Cu(II) onto m-ECCSB was spontaneous ($\Delta G^\circ = -8.990, -10.00$ and -10.593 kJ/mol), endothermic ($\Delta H^\circ = 15.674, 15.478$ and 15.699 kJ/mol) and ΔS° (0.0814 J/mol K) suggests an increased randomness at the solid/solution interface under the studied conditions.

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1. Introduction

Water pollution due to the release of various toxic chemicals from industrialization and urbanization is a global problem. Among the various notorious toxic chemicals, heavy metals, dyes, organics and pharmaceuticals are of highly concerned [1–17]. Metal ions are one of the most important water pollutants that are toxic to humans through the food-chain pyramid. Toxic heavy metal ions discharged into the environment through different industrial activities constitute one of the major causes of environmental pollution [18]. Copper is a widely used metal in various industries such as pulp, paper board, leather preserving, petroleum refining, plating, mining, smelting, brass manufacture, electroplating industries and copper coating sand fittings [19,20] and have been known to cause severe mucosal irritation, widespread capillary damage, hepatic and renal damage, and central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [21]. The World Health Organization (WHO) recommended a maximum acceptable con-

centration of Cu(II) in drinking water of 2.0 mg/L [22]. Therefore, it is necessary to treat wastewater containing copper before being discharged into the water streams.

The conventional processes used to remove heavy metal ions from the contaminated environments include reverse osmosis, adsorption, complexation, electrochemical techniques, filtration, solvent extraction and precipitation, coagulation, reduction, membrane processes and ion-exchange [23–31]. These methods are either inefficient or expensive when heavy metal exists in lower concentrations. However, recent studies have shown adsorption to be the most promising technique for metal ions removal due to convenience, easy operation, simplicity of design, can remove different type of pollutants and the adsorbent can be regenerated by some desorption process [32]. Among the currently available sorbents, chitosan is considered as a promising choice for effectively removing or even recovering target heavy metals from water. Chitosan biopolymer is an interesting, attractive and more effective sorbents because of their unique characteristics like non-toxicity, hydrophilicity, biocompatibility, biodegradability and biofunctionality [33]. The presence of amine ($-NH_2$) and hydroxyl ($-OH$) groups, which may serve as coordination sites to form complexes with various heavy metal ions in neutral solutions, makes chitosan as an excellent natural adsorbent. Chitosan

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offers other promising advantages over many biosorbents because it is a cost-effective and eco-friendly natural polymer and can be easily modified by chemical reactions. Many biopolymer modified materials are used to remove Cu(II) from aqueous water such as polyaniline graft chitosan beads [34], magnetic chitosan chelating resins [35,36], Carbon nanocomposites [37], chitosan-modified poly(methacrylate) nanoparticles [38], xanthate-modified magnetic chitosan [39], and L-arginine modifying magnetic chitosan [40]. However, the exploration and development of new adsorbents is endless. In this way many chitosan derivatives have been synthesized, by incorporating new functional groups onto chitosan backbone, with the aim of improving its adsorption capacity.

Different kinds of cross-linking agents such as glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether have been used in cross-linking reaction of chitosan. In this article, in order to enhance the metal (Cu(II)) uptake by chitosan, a novel modified adsorbent material has been synthesized, by the cross linker (epichlorohydrin) with the chitosan. However, an advantage of epichlorohydrin is that it does not eliminate the cationic amine function of chitosan [41,42]. Hence the amine groups were modified with thiophene-2-carboxaldehyde to introduce additional functional groups (sulphur) on the surface of the chitosan. Finally magnetic iron oxide nanoparticles were introduced into the polymer solution for enhancing the uptake of Cu(II) from aqueous solution. Nanoparticles are having high adsorption capacity due to its large surface area with smaller size. In this connection the utilization of nanoparticles are having greater attention in metal ion removal process. To the best of the authors knowledge, there is no investigation reported in the literature on the removal of Cu(II) by using m-ECCSB.

The purpose of this study is to synthesize, characterize and application of a novel m-ECCSB as an adsorbent material for the removal of Cu(II) ions from aqueous environment by batch adsorption system. In this regard, the present study is focused on the investigation of the effects of pH, agitation speed, adsorbent dosage, contact time, initial concentration and temperature on the adsorption efficiency of Cu(II) ions onto m-ECCSB. The pseudo-first-order, pseudo second-order and intraparticle diffusion kinetic rate equation were used to describe the kinetic adsorption process. Langmuir, Freundlich and D-R isotherm models were used to describe equilibrium isotherm data for the adsorption of Cu(II) onto m-ECCSB. Thermodynamic parameters such as standard Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were also studied for the removal of Cu(II) onto m-ECCSB.

Moreover m-ECCSB is economically attractive because preparation is easy, inexpensive and may be widely applicable for industrial ambience. It also offers minimization of chemical and biological sludge, and no additional nutrient requirements. On the economical front application and efficiency m-ECCSB proves to be a better adsorbent for the removal of Cu(II) ions from aqueous environment.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade. Chitosan with a degree of deacetylation of 90% was purchased from Tianjin umbrella science and technology Co., Ltd, China. Epichlorohydrin, thiophene-2-carboxaldehyde (Shanghai Macklin Biochemical's), HNO₃, HCl, glacial acetic acid, and NaOH were purchased from Tianjin guangfu technology development Co., Ltd, China. Cu(NO₃)₂·3H₂O were also obtained from Tianjin guangfu technology development Co., Ltd, China. FeCl₃·6H₂O (Aladdin industrial corporation, shanghai), FeCl₂·4H₂O was pur-

chased from the Sinopharm Chemical Reagent Co. Ltd. Double distilled water was used throughout the experiments.

2.2. Adsorbate preparation

The Cu(II) stock solution was prepared by dissolving the required amount of Cu(NO₃)₂·3H₂O in some double distilled water and making volume up to 1000 mL using distilled water. Cu(II) solutions of different concentrations (20–160 mg/L) were prepared by adequate dilution of the stock solution with distilled water.

2.3. Adsorbent preparation

2.3.1. Synthesis of Fe₃O₄ nanoparticles

Iron oxide nanoparticles were synthesized by an alkaline coprecipitation method and the process was depicted in Scheme 1A. FeCl₃·6H₂O (6 mmol, 1.622 g) and FeCl₂·4H₂O (3 mmol, 0.597 g) were dissolved in deionized water (200 mL). After stirring for 40 min at 320 K, 100 mL NaOH solution (0.24 mol/L) was added to the resulting complex drop wise. After adding base to the solution containing the iron salts, the resulting solution were stirred (350 K) for 45 min and turned into a black color. The black color precipitate were separated with a permanent magnet and washed 3 times with deionized water. Then Fe₃O₄ particle was oven dried at 370 K for 24 h. The dried Fe₃O₄ nano material kept in the glass vial for the characterization and further crosslinking studies.

2.3.2. Synthesis of m-ECCSB

To prepare ECCSB (epichlorohydrin crosslinked chitosan schiff's base), 2.0 g of chitosan was dissolved in 100 mL of 5% acetic acid solution under vigorous stirring at 30 °C for 1 h. To this 2.0 mL of epichlorohydrin was slowly added into the solution for cross-linking. The crosslinking reaction might be carried out between the hydroxyl groups of chitosan with the epichlorohydrin. ECH is a crosslinking mono-functional agent used to form covalent bonds with the carbon atoms of the hydroxyl groups of chitosan, resulting in the rupturing of the epoxide ring and the removal of a chlorine atom. Then 2.0 mL of thiophene-2-carboxaldehyde was added was added into the ECC solution and the mixture was kept at 70 °C to undergo cross-linking. Cross-linking reaction occurred for 12 h under vigorous stirring. thiophene-2-carboxaldehyde cross-links with epichlorohydrin crosslinked chitosan through Schiff's base formation between the free amino groups of chitosan and aldehyde groups of thiophene-2-carboxaldehyde as presented in Scheme 1B.

The preparation of magnetic ECCSB was carried out according to the following procedures; 2 g of the previously prepared iron oxide nanoparticles were added to the ECCSB (epichlorohydrin crosslinked chitosan schiff's base) solution and stir it to form a uniform dispersion system. A black hydrogel (m-ECCSB) was obtained and broken into smaller pieces with a spatula. Then the gel was washed with deionized water at least 3 times to remove the unreacted reagents. Finally, the resin was then dried in an oven at 60 °C for 24 h and kept in a vacuum desiccator for further analysis and use.

2.4. Analytical studies

X-ray Diffraction analysis was carried out in the 2θ range of 0–90° with Cu Kα radiation to identify the crystalline/amorphous forms of the pure chitosan, Fe₃O₄ and m-ECCSB. The presence of functional groups was identified using a Perkin Elmer 2000 FT-IR with KBr pellets in the range of 4500–400 cm⁻¹. The scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed using a Hitachi-S-4800, Philips Tecnai G2 F30 ST instrument to identify the surface morphology and elemental composition. The transmission electron microscopy (TEM)

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