



Removal of divalent manganese from aqueous solution using glycine modified chitosan resin



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ABSTRACT

Removal of Mn(II) ions from aqueous solution through adsorption on glycine modified chitosan resin (G@Chs) has been studied. Experiments were carried out as a function of pH, concentration of metal ion and contact time. Optimum Mn(II) uptake was observed at pH 6 and most of the Mn(II) were sorbed within 150 min. The isothermal data correlated with Langmuir model better than Freundlich model. Thermodynamic data indicated that adsorption process is exothermic and spontaneous reaction, while the kinetic data indicated that the adsorption follows the pseudo second order kinetics. The adsorption capacity of glycine onto modified chitosan resin was found to be 1.3 mmol/g, at 25 °C ± 1. Due to their outstanding adsorption capacities, G@Chs resin is an excellent adsorbent for the removal of Mn(II) ions. The resin regeneration was greater than 93% with 1.0 M HCl, and G@Chs could be repeatedly utilized for Mn(II) removal with negligible loss in sorption capacity.

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Introduction

Removal of heavy metal ions from various water resources has been a crucial issue. Heavy metals are generally present as pollutants in a variety of industrial effluents. Industries such as metal plating, metal finishing, rubber processing, fertilizers, mining as well as agriculture release these heavy metals into the surface and ground water [1]. Manganese is one of the important heavy metals found in groundwater, wastewater etc. Manganese can impair the quality of water from dual sources, natural and manufactured. Manganese can be present in water as a result of mineral dissolution and/or leaching from some rock and soils [2]. It could also be as a result of pollution emanating from industrial operations such as pyrolusite (MnO₂) treatment, steel alloy dry cells, glass and ceramics, paint and vanish, ink and dyes, metal galvanization plant effluents etc. [3]. Heavy metals such as Mn²⁺ are not biodegradable and thus tend to mount up in living organisms through the use of the heavy metal impaired water, and eventually causing various diseases and disorders [4]. Manganese is an oligo-element necessary for human survival but become toxic when the concentrations become too high in human body. It is

known that an excess Mn(II) in portable water causes problems in respiratory system and in the nervous system; it concentrated in brain especially in the basal ganglia, resulting in neurological disorders [5], and several reports are available on the effects of exposure to Mn(II) in water [5–7]. According to the World Health Organization, the maximum acceptable drinking water concentration in drinking water is 0.05 mg/L for manganese [8]. While the Egyptian legislation sets a limit of 0.4 mg/L for manganese [9]. It is therefore, necessary to proceed with the treatment of water contaminated by excess manganese so as to reduce their impact on the environment and to the human health. Different adsorbent have been carried out for adsorption of manganese ions: calcium silicate [10], clay [11], activated carbon [12], nut shells of *Tamarindus indica* [13], volcanic ashes [14] etc. In recent years, researchers have extensively focused on research into biosorbent such as chitosan because of its desirable properties like nontoxic, inexpensive, biocompatible and bio-functionality including antithrombogenic, homeostatic, and wound healing properties, antibacterial property and its low cost efficient [15–19]. Chitosan is a natural polymer derivative from *N*-deacetylation of chitin in alkaline medium [20]. It is the second most abundant aminopolysaccharide found in nature after cellulose. It is constituted of both glycosamine and acetylglucosamine moieties. Chitosan has been widely applied to the fields of food and pharmacy processing biotechnology and analytical chemistry. Chitosan shows high affinity for metal ions due to the amine and hydroxyl groups. These

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groups function as the coordination sites for heavy metal ions [21]. The removal of heavy metals (Cu, Ni, Co and Mn) was increased by the introduction of amino acids to chitosan, especially for Mn [22]. In this work, we synthesized chelating resin possessing glycine moieties, by using a cross linked chitosan as a base material for removal of Mn(II). The influences of the experimental parameters such as pH, temperature, contact time, initial concentration on adsorption will be studied. The kinetic models used to describe the rate data will be discussed. Both Langmuir and Freundlich isotherm models will be discussed, also the equilibrium isotherm modeling data and thermodynamic parameters will be calculated. Desorption studies will be carried out using suitable agents to regenerate the spend adsorbent.

Experimental

Chemicals

Chitosan, glycine, glutaraldehyde, dioxane, epichlorohydrin and manganese sulfate monohydrate were Aldrich products. All other chemicals were of analytical grade obtained from Merck Ltd., Germany and were used as received.

Surface modification and cross-linking of chitosan

Three grams of chitosan was dissolved in 20% aqueous solution of acetic acid and stirred until the solution became homogenous. Then 2 mL of glutaraldehyde solution (25%) was added, the obtained chitosan solution was stirred with heating until gelatinous product was obtained. The gel obtained was washed with distilled water several times and kept for use.

Synthesis of glycine-type chitosan resin

The modification of chitosan with glycine is schematically described in Scheme 1. A glycine moiety was introduced to the cross-linked chitosan in two steps according to the previously reported method [17] as follows:

Step 1: Cross-linked chitosan (5 g) was suspended in a mixture of distilled water (50 mL) and ethanol (50 mL), and then epichlorohydrin (10 g) was added to it. The mixture was then refluxed for 3 h. The product was filtered and washed with ethanol and distilled water to remove any residual reagents.

Step 2: 5 g of glycine suspended in dioxane (100 mL) were mixed with the produced chitosan, and then 40 mL of 1.0 M NaOH was added to the mixture. The reaction mixture was refluxed for 12 h, filtered and washed with water followed by acetone. The produced resin was dried in air and kept for use. The resin was referred by G@Chs.

FT-IR analysis

Infra red spectra were performed using Nicolet IR200 FT-IR Spectrometer.

Sorption experiments

Preparation of Mn(II) solutions

A stock solution of Mn(II) is prepared by dissolving an accurate quantity of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Merck Ltd., Germany). Stock solution (1×10^{-2} M) of Mn(II) was prepared, the range of concentrations prepared from stock solutions has been varied from 0.0001 to 0.01 M. Distilled water was used in preparing the stock solutions and also throughout the experimental analysis. The initial pH adjustments were carried out either by HCl and NaOH.

Batch studies

Batch adsorption was carried out by contact of dry resin (0.1 g) in 100 mL of 5×10^{-3} M Mn(II) solution taken in 125 mL Erlenmeyer flasks and agitated at 200 rpm on a shaking water bath model-1083 (Labortechnik mbH, Germany). Samples are withdrawn at periodic intervals and filtered. The concentration of Mn(II) ions remaining in the filtrate is analyzed by spectrophotometer (HANNA-HI 96709C) at 525 nm [23]. Quality control charts for Mn(II) analysis were done, and each data point was taken as the average of three measurements with standard deviation of $0.1 \pm 0.05\%$.

Effect of pH

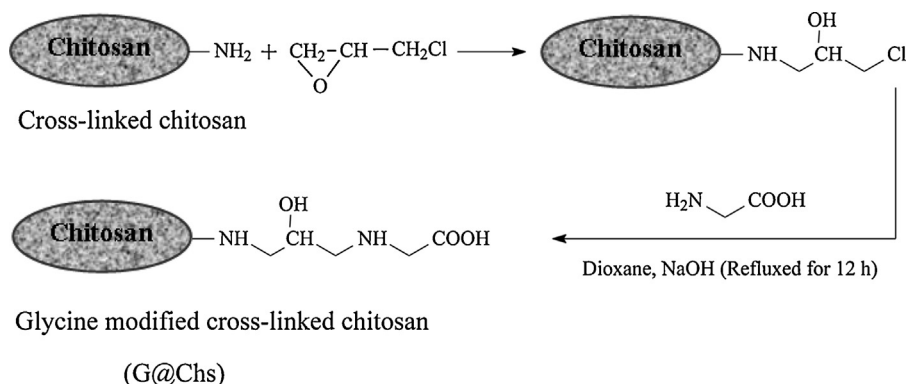
The uptake of Mn(II) by the investigated resin was studied at different pH values (1.0–8). The pH was adjusted using HCl or NaOH. 0.1 g of investigated resin was placed in a series of flasks. To each flask 100 mL of Mn(II) solution (5×10^{-3} M) was added. The contents of each flask were shaken for 150 min on a shaker at 200 rpm and at temperature $25 \pm 1^\circ\text{C}$ at desired pH. The resin was separated from the solution by filtration. Then the residual concentration of Mn(II) was estimated as above (Section Batch studies).

Adsorption isotherms

Complete adsorption isotherms were carried out by placing 0.1 g portions of dried resin in a series of flasks containing 100 mL of Mn(II) ions at pH 6. The temperature was thermostatically kept at 25 ± 1 , 35 ± 1 or $45 \pm 1^\circ\text{C}$ and equilibrium time 150 min. The residual concentration of Mn(II) was determined. The adsorption data were treated according to Langmuir equation [24]:

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e the adsorbed value of Mn(II) ions at equilibrium concentration (mmol/g), Q_{\max} is the maximum adsorption capacity



Scheme 1. Schematic description of the modification of chitosan with glycine.

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