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Optimization, isotherm, kinetic and thermodynamic studies of Pb(II) ions adsorption onto N-maleated chitosan-immobilized TiO_2 nanoparticles from aqueous media

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ABSTRACT

Chitosan, CS was chemically engineered by maleic anhydride via simple protocol to produce N-maleated chitosan, MCS which immobilized on anatase TiO_2 to synthesize novel eco-friendly nanosorbent (51 ± 3.8 nm), MCS@TiO_2 for cost-effective and efficient removal of Pb(II) ions from aqueous media. The chemical structure, surface properties and morphology of MCS@TiO_2 were recognized by FTIR, ^{1}H NMR, XRD, TEM, DLS and zeta-potential techniques. The relations between %removal of Pb(II) and different analytical parameters such as solution acidity (pH), MCS@TiO_2 dosage, time of contact and initial Pb(II) concentration were optimized using response surface methodology (RSM) and Box–Behnken design (BBD) statistical procedures. The fitting of the experimental data to four different isotherm models at optimized conditions was carried out by various statistical treatments including the correlation coefficient (r), coefficient of determination (r^2) and non-linear Chi-square (χ^2) test analyses which all confirm the suitability of Langmuir model to explain the adsorption isotherm data. Also, statistics predicted that the pseudo-second-order model is the optimum kinetic model among four applied kinetic models to closely describe the rate equation of the adsorption process. Thermodynamics viewed the adsorption as endothermic and feasible physical process. EDTA could release the sorbed Pb(II) ions from MCS@TiO_2 with a recovery above 92% after three sorption–desorption cycles. The novel synthesized nanosorbent is evidenced to be an excellent solid phase extractor for Pb(II) ions from wastewaters.

1. Introduction

Lead is one of the most extensive toxic metals released to the environment because of its wide use in many industrial applications such as storage battery, printing, pigments, fuels, photographic materials and explosives [1]. Industrial wastewater polluted with lead has endangered the human health and environment. The adverse effects of lead toxicity include impaired blood synthesis, hypertension, severe stomach ache, brain and kidney damage and miscarriage in pregnant women [2]. The permissible level for lead in drinking water is 5 ppm according to the US Environmental Protection Agency (EPA). A great deal of interest in the research of removing toxic heavy metals from industrial effluents has focused on using adsorption technique among different other conventional removal methods [3–12]. Chitosan, CS has gained considerable attention as a non-conventional adsorbent in water detoxification research due to its favorable properties such as non-toxicity, eco-friendliness, high availability, biodegradability, good biocompatibility, low cost and good adsorption properties [13–16]. CS is a naturally occurring linear binary cationic polysaccharide consisting of D-glucosamine and N-acetyl-D-glucosamine repeating units linked by β (1 → 4) glycosidic bond. Although, its backbone consists of hydrophilic amino and hydroxyl groups, CS is insoluble in water and most organic solvents due to its crystalline structure as a result of extensive intramolecular and intermolecular hydrogen bonding between its chains and sheets [17]. Hence, chemical modifications of CS become necessary to improve its water solubility, physicochemical properties and adsorption capacity by crosslinking, derivatization or addition of functional groups via saccharization, alkylation, acylation, metallization and quaternization of its amino groups [18–23].The engineered chemical modification via combining CS with maleic anhydride introduces polar functionality into its backbone that provides new biopolymer which is excellent scavenger for metal ions. On the other hand, titania-bio-based materials were also used as promising nanosorbents for the removal of many contaminants from wastewaters because of their hybrid properties and better performance. This work compiles the different desirable properties of N-maleated chitosan and nano-TiO_2 to produce one unique and accessible structure, MCS@TiO_2 as an innovative hybrid adsorbent with expected excellent sorption capacity for potential application in

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environmental remediation of Pb(II). In addition the investigated adsorption system was optimized using a statistical design to decrease the number of experiments, include the interactions among all analytical parameters and look for the best-fitting adsorption isotherm and kinetic models to know much about the mechanism of the sorbent–sorbate interaction. Hence, we modified chitosan with maleic anhydride and TiO_2 by a new simple synthetic procedure for enhancing its adsorption capacity towards Pb(II) ions. Various spectroscopic techniques were used to elucidate the structure and morphology of the fabricated nanosorbent. Thermodynamic study was done to add more information about the nature, spontaneity and thermic behavior of the adsorption process. Three adsorption–desorption cycles were carried out to judge its beneficial application as a wastewater detoxifier of Pb(II) ions.

2. Experimental

2.1. Materials

Anatase TiO_2 nanopowder (99%, 10–25 nm, 250 $m^2\ g^{-1}$ surface area and 0.12–0.18 g cm^{-3} bulk density) was supplied from the US research nanomaterials, Inc. (Houston, USA). CS (deacetylation degrees >90% and average molar mass is 111 kDa) and other used chemicals as maleic anhydride, epichlorohydrin, acetone, diethyl ether, DMSO, EDTA, $Pb(NO_3)_2$, HNO_3, HCl and NaOH in this work were purchased from Sigma-Aldrich Chemical Co (St. Louis, USA). The pH of solutions was adjusted by adding appropriate amounts of HNO_3 or NaOH. All glassware was washed with HCl acid (1.0 M) before and after each experiment to avoid binding to metals. Double distilled water was used throughout this work.

2.2. Apparatus

A centrifuge model 236HK (Hermle, Germany) was used to separate the solid samples. A spectrophotometer model 8400S (Shimadzu, Japan) with KBr powder of spectroscopic grade was used to determine the FTIR (400–4000 cm^{-1}) spectra of the investigated compounds. A freeze-dryer model FDU (Operon, South Korea) is used to lyophilize MCS. An Orion pH-meter model 420A (Thermo Scientific, USA) determines the pH of solutions. The size of nanoparticles was measured using DLS particle size analyzer model NanoBrook 90Plus (Brookhaven Instruments Corporation, USA). The nanoparticle morphology was observed using TEM model CM200 (Philips Scientific, UK). A diffractometer model D/MAX 2500V (Rigaku, Japan) with CuKα radiation (λ = 1.5406 nm) was used to analyze the samples. The electrostatic surface potential was measured by zeta potential analyzer model delta 440sx (Beckman Coulter, USA).The ^1H NMR spectra were determined on 300 MHz model AV 3000 Supercon NMR system (Bruker, Germany). The residual Pb(II) ions concentrations were determined using an atomic adsorption spectrophotometer (AAS) model PU9400 (Philips Scientific, UK).

2.3. Preparation of N-maleated chitosan, MCS

MCS was prepared by a similar reported protocol [24,25]. A sample of 1.5 g of CS was treated with 90 mL of DMSO and constantly stirred at room temperature. Then, to the dispersion solution formed, 3 g of maleic anhydride in DMSO solution was added to perform the required reaction at 60 °C for 8 h. The reaction product was cooled to room temperature and subsequently precipitated in 250 mL acetone. Finally, the solid product was filtered, washed with acetone and diethyl ether and then lyophilized for three days and dried under vacuum to get MCS. The molecular structures and brief synthetic route for the synthesis of MCS are shown in Fig. 1.

2.4. Preparation of N-maleated chitosan-immobilized TiO_2 nanosorbent, MCS@TiO_2

A sample of 0.5 g MCS was dissolved in 3% acetic acid. Then 0.2 g of anatase TiO_2 was added to this formed solution and dispersed through ultrasonication for 15 min. The mixture was stirred continuously for 45 min followed by the addition of 1 mL epichlorohydrin and 0.5 mL OP emulsification and then stirred for 5 h at room temperature. The solution was dropped into 0.1 M of NaOH as a solidifying solution. The gelled MCS@TiO_2 spheres were formed instantaneously, which remained in the alkaline solution for 12 h and then were washed with distilled water. The wet spheres were put into a flask with 100 mL of 0.1% (g/g) EDTA stirred at 30 °C for 4 h, and then washed with distilled water. The solid MCS@TiO_2 was separated by centrifugation, freeze-dried and kept in a desiccator for adsorption experiments.

2.5. Batch adsorption studies

A series of batch contact experiments were conducted to explore the effect of medium acidity (pH), contact time, quantity of MCS@TiO_2 adsorbent, initial Pb(II) concentration and temperature. These batch adsorption experiments were performed in 125 mL stoppered bottles by agitating 25 mg of MCS@TiO_2 in 100 mL of known varied initial concentrations (0–200 mg L^{-1}) of Pb(II) solutions in a thermostated shaker (200 rpm) at adjusted pH (6.0) and temperature (20, 30, and 40 °C).

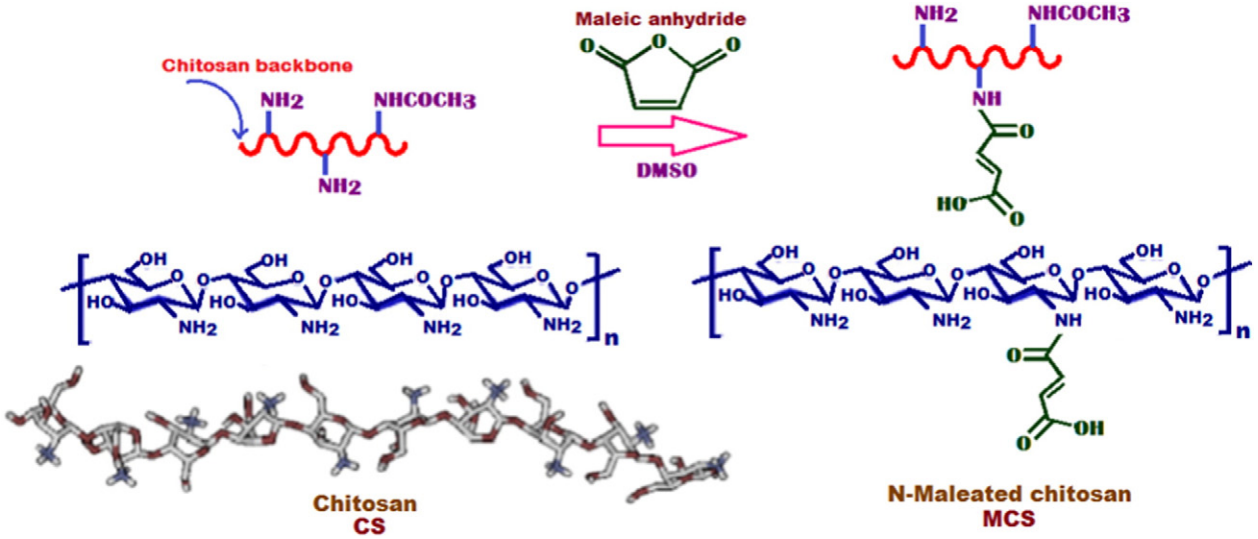

Fig. 1. Molecular structure of CS and synthetic route to prepare MCS.