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Removal of Heavy Metal Ions by Polymer Bound Tris-amine Microspheres

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Abstract

In this work, polystyrene tris (2-aminoethyl) amine was used for the removal of Cr (VI) from aqueous solutions. The influence of pH, contact time, adsorbent dosage and initial Cr (VI) concentration on adsorption was investigated. FT-IR and SEM analyses were performed on the adsorbent before and after Cr (VI) binding. Maximium adsorption of Cr (VI) was achieved at pH 5 and after a contact time of 120 minutes with 10 g/L adsorbent dosage. The percentage of Cr (VI) removal decreased from 96.74% to 40.74% when the initial Cr (VI) concentration was increased from 10 to 80 mg/L at pH 5 and 25±1°C as determined by UV-Visible spectroscopy. The adsorption of Cr (VI) was evaluated using Langmiur and Freundlich isotherm models, the data fit Langmiur isotherm model and the maximum adsorption capacity was 312.27 mg/g at pH 5. FT-IR spectra indicated the complexation of Cr (VI) with the adsorbent and the reduction of Cr (VI) to Cr (III) by the adsorbent after complexation. SEM and EDS analyses confirmed the complexation of Cr (VI) to the adsorbent. Desorption test indicated 89.3% removal of chromium from the adsorbent.

ازالة الكروم السداسي من المحاليل المائية عن طريق بولي ستيرين ترس-٢- أمين ايثل أمين

الملخص بالعربي

في هذا العمل، تم استخدام بولي ستيرين ترس-٢- أمين ايثل أمين لازالة الكروم السداسي من المحاليل المائية. تمت دراسة أثر الحموضة، وقت الاتصال، كمية المادة الرابطة و التركيز الاولي للكروم على عملية الامتصاص السطحي. تم اجراء تحليل بجهاز مطيافية الاشعة تحت الحمراء و مجهر المسح الالكتروني على المادة الرابطة قبل و بعد ربط الكروم السداسي. عملية الامتصاص السطحي الاقصى حصلت على درجة حموضة تساوي ٥ و بعد وقت اتصال يساوي ١٢٠ دقيقة بكمية مادة رابطة تساوي ١٠ غم.لتر$^{-1}$. نسبة الكروم المزالة انخفضت من ٩٦.٧٤% الى ٤٠.٧٤% عندما تم رفع تركيز محلول الكروم السداسي من ١٠ الى ٨٠ مغم.لتر$^{-1}$ على درجة حموضة ٥ و درجة حرارة ٢٥±١ °مئوية كما حدد عن طريق جهاز الاشعة فوق البنفسجية- الاشعة المرئية. تم تقييم عملية ربط الكروم السداسي باستخدام نموذج لانغمير و فريندلش الايسوثرمي، كانت النتائج تتناسب مع نموذج لانغمير الايسوثرمي وكانت قدرة المتصاص السطحي الاقصى تساوي ٣١٢.٢٧ مغم.غم$^{-1}$ على درجة حموضة ٥ . أشار جهاز مطيافية الاشعة تحت الحمراء الى ارتباط الكروم السداسي مع المادة الرابطة تلاها حصول عملية الاختزال للكروم السداسي الى الكروم الثلاثي. أكد مجهر المسح الالكتروني و منظار الطيف الالكتروني المتبدد عملية ربط الكروم السداسي على المادة الرابطة . أشار اختبار اعادة ازالة الكروم السداسي عن المادة الرابطة الى نسبة ازالة تساوي ٨٩.٣%.

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1. Introduction

Chromium exists in the environment in two main oxidation states Cr (III) and Cr (VI) [14]. Cr (III) is an essential element in humans and is much less toxic than Cr (VI), it is required to potentiate insulin and for normal glucose metabolism [16, 17]. Cr (III) is poorly adsorbed by any route so the toxicity of chromium is attributable to the Cr (VI) form [15]. Cr (VI) can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin. If Cr (VI) is reduced to Cr (III) extracellularly, the toxicity is not observed. Cr (VI) can be reduced intracellularly by hydrogen peroxide, glutathione reductase and ascorbic acid to produce reactive intermediates. Any of these species could attack DNA, proteins and membrane lipids thereby disrupting cellular integrity and functions. Exposure to chromium VI can cause respiratory, renal, hepatic, gastrointestinal, cardiovascular and hematological problems. Also Cr (VI) is considered to be carcinogenic [21, 22].

Cr (VI) is introduced into natural waters by a variety of industrial wastewaters including those from textile, dyes and pigment production, film and photography, galvanometry, leather tanning, electroplating and metal finishing industries [19].

A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption. Most of these methods have a lot of disadvantages including high operational cost [20].

Recently, adsorption was reported to be a promising technique for chromium removal. Specific polymer sorbents consist of a metal chelate forming agent which interacts specifically with the heavy metal ions, and a carrier matrix which may be an inorganic material, or polymeric microspheres that contain functional groups that can bind to the heavy metal ions [23].

Hundreds of works have been published in international journals devoted to Cr (VI) biosorption. Nuria Fiol etal used grape stalks and yohimbe bark wastes to remove Cr (VI) and Cr (III) from aqueous solutions. The sorbents were cut, sieved and then shaked with chromium solutions. The total concentration of chromium remaining in solution after sorption was determined by flame atomic absorption spectroscopy. Cr (VI) was determined colormetrically by 1, 5-diphenylcarbazide method. Cr (III) was determined as the difference between total chromium and Cr (VI) concentration. FTIR and XPS analyses were performed on solid phase to determine the main functional groups that might be involved in metal uptake and to confirm the presence of Cr (III) on sorbents [5].

Nuria Fiol etal found that Cr (III) appears in solution few seconds after contacting grape stalks and yohimbe bark with Cr (VI) solution. So both sorbents have the ability to reduce Cr (VI) to Cr (III). The sorption of Cr (VI) on yohimbe bark was faster than grape stalks and the sorption process was completed after 24 hours for both sorbents. The sorption of Cr (III) was faster than Cr (VI) and equilibrium was attained after 10 hours [5].

Carlos Escudero etal studied the kinetics of Cr (VI) sorption onto grape stalk waste in a stirred batch reactor. Experiments were carried out at different temperatures but at constant pH (3±0.1). A model has been developed to predict Cr (VI) sorption onto grape stalks on the basis

of (1) irreversible reduction of Cr (VI) to Cr (III) reaction, whose reaction rate is assumed to be proportional to the Cr (VI) concentration in solution and (2) Adsorption and desorption of Cr (VI) and formed Cr (III) assuming that all the processes follow Langmiur type kinetics [2].

Carlos Escudero etal found that the Cr (III) formed due to reduction is partially adsorbed onto grape stalk waste. The rate constants values put into evidence that reduction is the main reaction. The rest of the processes are affected by this reaction. The proposed model fits adequately the obtained experimental data for total chromium, Cr (VI) and the calculated Cr (III) [2].

V. Vinodhini etal investigated the removal of Cr (VI) from aqueous solutions using biowaste materials (neem sawdust, mango sawdust, wheat shell, sugar cane bagasse and orange peel). The influence of contact time, pH, adsorbent dosage and metal initial concentration was investigated. Neem sawdust showed the highest Cr (VI) removal capacity. The sequence of Cr (VI) removal was NS>MS>WS>SB>OP. Percentage removal of Cr (VI) decreased with increase in pH. Maximum adsorption of Cr (VI) ions was observed at pH=2 for all the biosorbents. The adsorption capacity increased with increase in time, biomass dosage and metal initial concentration. The biosorption equilibrium data fitted well to the Langmiur isotherm [7].

S. Dhanakumar etal investigated the removal of Cr (VI) from aqueous solution by using cooked tea dust as adsorbent. The cooked tea dust was agitated with aqueous solutions of Cr (VI) at varying pH (2-11), agitation time, particle size and adsorbent dosage at room temperature in a mechanical shaker. Cr (VI) was estimated spectrophotometrically using 1, 5-diphenylcarbazide method. FTIR spectra were obtained for cooked tea dust before and after adsorption [6].

S. Dhanakumar etal found that the removal rate of Cr (VI) was rapid during the first 10 minutes of agitation then it slowed down until it reached equilibrium. The removal rate of Cr (VI) increased with increase of adsorbent dosage and decreased with increase of pH, adsorbent particle size and Cr (VI) initial concentration. Results conformed into both Langmuir and Freundlich adsorption models for adsorption equilibrium of Cr (VI) onto cooked tea dust. The Langmuir adsorption capacity was found to be 30.3 mg/g while Freundlich constants k_f and n were 7.524 and 2.673 respectively. Desorption ratio was 82.28% using NaOH [6].

M. Seyf-laye etal used activated charcoal for the removal of Cr (VI) from aqueous solutions. The effect of pH, contact time, initial chromium concentration and adsorbent amount were investigated. To model the adsorption behavior, three adsorption isotherms (Langmuir, Freundlich and Temkin) were studied and their correlation with experimental data was assessed. Various kinetic models such as pseudo first order, pseudo second order and Elovich model were used to evaluate the mechanism of Cr (VI) adsorption on activated charcoal [1].

M. Seyf-laye etal found that maximum Cr (VI) adsorption was between pH 1-3 after a contact time of 120 minutes. Percent removal of Cr (VI) decreased as the initial Cr (VI) concentration increased and it increased as the amount of activated charcoal increased. The kinetics of Cr (VI) adsorption using activated charcoal was explained by pseudo second order kinetic model, the rate constant of adsorption K_2 was 0.1800 g/Kg.min for an initial Cr (VI) concentration of 0.1 mg/ml. The adsorption fit well with Langmuir and Freundlich isotherm models, the maximum adsorption capacity obtained using the Langmuir isotherm model was 45.24 g/Kg at pH=2 [1].

Erhan Demirbas etal investigated the adsorption kinetics for the removal of Cr (VI) from aqueous solutions using activated carbons prepared from agricultural wastes (Cornelian cherry, Apricot stone and almond shells). The effect of pH, contact time, initial Cr (VI) concentration and adsorbent particle size were studied. The kinetics of Cr (VI) adsorption on the activated carbons was analyzed using pseudo first order, pseudo second order, Elovich and intraparticle diffusion kinetic models. Almond shell carbon was the most effective for which the removal reached 99.99% at 25°C. Adsorption was highly pH dependent and the optimum pH was found to be 1. The percent removal decreased with increase in adsorbent particle size, pH and initial Cr (VI) concentration. Results showed that the pseudo second order kinetic model correlate the experimental data well [3].

V. Vinodhini etal investigated the mechanism of Cr (VI) biosorption by Neem sawdust using different chemical and instrumental techniques in order to assist in the elucidation of the role of major constituents of Neem sawdust in chromium removal process. Three biosorbents were used (Raw Neem sawdust, Neem sawdust without cellulose and Neem sawdust without lignin) in a batch equilibrium studies, contacted with various concentrations of Cr (VI) solutions ranging from 10-150 mg/L at pH 2 with a contact time of 2 hours. FTIR analysis, EDAX analysis and ESR analysis were carried out on Neem sawdust before and after Cr (VI) adsorption. FTIR analysis showed that the bonded- OH groups, C=O groups, SO_3 stretching, C-O stretching and C-N stretching were involved in Cr (VI) biosorption. EDAX showed that ion exchange is not the mechanism involved in adsorption of Cr (VI). ESR analysis confirmed that Cr (VI) was reduced to

Cr (III) on lignin component of Neem sawdust. The batch equilibrium studies showed that lignin is the major component for Cr (VI) adsorption on Neem sawdust [8].

Haifa Zghida etal studied the sorption of chromium oxy- anions onto cationized ligno-cellulosic material (cotton, wood sawdust and maize-cob flour). Quaternary ammonium groups were grafted onto the ligno-cellulosic material, those groups form the binding sites for the oxy-anions containing chromium atoms. Adsorption isotherms were calculated using Langmuir, Freundlich and Jossen equations. Cationized ligno-cellulosic materials were able to sorb chromium; adsorption proceeded very quickly and reached a limit value dependent on the rate of ammonium grafting. The Jossen model was the most adequate to describe these adsorptions. The regeneration of the ammonium groups was done using solution of KCL at 2, 3 and 4 M. Desorption percentage was 95% using 4M KCl solution [4].

5.Conclusion

Polystyrene tris-2-(aminoethyl)amine has been successfully used to remove Cr (VI) from aqueous solutions. The removal of Cr (VI) was best at pH 6, and the percentage of Cr (VI) removed was dependent on adsorbent dosage, contact time and initial Cr (VI) concentration. During the adsorption process the detoxification of Cr (VI) occured by its reduction to Cr (III) by the electrons on the nitrogens of the polystyrene tris-2-(aminoethyl)amine . FT-IR analysis revealed that the adsorbent gets oxidized in the process of removal of Cr (VI) concomittant with the reduction of Cr (VI) to Cr (III). The Langmuir isotherm model agreed with the experimental data and the maximum adsorption capacity was 312.27 mg/g which is considered to be very high compared to other adsorbents.