



Comparison of heavy metal ions removal from industrial lean amine solvent using ion exchange resins and sand coated with chitosan



Priyabrata Pal, Fawzi Banat*

Department of Chemical Engineering, The Petroleum Institute, P.O.Box 2533, Abu Dhabi, United Arab Emirates

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ABSTRACT

The accumulation of heavy metal ions in natural gas sweetening unit causes problems such as corrosion, foaming and fouling of the equipment. Heavy metal ions being chelated to lean amine solvent cannot be removed from the solvent by simple heating in the regenerator, hence requiring new approaches for heavy metal ions removal from aqueous solution of lean amine (methyldiethanolamine) solvent is mandatory. In this study, three different grades of commercial ion exchange resins (A–C) including chitosan coated Resin C and sand coated with chitosan (SCC) were tested to remove major heavy metal ions from raw industrial lean amine (MDEA) solution employing the principles of adsorption. Finally, Resin C and SCC were used for elaborate batch and continuous adsorption studies. SEM and FTIR analysis mapped the surface morphology changes and coating of chitosan before adsorption process over the adsorbent. The equilibrium batch sorption studies for heavy metal ions removal were fitted into Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms. The Langmuir model predicted maximum uptake capacity for chitosan coated resin C and SCC (in brackets) 38.022 (14.184) $\mu\text{g/g}$ for chromium, 59.88 (75.7575) $\mu\text{g/g}$ of iron and 22.47 (185.185) $\mu\text{g/g}$ of lead having total maximum metal removal of 6.858 (5.0226) $\mu\text{equivalence/g}$. The sorption kinetics obeys pseudo-first-order having rate constant 0.0111 min^{-1} (0.0095 min^{-1}) for chromium ions. The negative values of Gibb's free energy explains spontaneity of the reaction with endothermic heat of adsorption for the removal of heavy metal ions using resin C and SCC. The breakthrough curves for removal of metal ions in column bed with 2.54 cm column diameter and flow rate of 4.5 ml/min was achieved within 8 h. The parameters k and τ for chitosan coated resin C and SCC were determined to be 0.014 (0.015) min^{-1} and 551.25 (525.7867) min.

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1. Introduction

In natural gas sweetening plant aqueous amine such as methyldiethanolamine (MDEA) solution is used to scrub natural gas. The rich MDEA solution is fed to a regeneration column where heat is applied to strip the acid gas components out of the MDEA solution. To maintain a constant concentration of MDEA solution, demineralized water (as make-up water) and MDEA are added regularly in the process. As the plants are running continuously, the traces of heavy metal ions present at the beginning of the operation keep on accumulating as contaminant which may come from make-up water and metal corrosion and erosion caused in the process. There are different techniques for metal ions removal such as chemical precipitation, ion exchange, membrane filtration, electro-

dialysis and reverse osmosis (Inoue et al., 2010; Koter and Warszawski, 2006; Vinodh et al., 2011; Tanaka, 2009; Issabayeva et al., 2006). However, these methods have high operational cost and inefficient in the removal of some heavy metal ions (Salehi and Madaeni, 2010; Post et al., 2009). In contrast, adsorption processes are capable of achieving very low metal ion concentrations (Burns and Gregory, 1995), low operation and installation costs with reduced regeneration chemical cost (Cummings et al., 2007). Few research works were conducted to remove metal ions from industrial amine solutions. Cummings and Smith (2010) used continuous adsorption studies passing the alkanolamine solutions over cation bed where positively charged contaminants such as ferrous ions and sodium ions were exchanged with protons. Audeh and Yan (1994) showed that weakly acidic cationic resins with carboxylic acid functionality outperform strongly acidic resins with a sulfonic acid groups.

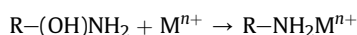
Chitosan is derived from N-deacetylation of chitin, the major component of the shells of crustacean organisms and one of the

* Corresponding author. Tel.: +971 552640865.

E-mail address: fbanat@pi.ac.ae (F. Banat).

most abundant naturally occurring biopolymer. Chitosan have properties such as non-toxicity, biocompatibility, high chemical reactivity, chirality, chelation and adsorption (Crini, 2005, 2006; Felse and Panda, 1999). The presence of both amine and hydroxyl groups makes chitosan unique among biopolymers for its affinity for heavy metal ions (Laus et al., 2010; Zhou et al., 2010; Kumar et al., 2009; Fan et al., 2011). The production of chitosan beads involves the dissolution of chitosan in acetic acid solution followed by a precipitation process for injecting the chitosan solution into a dilute sodium hydroxide solution (Rorrer et al., 1993). However, the chitosan beads have the disadvantage of poor chemical resistance and mechanical strength which significantly reduces the recycle life of the chitosan beads. To improve these properties, chitosan was coated on resin beads and on sand to obtain good mechanical and chemical properties and compare their adsorption properties.

In the developed chitosan coated resin beads and SCC, it was expected that nitrogen atom of amino groups and the oxygen atom of the hydroxyl groups in chitosan acted as adsorption sites for heavy metal ions. Both nitrogen and oxygen atom possess lone pair of electrons, can bind a positively charged metal ion through the electron pair sharing. The easy release of lone pair from nitrogen atom makes it the main binding site and forms stable metal complex. With the above consideration, the following chemical reactions are proposed to account the mechanism of heavy metal ions adsorption:



where R represents all other components in chitosan coated resin beads and M^{n+} is the metal ions having valence state of n .

In the present study three commercially available ion exchange resins (A–C) were tested in the removal of metal ions. Amongst all metal ions present in the amine solvents, the amount of heavy metals present were maximum and hence its removal was the major aim of this work along with low level removal of other ions. MDEA containing both amine and hydroxyl group adhere heavy metal ions strongly. Thus bare ion-exchange resins cannot always successfully remove heavy metal ions from this lean amine solvent overcoming the chelation. The novelty of this research work lies in the use of chitosan coated ion-exchange resin (best selected among the three selected resin) and the sand coated with chitosan (SCC) which were used as an adsorbent for the removal of heavy metal ions (mostly chromium, iron and lead) accumulated in lean MDEA solution in gas sweetening process. Based upon extensive literature survey, it can be concluded that this work is possibly the first of its kind, where removal of metal ions from direct raw industrial lean MDEA solutions (obtained from Gasco Habshan, Abu Dhabi) were done. FTIR studies and SEM analysis were carried out to study the underlying principle of adsorption. Further the kinetic and equilibrium parameters in the batch adsorption studies for the removal of heavy metal ions and continuous adsorption experiments based on column studies were also investigated. The adsorption isotherm models like, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) were used to verify the mechanism of the adsorption process. The breakthrough curve was achieved using continuous column experiments and fitted in the model equations.

2. Materials and methods

2.1. Materials

Lean amine solvents were obtained from the Gasco, Habshan, Abu Dhabi containing 45 weight% methyldiethanolamine (MDEA). Three commercially available cation exchange resins were obtained from Shijiazhuang Jihai Resin Technology Co., Ltd., China (D303)

and Hangzhou Zhengguang Resin Co., Ltd., China (ZGC151MB and ZGC151) to check their removal efficiencies in removing metal ions present in lean amine (MDEA) industrial samples. Chitosan and all other chemicals used in this study were purchased from Sigma Chemical Co., USA. Chitosan coated ion-exchange resins were treated to regenerative form before their use in ion exchange batch sorption experiments. Two ICP standard solutions were obtained from Perkin, Elmer. Sand was taken from the campus area of the Petroleum Institute, Abu Dhabi.

2.2. Instrumentation

Elemental analysis was carried out using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Optima 8000; Perkin Elmer). The FTIR studies of chitosan coated ion-exchange resins and SCC were carried out using FTIR, Nicolet, iS10, Thermo Scientific instrument using OMNIC software. Scanning Electron Microscopy (SEM) was carried out with FEI Quanta 200, The Netherland. The energy dispersive X-ray Spectroscopy was carried out using (Oxford-EDX, UK). Surface area of the sand coated with chitosan was measured by multipoint BET (Brunauer, Emmett, and Teller) method using Quanta chrome Autosorb 1(USA), instrument.

2.3. Characterization

The surface area for sand coated with chitosan (SCC) was found to be $0.5901 \text{ m}^2/\text{g}$ having pore volume of $2.811 \times 10^{-4} \text{ cc/g}$. The value obtained was higher than the previous work (Wan et al., 2010; surface area of chitosan coated sand $0.3978 \text{ m}^2/\text{g}$) with technical grade sand coated with chitosan. The physical and chemical properties of the ion exchange resins are shown in Table 1.

2.4. Methodology

2.4.1. Pretreatment and intake capacity of the resin

The fresh commercial resins were treated to regenerative form before their use in batch adsorption experiments. They were converted to protonated form using 0.1 (M) hydrochloric acid solutions. 10 g of each ion exchange resins were added to 100 ml hydrochloric acid solution and stirred at 400 rpm for 24 h at room temperature. The resins were washed with deionized water, dried at 50°C and then used for adsorption studies.

2.4.2. Chitosan coating on resin C and sand

At first, the bare resin C was coated with chitosan. 1.0 g chitosan powder was added to 100 ml 5% acetic acid solution and left overnight in stirring condition to dissolve completely. 10 g of resin C

Table 1
Physical and chemical properties ion exchange resins, as given by the supplier.

Characteristics of resins	D303 (resin A)	ZGC351 MB (resin B) and ZGC351 (resin C)
Appearance	White spherical beads	Light yellow spherical beads
Polymer Matrix Structure	Styrene-divinylbenzene	Styrene-divinylbenzene
Type	Macroporous strong acidic	Macroporous strong acidic
Functional Group	$R-(SO_3)-H^+$	$R-(SO_3)-H^+$
% Moisture Content	50–60	55–65
Capacity in Volume	$\geq 1.00 \text{ mmol/ml}$	$\geq 1.00 \text{ mmol/ml}$
Density	1.0 g/ml	1.05–1.08 g/ml
Effective Particle Size	0.45–0.65 mm	0.40–0.70 mm
Specific surface area	$16.19 \text{ m}^2/\text{gram}$	$17.58 \text{ m}^2/\text{gram}$
Pore diameter	46.54 nm	36.911 nm
Pore volume	0.18 ml/g	0.162 ml/g

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