



Gold Nanoparticles Encapsulated Alginate Microspheres as an Adsorbent for the Separation of Mn (II) Ions from the Aqueous Solutions

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Abstract: Gold nanoparticles encapsulated alginate microspheres were synthesized and evaluated as a nanoadsorbent for removing Mn (II) from aqueous solutions. Gold nanoparticles were prepared and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and FT-IR. The adsorption of Mn (II) ions was examined by batch equilibrium techniques. The effects of pH, initial Mn (II) concentration, adsorbent dosage and contact time on the efficiency of Mn (II) removal were studied for the batch method. The equilibrium data analyzed by using Langmuir and Freundlich isotherm models showed better agreement with the latter model. Repeated adsorption and desorption cycles were performed to examine the stability and reusability of the nanoadsorbent. The result of this study proved high stability and reusability of Gold nanoparticles encapsulated alginate microspheres as an adsorbent for Mn (II) ions.

I. INTRODUCTION

Contamination of water with toxic metal ions (Hg(II), Pb(II), Cr(III), Cr(VI), Ni(II), Co(II), Cu(II), Cd(II), Ag(I), As(V) and As(III)) is becoming a severe environmental and public health problem. In order to achieve environmental detoxification, various techniques like adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, floatation, oxidation and biosorption processes are extensively used [1-3]. Among these, adsorption is a conventional but efficient technique to remove toxic metal ions and bacterial pathogens from water. Development of novel and costeffective nanomaterials for environmental remediation, pollution detection and other applications has attracted considerable attention. Recent advances suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration or other products resulting from the development of nanotechnology [4-5].

Nanotechnology has the potential to bring in solutions to minimize or eliminate the use of toxic materials and the generation of undesirable byproducts, as well as, sensitively detect (and monitor) specific polluting agents well before any major environmental disaster occur. The chemical inertness and resistance to surface oxidation make production of gold nanoparticles easier in comparison to other metal nanoparticles. The application of metallic and organic nanomaterials based Chemistry for waste water treatment is summarized for three major types of contaminants: halogenated organics including pesticides, heavy metals and dyes. Besides the above efforts for the removal, the ultra low concentration detection of such species, using metal nanoparticles are summarized.

It is vital to summarize a few of the advantages of nanomaterial chemistry with respect to conventional technologies. The surface-to-volume ratio increases drastically with the reduction of the size of the adsorbent particle from bulk to nano dimensions. It leads to the availability of higher numbers of atoms/molecules on the surface for adsorption of contaminants. Accordingly the surface energy available with each adsorbent particle also increases significantly. This provides many advantages to drinking water purification:

- Effective contaminant removal even at low concentrations;

- Less waste generation post-treatment as less quantity of Nanomaterial will be required in comparison with its bulk form. This happens since more adsorbent atoms/molecules are present per unit mass of the adsorbent and thus are actively utilized for adsorption.

Hence, an applied strategy for detection of heavy metal ions in water has been developed employing approx 50 nm gold nanoparticles capped with a biopolymer called Alginate. Polymer capping of nanoparticles serves a two-fold purpose, that of stabilization and surface functionalization for application as sensors. Alginate is widely used as a chelating agent for removal of heavy metal contaminants in wastewater. Alginate has free acidic groups in its monomer, which gets deprotonated in dilute basic media. These deprotonated acidic groups form the multiple bonding sites that are useful in chelating heavy metals like Mn2+, Cu2+ and Zn2+ [6]. $(Na - Alg)n + n M^{2+} = (M - Alg2)n + n (2Na^{+})$

Manganese compounds are less toxic than those of other widespread metals such as iron, nickel and copper compounds. However, manganese is toxic in excess.

The usual method followed for metal nanoparticle synthesis is reduction of metal salts (precursors). During the reduction process, the growth kinetic parameters are controlled by a combination of low precursor concentration (increasing the diffusion distance), nature of solvent (higher solvent viscosity), slow acting reducing agent (reduced electrochemical gradient) and appropriate protection of the growth surface with a stabilizing agent (controlling surface reactivity).

In this work, the synthesized nanoparticles were capped with alginate, which is well known as a heavy metalchelating agent [7]. Polymers serve dual-purpose, one of providing sufficient steric or electrosteric hindrance ensuring stability of the colloids and also to functionalize the nanoparticles for sensing applications [8]. The present work purposes to investigate the removal of Mn (II) ions from aqueous solution by adsorption onto the gold nanoparticles encapsulated alginate microspheres.

Alginate is a polysaccharide biopolymer composed of anionic blocks of $(1\rightarrow 4)$ linked -l-gluronic acid (G) and -d-mannuronic acid (M). Alginate (alginate salts) shows high affinity to metal ions. Similar approaches for functionalization of noble metal nanoparticles have been developed using various other organic molecules (aliphatic and aromatic) containing a wide variety of functional groups ;e.g., cyano (–CN), mercapto (–SH), carboxylic acid(–COOH) and amino (–NH2) are known to have a high affinity for gold and thus are useful as surface protective functional groups [9–15].

II. EXPERIMENTS

A. Materials

Tetrachloro auric acid, Manganese Sulphate monohydrate, Sodium Alginate, Trisodium Citrate and Calcium Chloride of A.R. grade were purchased from Molychem, Mumbai, India. Double distilled water was used throughout the experiment.

B. Preparation of Adsorbent

Beads of Sodium Alginate is prepared by dissolving it in required amount of double distilled water. It is left overnight for deaeration. The uniform sized beads are prepared by adding the solution dropwise in Calcium Chloride solution with the help of a syringe. The beads so prepared get crosslinked with calcium ions. Such beads are mixed with tetrachloro auric acid and trisodium citrate dihydrate to produce in-situ gold nanoparticles. Gold nanoparticles formation is based on the well documented Turkevitch process i.e. by adding tetrachloro auric acid or gold chloride trihydrate with trisodium citrate dihydrate. The colour transition from colourless to dark red beads during brisk boiling in magnetic stirrer indicates the formation of gold nanoparticles. It is washed several times thoroughly with double distilled water and stored for further experiment.



Fig. (1) A photograph showing the swollen (A) Alginate and (B) Gold encapsulated Alginate polymeric beads

C. Preparation of stock solution

The stock solution of Mn (II) of $(1000 \text{ mg dm}^{-3})$ was prepared by dissolving 0.307 g. of MnSO₄.2H₂O (AR) in 100 ml. distilled water. Suitable concentrations of Mn working solutions were prepared by diluting the stock solution with deionized distilled water.

(**Other solutions prepared are:** - 0.001 M HAuCl₄ solution, 1% Trisodium Citrate solution, 0.5 M Calcium Chloride solution)

D. Adsorption experiments

The adsorption experiment was carried out by batch method. Batch experiments were conducted by varying contact time, pH, initial metal ion concentration and adsorbent dosage. The experiments were carried out in a conical flask containing the swollen biopolymeric beads (0.1 g) and 10 ml solution of MnSO₄.2H₂O solution (2 mg dm⁻³ concentration) at constant pH 8 and room temperature $(25^{\circ}C)$ with constant stirring using mechanical shaker for 5 hrs. The amount of Manganese present in the colourless solution was assayed Atomic spectrophotometrically using Absorption Spectrophotometer [16]. The amount of adsorbed Mn (II) was calculated by the following mass balance equation:

Adsorbed amount (mg/g) = $\frac{(\text{Ci} - \text{Cf}) V}{M}$ (1)

Where C_i and C_f being the initial and final concentrations of K_2CrO_7 solution (mg ml⁻¹), V being the volume of adsorbate solution and m is the weight of swollen beads.

1) Factors affecting adsorption

a) Effect of pH: In the present study, the effect of pH has been observed by varying the pH of suspension in the range 3.0 to 9.0, using 0.1 M HCl and 0.1M NaOH solution. The results clearly reveal that the optimum adsorption is noticed at pH 5.0 while the adsorption of Mn (II) ions decreases on both sides of the optimum pH. The increase in adsorption of Mn (II)ions due to increase in pH may be explained on the basis of a decrease in competition between proton and positively charged metal ions at the surface site and also decrease in positive charge near the surface which results in a lower repulsion of the Mn (II) ions. At pH below 5, the adsorption experiments could not be performed due to the dissolution of the polymeric beads in the solution.



b) Effect of concentration: When the concentration of Manganese Sulphate is raised in the range 0.5 to 2.0 mg dm⁻³, the amount of adsorbed Mn (II) ions is found to increase. The observed increase is quite obvious, as on increasing the concentration of solute, greater number of metal ions arrives at adsorbent interface and thus get adsorbed. This is a common finding and has been largely reported in the literature [17]. The highest uptake of Mn (II) ions by the adsorbent was found at 1.0 mg dm⁻³ initial Manganese ion concentration.



c) Effect of Time: - When the shaking time was increased from the range 30 min to 240 min, the amount of adsorbed Mn (II) ions is found to increase. The observed increase is quite obvious, as on increasing the shaking time of solute, greater number of metal ions arrives at adsorbent interface and thus get adsorbed. The highest uptake of Mn (II) ions by the adsorbent was found at 180 minutes.



E. Desorption experiments

The desorption studies of Mn (II) ions were conducted by batch method under similar conditions. In order to desorb the metal ions, the beads loaded with Manganese were exposed to 10 ml of 0.1 M HNO₃ for 15 minutes, centrifuged and washed with double distilled water. The beads were then again exposed to HNO₃ to strip off any remaining Manganese and then used again for further experiments. The desorbed beads were verified by the above adsorption process.

F. Adsorption isotherms: Adsorption data for wide range of adsorbate, concentration and adsorbent dosage have been treated by Langmuir and Freundlich isotherms, two widely used models.

1. Langmuir isotherm: The Langmuir isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface. Langmuir isotherms were obtained by batch method taking a fixed initial adsorbent dose (0.1 g) and varying the adsorbate concentration of Mn (II) at fixed pH 8 and time (30 minutes). The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phase. The linearised Langmuir adsorption isotherm is given by equation(2)

$$\frac{Ce}{a} = \frac{1}{a_s}K + \frac{Ce}{a_s}$$
(2)

Where, 'a' is the adsorbed amount of Mn (II) ions (mg g^{-1}) at equilibrium concentration C_e, a_s (mg dm⁻³) is the adsorption capacity and K is the adsorption coefficient.

2) Freundlich isotherm: The Freundlich isotherm has the following equation (3)

$$a = K_f C e^{1/n}$$
(3)

Where, 'a' is the adsorbed amount of Mn (II) ions, C_e represents the equilibrium concentration, K_f and n are Freundlich constants. K_f is the predicted quantity of sorption per gram of the biopolymeric beads at unit equilibrium concentration of Mn (II) ion solution, and 1/n is the measure of the nature and strength of the adsorption process and the distribution of active sites. If 1/n < 1, the bond energies increase with the surface density, if 1/n > 1, the bond energies decrease with the surface density and when n =1, all surface sites are equivalent.

The linearised form of Freundlich adsorption isotherm was used to evaluate the sorption data, represented as-

$$\log a = \log Kf + (1/n) \log Ce \qquad (4)$$

By plotting log C_e vs. log a, the values of K_f and n were calculated from the slope and intercept of the Freundlich plots.

3) Modified Freundlich: The biopolymeric beads are multifunctional in nature and therefore may be considered responsible to cause the adsorption process heterogeneous, i.e. not mono energetic. Thus, the following modified Freundlich equation using statistical mechanics may be applied in the present case.

$$\log\left(\frac{a_{s}}{a}\right) = \beta \log C_{e} + \log \frac{A}{a_{s}}$$
(5)

Where, β and A are empirical constants which can be determined through linear regression analysis. These empirical constants provide a means for visualizing the

general sorption process relative to the distribution of sorptive energies by the exchange surfaces.



G. Adsorption kinetics

The progress of adsorption process was monitored at different time intervals (10 - 240 minutes). It was observed that the adsorbed amount of Mn (II) ions constantly increases with increasing time. The kinetic model proposed by Bajpai et.al. [18] may be applied, to study the dynamic nature of the adsorption process as in equation (6).

$$\frac{1}{c} = k_1 \frac{t}{c_0} + \frac{1}{c_0}$$
(6)

where C = concentration of adsorbate solution at any time t, and $C_0 =$ the initial concentration of adsorbate solution. k_1 is the rate constant for adsorption. By plotting 1/C vs. t, the value of K was calculated.

1) Pseudo first order: The kinetics of sorption of Mn (II) ions was studied using pseudo first order equation (7) given by Lagergreen:

$$\frac{d_a}{d_t} = K_{ad} (a_s - a)$$
(7)

where, a_s and a represent the adsorption capacity at (mg/g) equilibrium and at time t respectively, K_{ad} is Lagergreen rate constant of pseudo first order adsorption. After integration and applying boundary condition t = 0 to t = t and $q_t = q$, the integrated form of equation becomes as follows (8).

$$\log(a_s - = \log a_s - \frac{K_{ad}}{2.303}$$
 (8)

when the value of log (a_s-a) is linearly correlated with t and a plot of log $(a_s - a)$ against t gives a straight line, the value of K_{ad} can be calculated.

2) Pseudo second order: The Pseudo second order adsorption kinetics rate equation is expressed as in equation (9).

$$\frac{da_{t}}{d_{t}} = K_{2} (a_{s} - a_{t})^{2}$$
(9)

where K_2 is the rate constant of Pseudo second order adsorption. The boundary condition t = 0 to t = t and $a_t = 0$ to $a_t = a_t$, the integrated form may be written as equation (10)

$$\left(\frac{1}{a_{s}-a_{t}}\right) = \frac{1}{a_{s}} + Kt$$
 (10)

This is the integrated rate law for a Pseudo second order kinetics.



H) Characterization of microspheres

(1) **TEM Analysis:** The particles size determination was carried out using the TEM image. Transmission electron microscopy (TEM) was performed by using a TECNAI-G20 transmission electron microscope with an acceleration voltage of 200 kv. The sample prepared for the TEM measurements was done by dispersing a drop of the sample solution on glass grids (AIIMS, Delhi).

2) FTIR Analysis: FTIR spectra of unabsorbed (bare) and Mn (II) adsorbed biopolymeric beads was recorded on a Perkin Elmer spectrophotometer (Dr. M. K. Deb, PRSU, Raipur).

3) XRD Analysis: The crystalline nature of composite beads of Gold nanoparticles encapsulated alginate microspheres and alginate alone was studied on a rotating X-ray diffractometer (NIT, Raipur).

I) Results and discussions

1) TEM Analysis: The TEM image shows the spherical structure and narrow size of the Au. According to the image, the average size of Au nanoparticles was estimated at 11.77 nm as in fig. 2



2) FTIR analysis: Fourier transforms infrared spectroscopy (FTIR) spectra of unadsorbed (bare) and Mn (II) adsorbed beads are shown in fig. 3. The FTIR analysis indicated the band at 2923.61 cm⁻¹, assigned to C-H bond of methylene groups. The sharp peak appearing at 1652.73 cm⁻¹ may be attributed to >C=O group. The absorption peak around 3446.24 cm⁻¹ may be assigned to -OH stretching, while a peak around 1070.32 cm⁻¹ may be due to the C-O stretching. The characteristic peak at 561.19 cm⁻¹ indicates the coating of Au nano particles on alginate because the surface of alginate with negative charges has an affinity towards Au nanoparticles by the electrostatic interaction and chemical reaction through glutaraldehyde crosslinking.

After adsorption the specific band at 1070.32 cm⁻¹ (C-O str.) was shifted to 1072.24 cm⁻¹ and a peak appearing at 2991.1 cm⁻¹ (C-H str.) shifted to 2998.82 cm⁻¹, which may be due to binding of metal ions to adsorbent surface.



3) XRD analysis: The XRD pattern of composite beads of Gold nanoparticles encapsulated alginate microspheres is shown in fig. 4. Powder XRD was carried out to identify the nano crystalline structure of the gold species and amorphous nature of Alginate.



J) Conclusion

Biopolymeric beads composed of Gold nanoparticles encapsulated alginate microspheres prove to be effective adsorbent for removal of Manganese ions from their aqueous solution. The adsorption of Mn (II) ions is significantly affected by pH of the metal ion solution, when varied in the range 4 to 10. It was noticed that the maximum adsorption was obtained at pH 5 at room temperature. The polymeric adsorbent beads composed nanoparticles encapsulated of Gold alginate microspheres could be repeatedly used in the adsorption studies by adsorption and desorption cycle without detectable losses in their initial adsorption capacities.

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