A Justificative Study of the Colorimetric and AAS method for the Adsorbent Gold Nanoparticles Encapsulated Alginate Microspheres applied for Remediation of Toxic Metals in the Aqueous Solutions

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Abstract

Gold nanoparticles encapsulated alginate microspheres were synthesized and found as a nanoadsorbent for the removal of Manganese metal ion from aqueous solutions. Gold nanoparticles were prepared and characterized by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Fourier Transform Infra-Red Spectroscopy (FT-IR). The adsorption of Manganese metal ion was examined by batch technique. The effects of pH, initial Manganese metal ion concentration, adsorbent dosage and contact time on the efficiency of Manganese metal ion removal were studied for the batch method. Batch technique was processed simultaneously and analysed using both Colorimetric and AAS method. The result of this study proved AAS method to be better for the removal of Gold nanoparticles encapsulated alginate microspheres as an adsorbent for Manganese metal ion. But both these methods have their own advantages and limits as well.

Index Terms: *Adsorption; Nanoparticles; Alginate*

1. Introduction: -

Water pollution by toxic metals remains a serious environmental problem and can be detrimental to plants, animals, and human beings alike. Different governments have set up environmental laws to determine amount of heavy metal ion in drainage, considered to be non-detrimental to the environment.

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 cost-effective 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 sorted 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.

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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.

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 Mn^{2+}, Cu^{2+} and Zn^{2+} [6].

$$(Na - Alg)_n + n\,M^{2+} = (M - Alg_2)_n + n\,(2Na^+)$$
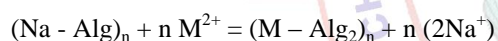
Manganese compounds are less toxic than those of other widespread metals such as iron, nickel and copper compounds. However manganese is toxic in excess. Problems that are caused by Manganese (II) are

-Skin rashes

-Upset stomach and ulcers

-Respiratory problems

-Weakened immune systems

-Kidney and liver damage

-Alteration of genetic material

-Lung cancer

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 metal-chelating 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 and subsequent comparison of the vitality of the two methods namely Colorimetric and AAS method.

Alginate is a polysaccharide biopolymer composed of anionic blocks of (1→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].

2.Experiments:-

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.

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 gel 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

Preparation of stock solution: - The stock solution of Mn (II) of (1000 mg dm^{-3}) was prepared by dissolving 0.307 g. of MnSO$_4$.2H$_2$O (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 HAuCl$_4$ solution, 1% Trisodium Citrate solution, 0.5 M Calcium Chloride solution**)**

Special Reagent for Colorimetric method: 400 ml. of conc.HNO$_3$ is added with 200 ml. of distilled water and subsequently 75g. of HgSO4, 200 ml. of 85% conc. H$_3$PO$_4$ and 35 g. of AgNO$_3$ was added. The solution was cooled and made upto 1000 ml. with distilled water.

Procedure of Colorimetric Analysis: About 1.25 ml. of the above prepared Special Reagent was added to 25 ml. of the sample solution and vigorously boiled to reduce the solution to 10 ml. when (NH$_4$)$_2$S$_2$O$_8$ was added quickly and the solution cooled down immediately. The persistent pink colour appears which is measured spectrophotometrically using VISISCAN-167.

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 MnSO$_4$.2H$_2$O solution (2 mg dm^{-3} concentration) at constant pH 8 and room temperature (25^{0}C) with constant stirring using mechanical shaker for 5 hrs. The amount of Manganese present in the colourless solution was assayed colorimetrically using VISISCAN-167 and spectrophotometrically by Atomic Absorption Spectrophotometer [16]. The amount of adsorbed Mn (II) was calculated by the following mass balance equation:

Adsorbed amount (mg/g) $= \dfrac{(C_i - C_f)V}{M}$

(A)

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.

3.Factors affecting adsorption:-

Effect of concentration: - When the concentration of Manganese Sulphate is raised in the range 0.5 to 4.0 mg dm^{-3} for AAS analysis and 0.0005 to 0.05 mg dm^{-3} for colorimetric analysis, the amount of adsorbed Mn (II) ions is found to increase and then tended to decrease for both the analysis. 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 initial Manganese ion concentration, which was found to decrease at higher concentrations, may be
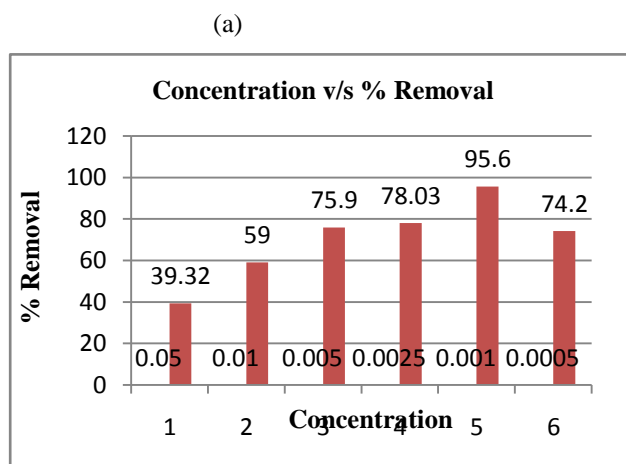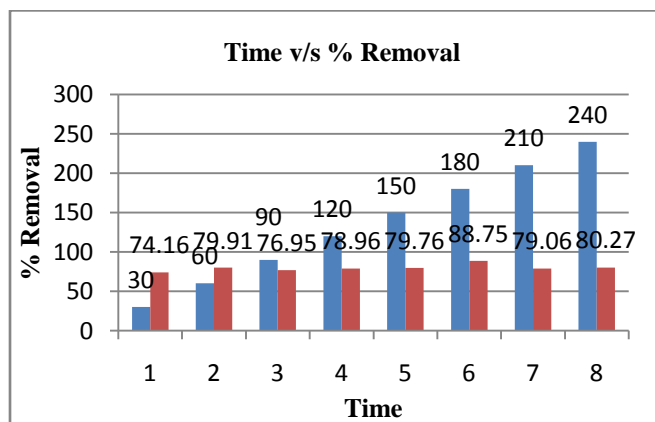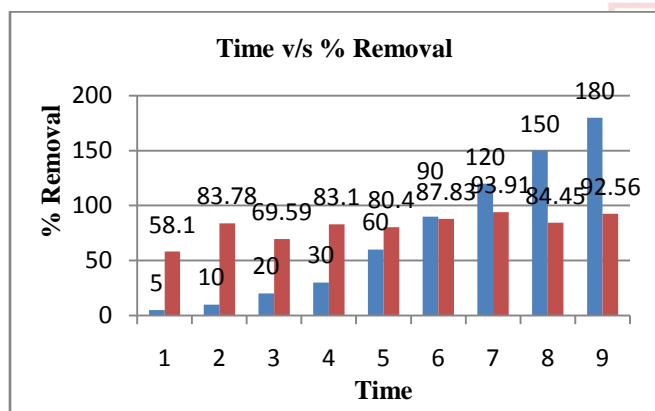
(a)

(b)
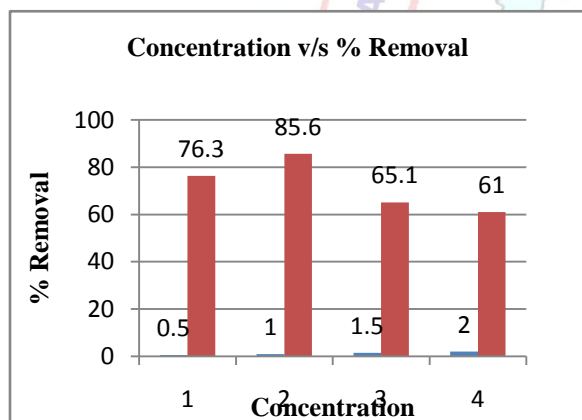
Fig. (2) Effect of concentration on the adsorption of Mn (II) ions onto Gold nanoparticles encapsulated alginate microspheres composite beads = 0.1 g. at room temp.for (a) AAS METHOD and (b) COLORIMETRIC METHOD

Effect of Time: - When the shaking time was increased from the range 5 min to 150 min for colorimetric method, the amount of adsorbed ions is found to increase when greater number of metal ions arrives at adsorbent interface and thus get adsorbed which was found to decrease at larger time span, may be due the progressive saturation of binding sites. Whilst ranging from 5 min to 300 min for AAS method, the amount of adsorbed ions is found to increase.

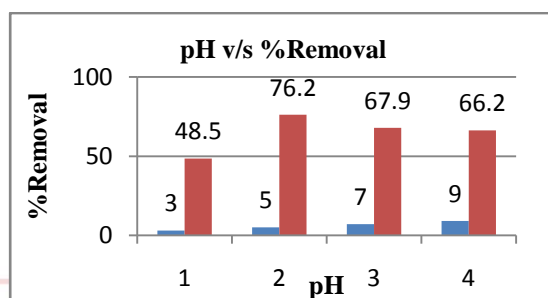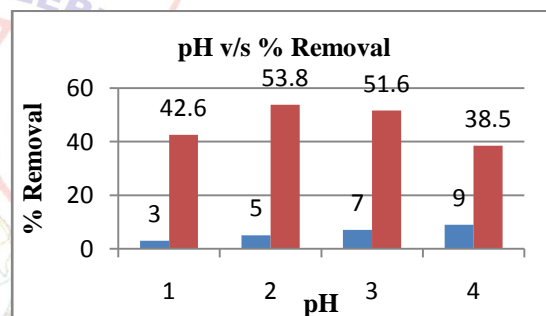due the progressive saturation of binding sites.

(a)

(b)

Fig. (3) Effect of time on the adsorption of Mn (II) ions onto Gold nanoparticles encapsulated alginate microspheres composite beads = 0.1 g. at room temp.for (a) AAS METHOD and (b) COLORIMETRIC METHOD

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.

(a)

(b)

Fig. (4) Effect of pH on the adsorption of Mn (II) ions onto Gold nanoparticles encapsulated alginate microspheres composite beads = 0.1 g. at room temp.for (a) AAS METHOD and (b) COLORIMETRIC METHOD

Effect of colour and size of the beads: - The similar experiments performed with an appreciable change in the size and the colour of the beads showed no remarkable change in the adsorption characteristics highlighting the fact that once the active sites of the nanoparticles are filled, any further change is rarely feasible.

4.Characterization of microspheres:-

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).

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).

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).

5.Results and discussions: -

XRD analysis: - The XRD patterns of composite beads of bare alginate and Gold nanoparticles encapsulated alginate microspheres are shown in fig. 5 (a) and (b) respectively. Powder XRD was carried out to identify the nano crystalline structure of the gold species and amorphous nature of Alginate.
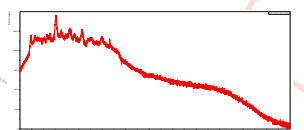

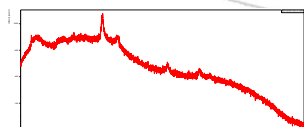Fig. (5) (a) XRD pattern of bare Alginate

Fig. (5) (b) XRD pattern of Gold nanoparticles encapsulated alginate microspheres

FTIR analysis: - Fourier transforms infrared spectroscopy (FTIR) spectra of unadsorbed (bare) and Mn (II) adsorbed beads are shown in fig. 3 (a) and (b) respectively. The FTIR analysis indicated the band at 2923.61 cm^{-1}, assigned to C-H bond of methylene groups. The sharp peak appearing at 1652.73cm^{-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.
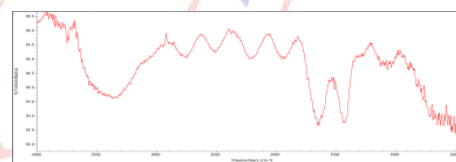

Fig. (6) (a)

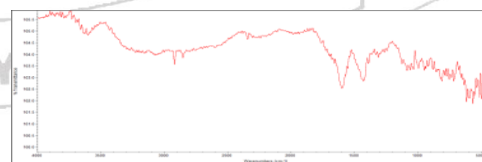Fig. (6) (a) FTIR spectra of bare Alginate

Fig.(6) (b)

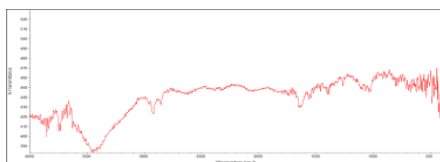Fig.(6)(b) FTIR spectra of Gold nanoparticles encapsulated alginate microspheres

Fig. (6) (c)

Fig. (6) (c) FTIR spectra of Mn (II) adsorbed Gold nanoparticles encapsulated alginate microspheres

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.
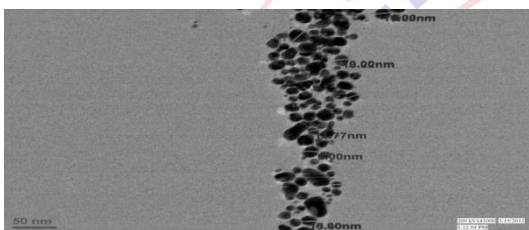

Fig. (7) TEM images of bare nanoparticles of Gold nanoparticles encapsulated alginate microspheres

6. Conclusion

Biopolymeric beads composed of Gold nanoparticles encapsulated alginate microspheres prove to be effective adsorbent for removal of Manganese ions from their aqueous solution. It can however be shown that both the methods have their own limitations and advantages based on the prevalent conditions. Though AAS being sophisticated, is comparatively a better method as compared to Colorimetric method but based on the economical viability of the instrument, Colorimetric method cannot be underestimated under the present

available conditions. Again, the utmost sensitivity and care required to process out the Colorimetric method can't be overlooked or surpassed which questions the reproducibility of the process. Hence, both the methods seem to validate the usefulness and applicability of the chosen method under its own specific conditions.

Table 1: Comparison Of Parameters w.r.t. AAS and COLORIMETRIC method:

S.No.	Parameters	AAS		Colorimetric method	
		Conc.	Time	Conc	Time
1.	AA*	128.47 mg	3.13 mg	0.0095 mg	0.0093 mg
2.	EC**	0.144 ppm	0.112 ppm	43.5 ppb	60.9 ppb

Where AA* stands for ADSORBED AMOUNT and

EC** for EQUILIBRIUM CONCENTRATION

Table 2: Comparison Of Factors Against % REMOVAL w.r.t. AAS and COLORIMETRIC method:

S.No.	FACTORS	AAS METHOD (% R)*	COLORIMETRIC METHOD (% R)*
1.	pH	76.2	53.8
2.	Conc.	85.6	95.6
3.	TIME	88.75	93.91

Where (% R)* implies Percentage Removal

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