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Waste Water Treatment Through Dendrimer – Conjugated Magnetic Nanoparticles

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Abstract: Water treatment by the use of nano technology has been an encouraging progress, though nano membranes and nanofilters are used in the treatment of water, the technology of metal ion removal by the use of a nanoadsorbant is at a neonatal stage in India, though it has been prôposed that the nanoadsorbants have a tremendous potential for effective physical as well chemical treatment of water. The aim of the present study was to synthesize silica based PAMAM dendrimer (nanoadsorbant) with ester and amino groups at the outer surface, to evaluate its metal binding properties from tannery effluent using Atomic Absorption Spectroscopy. The synthesis of dendrimer is usually carried out in two ways namely convergent technique and divergent technique. In the divergent technique, the dendrimer is assembled from a multifunctional core, which is extended outward by a series of reactions, commonly a Michael reaction. In the case of convergent technique, Dendrimers are built from small molecules that end up at the surface of the sphere, and reactions precede inward building inward and are eventually attached to a core. PAMAM is normally synthesized by divergent methods starting from ammonia or ethylenediamine initiator core reagents. PAMAM is found to have high surface functionality, which is very helpful in the adsorption of metal ions. PAMAM belong to the class of water soluble polymers which is a criteria much needed for the agent in the treatment of water. They can act as flocculants for dye industry waste water treatment. Amine terminated PAMAM dendrimers exhibit and high affinity for adsorption of metal ions to their surface via co ordination to the amine or the acid functionality. It is pH independent in its action. Silica gel being an adsorbent with excellent thermal and mechanical stability, used in most chromatographic techniques. All of the ester and amino terminated PAMAM dendrimer presented regularities in adsorption of metals like chromium, zinc and iron. The adsorption of ester and the amino terminated products increased with the increase in the increase in the grafting percentage and the addition of the surface functional groups. From this it can be concluded that the amine and the ester groups are alone responsible for the easy and efficient adsorption of the metal ions, the amine terminated groups exhibiting higher adsorption due to its co ordination and acid functionality.

Key Words: Heavy metal removal**,** Modified silica-gel; Polyamidoamine-typed hyperbranched polymer Preparation, Adsorption.

1. Introduction

Water resources are of critical importance to both natural ecosystem and living beings. This important natural resource is being contaminated every day by various anthropogenic activities such as rapid growth of population, urbanization and industrialization that ultimately make the environment polluted[1]. There are greater concerns about heavy metal contamination. Environmental pollution from industrial wastewater particularly in developing countries like India is of major concern. High levels of heavy metals can damage soil fertility and may affect the flora and fauna. Industrial effluents discharged from various industries like textile, tannery, sugar processing, dye and distilleries contain higher amount of metals like chromium, copper, nickel, lead, zinc, mercury and cadmium and results in a series of well documented problems in living beings because the heavy metals cannot be completely degraded[2]. Hence it is necessary to treat the effluent to reduce the concentration of heavy metal contamination and different systems like mechanical systems, aquatic systems and terrestrial systems were primarily used[3]. At present, many physiochemical methods like distillation, reverse osmosis, carbon adsorption, ion exchange resins and nanofiltration are used[1]. Major drawbacks of these methods include sludge formation, handling, disposal problems, and technical constraints. This necessitates cost effective, innovative and most advantageous methods for treatment of waste water containing heavy metals[5,6,10,11].

2.Materials And Methods

Ethanol, Tetra Hydro furan, methanol, ethylene diamine, methyl acrylate, toluene were purchased from Loba Chemicals, and amino propyl triethoxysilane (APES) was purchased from Synergy Scientific Services. Tannery effluent was obtained from tanning industries in Sembattu region of Tiruchirappalli. All the other solvents and reagents were of analytical or high performance liquid chromatography grade.

3. Experiment Methodology

3.1. Preparation Of Ester And Amino Terminated Pamam Dendrimers[4,7,8,9] :

The general scheme of synthesizing ester and amino terminated PAMAM dendrimers is by the introduction of amino groups onto the silica gel surface followed by the Michael's addition of methyl acrylate to amino groups on the silica gel surface and ends with the terminal ester group amidation by ethylene diamine, given as[4,7,8,9]:

3.2. Preparation Of SiO_2-G0

Introduction of amino groups onto the silica surface was achieved by the treatment of surface silanol groups with Amino Propyl TriEthoxy Silane (APES). A suspension of 50.0 g of silica-gel and 50 ml of APES were stirred at 70^0C in the 150 ml of toluene solution for 6 hours in a round bottomed flask mounted on a magnetic stirrer provided with a heater. The rate of mixing was controlled by the RPM controller provided. The RPM was generally maintained around 900 rpm. Condensing system was used to prevent toluene loss due to vaporization, since it is a highly volatile compound. The product was then filtered off, packed in a thimble bag and then transferred to a Soxhlet extraction apparatus for reflux-extraction in toluene and ethanol for 10 hours, respectively. The product thus extracted was dried under vacuum at 50^0C over 48 hours.

3.3. Preparation Of SiO_2-G0.5:

A mixture of 40 g of SiO_2-G0 and 31 ml of Methyl Acrylate (MA) were added to a 500 ml flask with 240 ml of methanol as solvent. The mixture was stirred at 50^0C for 3 days to react sufficiently under nitrogen atmosphere condition, brought about by purging the round bottomed flask with nitrogen gas after the reactants are added followed by the continuous passage of nitrogen gas into the round bottomed flask, at the time of reaction. The solid product was then filtered off, packed in a thimble bag, and transferred to the Soxhlet extraction apparatus for reflux extraction in ethanol and tetrahydrofuran for 24 hours, respectively. After extracting, the product was dried under vacuum at 50^0C over 48 h and SiO_2-G0.5 was obtained

3.4. Preparation Of SiO_2-G1.0

The reaction was carried out under a nitrogen atmosphere, a suspension of 30 g of SiO2-G0.5 and 300 ml of EDA was stirred at room temperature about 25^0C in a flask using 200 ml of methanol as solvent for 5 days. The product was filtered off , packed in a thimble bag and transferred to the Soxhlet extraction apparatus for reflux-extraction in ethanol and tetrahydrofuran for 24 hours, respectively and then was dried under vacuum at 50^0C over 48 hours. The product SiO_2-G1.0 was obtained.

3.5. Preparation Of SiO_2-G1.5:

Under a nitrogen atmosphere, the reaction involved mixing of a suspension of 19.4 g of SiO_2-G1.0 and 62 ml of Methyl acrylate in 120 ml of methanol solvent. The reactant mixture was stirred for 4 days at 50^0C and then the product SiO_2- G1.5 was filtered off , packed in a thimble bag and transferred to the Soxhlet extraction apparatus for reflux-extraction in ethanol and tetrahydrofuran for 24 hours, respectively and then was dried under vacuum at 50^0C over 48 hours. The product SiO_2-G1.5 was obtained

3.6. Preparation Of SiO_2-G2.0

The Reaction was carried out under a nitrogen atmosphere and 11.4 g of SiO2-G1.5, 150 ml of Ethylene Diamine were mixed with 70 ml of methanol as solvent .The mixture was stirred at 25^0C for 7 days .The solid product was then filtered, packed in a thimble bag and transferred to the Soxhlet extraction apparatus for reflux-extraction in ethanol and tetrahydrofuran for 24 hours, respectively and then was dried under vacuum at 50^0C over 48 hours. The product SiO_2-G2.0 was obtained.

4. Treatment Of Effluent:

An accurately measured quantity of around 20ml tannery industry effluent was taken in four different centrifuge tubes and to the said effluent around 0.25g of SiO_2.G0.5 and SiO_2.G1 SiO_2.G1.5 and SiO_2.G2 were added separately, and shaken vigorously in a vortex shaker for about 15 minutes, to bring about good contact between the dendrimer nanoparticles and the heavy metal ions to facilitate a greater extent of adsorption of the metal ions in the effluent. Then the treated effluent is centrifuged, at a temperature of about 20^0 C and a speed of about 7000 rpm, such that the treated water and the added PAMAM dendrimer settle separately, for the dendrimer to be reused.

5. Characterization Of Ester And Amino Terminated Pamam Dendrimer:

5.1. Fourier Transform Infra Red Spectrophotometer (FTIR):

FTIR was used to measure changes in the chemical structure of the silica gel based ester and amino group terminated PAMAM dendrimer on which all the functional groups are added in a step wise manner. Infrared spectra were recorded on a Nicolet MAGNA IR 550 (series II) spectrophotometer, using ATR attachment at room temperature. The spectrum was acquired at 400-4000 cm-1 wave numbers with a 4 cm-1 resolution using EZ OMNIC 6.0 (Thermo Nicolat) software.

5.2. Scanning Electron Microscope (SEM):

The shapes and the surface morphology of the samples were examined on a Scanning Electron Microscope (SEM), to make sure that the synthesized particles are of nano size.

5.3. Characterization Of Tannery Effluent

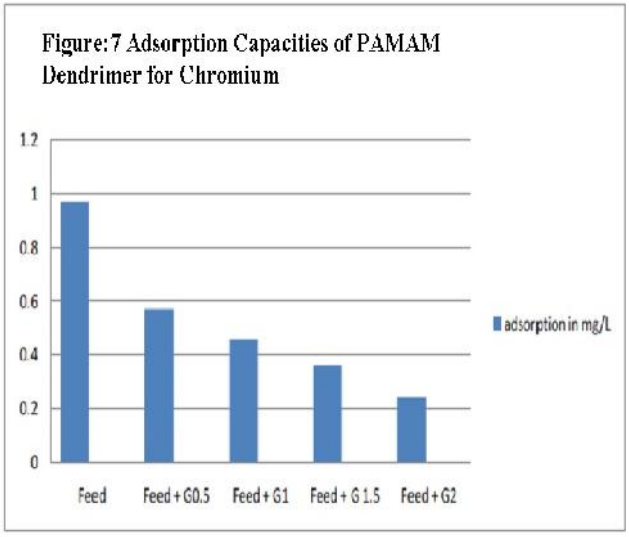
The tannery effluent was characterized by Flame method of the Atomic Absorption Spectroscopy, at Ekdant Enviro Services Private Limited, Anna Nagar, Chennai. The feed was treated with the progressing generations of the dendrimers. Five samples were analyzed against different standards for the evaluation of chromium ion concentration in the sample. From the observed absorbance values, as given in the table.

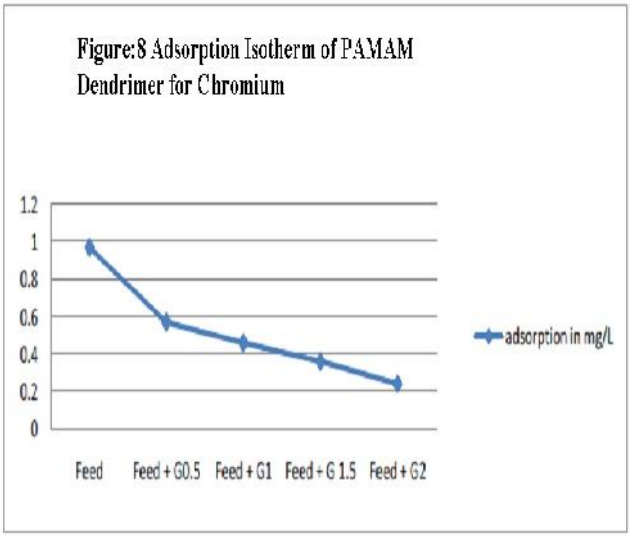
As seen in the table, the amount of the chromium metal ion concentration has been found to be decreasing with the progressing generation of the dendrimer thus proving the PAMAM dendrimers to be good absorption species.

The adsorption capacities and the isotherm of the PAMAM dendrimer for chromium are as shown in the Figures 7 and 8.

Table 1: Atomic Absorption Spectroscopy report for tannery effluent:

Sample	Reference Standard		Tannery Effluent Sample Collected	
	Amount of Cr in mg/L	Absorbance	Amount of Cr in mg/L	Absorbance
Feed	0.10	0.01	0.97	0.10
Feed+G0.5	0.20	0.02	0.57	0.05
Feed+G1	1.00	0.10	0.46	0.04
Feed+G1.5	2.00	0.20	0.36	0.03
Feed+G2	3.00	0.30	0.24	0.02





5.3.1. Atomic Absorption Spectroscopy (AAS):

Atomic Absorption spectrophotometer was used to measure the concentration of metal ions before and after the treatment of the effluent and the plant extract with the dendrimer samples.

6. Result And Discussion

6.1. Characterization Of The Pamam Dendrimer:

Nanoadsorbants have been characterized by using a wide range of techniques. The characterization of nanoadsorbants is a difficult task owing to their complexity, variety of structures and components involved in these systems, as well as the limitations associated with each technique, but such knowledge is essential for their successful commercial exploitation.

6.2. scanning electron microscope (SEM):

Scanning Electron Microscopy analysis was carried out at 10Kv. The results of the scanning electron microscopy can be observed in the Figures 1 and 2.The figures reveal that the particle appearances of the G1 and G2 dendrimers were very similar, thus demonstrating that the particles of the dendrimer samples have good mechanical stability, and they had not been destroyed during the whole reaction.

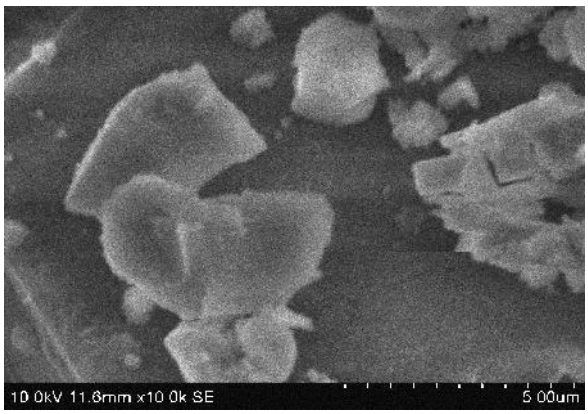


Figure 1: SEM image of G1 PAMAM dendrimer

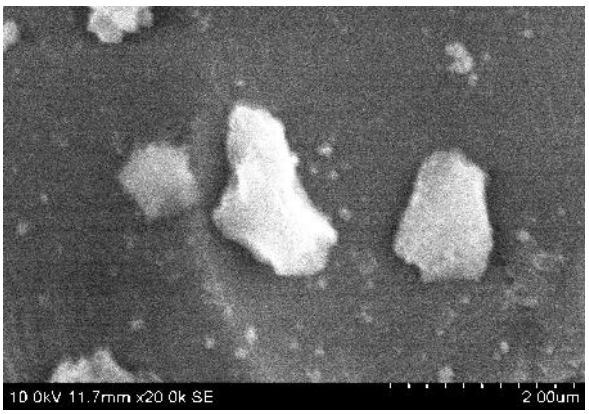


Figure 2: SEM image report of G2 PAMAM dendrimer

6.3. Fourier Transforms Infrared Spectroscopy:

The surface attachment of the amino groups on the surface of the silica gel was characterized by FTIR spectrum for the G0 and G 0.5 of the PAMAM dendrimer (Fig. 3and 4) Thirteen characterization peaks at 3378.84, 3164.05, 3612.23, 3718.89, 3942.27, 3812.66, 2677.37, 1408.30, 1078.38, 1602.21, 727.43, 626.35, 487.43 were observed to be NH bending (Primary and Secondary amides), NH stretching vibrations(Primary amides and Secondary amides), C-N stretching band, conforming primary amine, C-N Stretching vibrations indicating primary and secondary amides, OH stretching vibrations showing the vibrations of the SiOH group and the torisonal oscillation of NH_3 group.

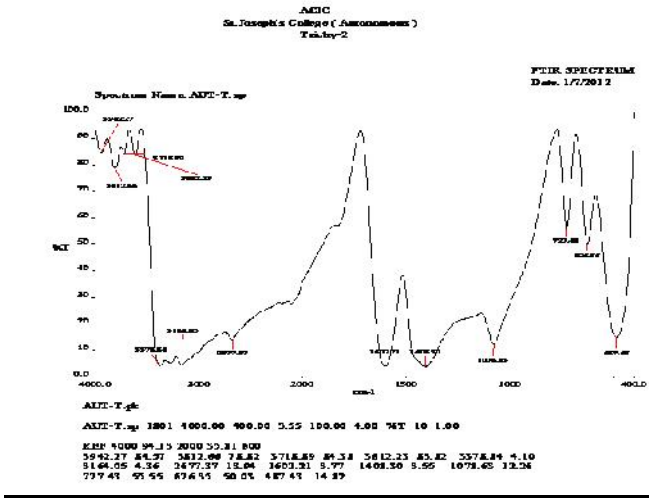


Figure 3: FTIR Spectrum of G0 PAMAM Dendrimer

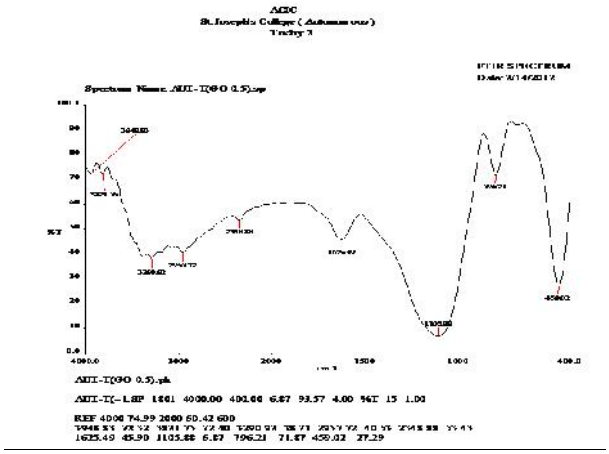


Figure 4: FTIR Spectrum of G0.5 PAMAM Dendrimer

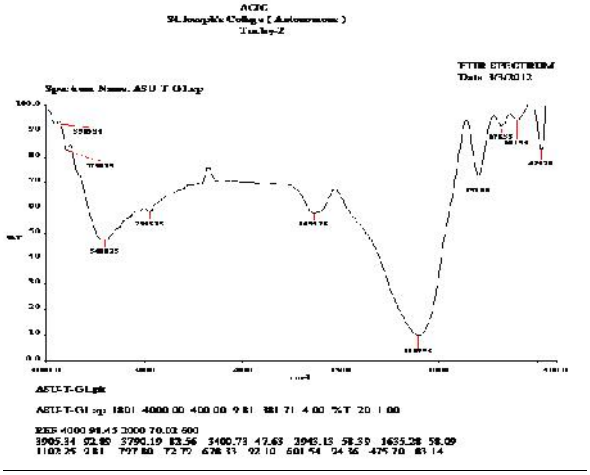


Figure 5: FTIR Spectrum of G1 PAMAM dendrimer

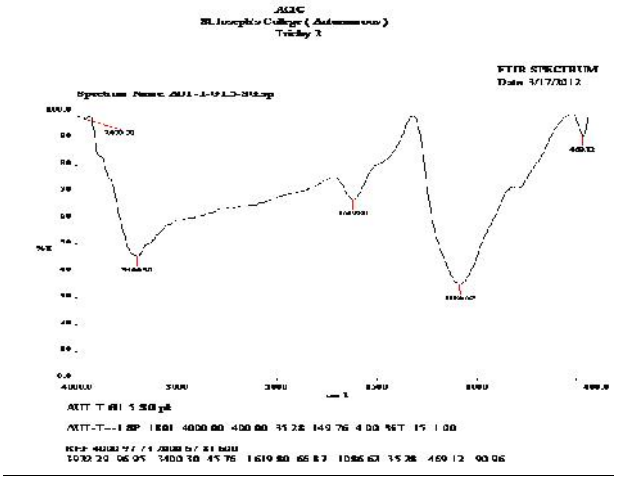


Figure 6: FTIR Spectrum of G1.5 PAMAM dendrimer

Conclusion

Ester and amino terminated PAMAM dendrimer was synthesized by divergent method of synthesis and they were grafted successfully on the surface of the silica gel. The percentage of grafting of the ester and amino group terminated PAMAM dendrimer on the surface of the silica gel increased with the increase in the number of generations as given by the FTIR reports. And the monitoring by FTIR showed that it needed at least 5 and 7 days for G0.5 and G1 to be converted to G1.5, and G2 respectively. SEM analysis report makes it is evident that the size range of the PAMAM dendrimer is around 1nm and the pore surface diameter decreased after the series of grafting reactions. All of the ester and amino terminated PAMAM dendrimer presented regularities in adsorption of metals like chromium. The adsorption of ester and the amino terminated products increased with the increase in the increase in the grafting percentage and the addition of the surface functional groups. From this it can be concluded that the amine and the ester groups are alone responsible for the easy and efficient adsorption of the metal ions, the amine terminated groups exhibiting higher adsorption due to its co ordination and acid functionality.

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