Preparation Of Fe-Loaded Polyacrylamide Grafted Shellac For The Removal Of Cadmium (II) Ions From Aqueous Solution

[1]M M Sajeevan, [2] Ajmal Thayyullathil, [3]C M Naseera

[1,2,3] Assistant professor, Department of Chemistry, Government College Madappally, Calicut University, Kerala-673102, India.

Abstract:

Pollution adversely affect the aquatic life and human beings. Removal of hazardous materials from waste water is very important for aquatic life as well as human life. Many methods including adsorption are used for the removal o toxic metal ions and dyes from waste water. The adsorbent binds with metal ions and dyes and remove them. A novel adsorbent, shellac and its iron loaded derivative was prepared. The iron loaded polyacryamide grafted shellac was used to remove cadmium from waste water. The synthesised iron loaded polyacrylamide grafted shellac was characterised by FTIR and XRD. Shellac and shellac derivative are efficient adsorbent for the removal of toxic metal ions from waste water. The amount adsorbed was found higher than that observed in conventional adsorbents.

Index Terms: Shellac, Polygrafted, Iron loaded shellac.

Abbreviations

SH- Shellac

PGSH- Polyacrylamidegrafted Shellac

Fe-PGSH- Iron loaded polygrafted shellac

FTIR-Fourier transform infrared

XRD- X-ray diffraction

Introduction.

Pollution is one of the major problems facing by the living world. Major pollutants involved in water pollution are heavy metal ions such as Co, V,Cd,Crand Pb, and dyes such as methylene blue and Indigo. Many industrial uses of metals and other domestic process like incineration of wastes, burning of fuels, smelting process are causing pollution (1).At high concentrations the heavy metal causes toxic effects. Lead causes kidney damage, encephalopathy, behavioural disturbances and anaemia(2). Chromium(VI) ions produce respiratory cancers(3) and cadmium causes nephrotoxic effects(4). Among the heavy metal ions vanadium is one of the most important and hazardous metal which causes breathing disorders and paralyzes ,and also affect liver and kidney(5). So the removal of Vanadium from industrial waste water is very important as far as the aquatic life as well as human life is concerned.

Varieties of methods are used for the determination of vanadium. It includes graphite furnace atomic absorption spectroscopy(6), spectrophotometry(7) ,eletro thermal atomic absorption spectroscopy(8),inductively coupled plasma optical emission spectroscopy(9),inductively coupled plasma mass spectrometry(10) and neutron

activation analysis(11). Spectrophotometry is the simple and most commonly used method for the determination of vanadium. Vanadium 5+ can be determined by spectrophotometry based on N-(1-naphthalene-1-yl) ethane-1,2-diamine hydro chloride (NEDA)(12),dopamine hydrochloride(DPH)(13). Semicarbazide and their metal complexes are used for the extraction of $V5^+$(14)

Adsorption is one of the best methods used to remove heavy metals and dyes from waste water. Charcoal, coconut husk ash and rice husk ash are the important adsorbents used for the removal of heavy metals and dyes from industrial waste water. Adsorption of heavy metals by organic materials is accomplished by the application of polymeric ion exchangers. The interaction between the adsorbents and metal species is favoured through ion exchange mechanism. If we use chelating adsorbents the metal species can directly attached through chelation or complex formation mechanism(15). Naturally occurring materials like chitosan or modified materials like cross linked carboxy methyl chitosan are also used for the adsorption of heavy metals(16)

Recently, different types of iron loaded materials are, especially both biopolymers and synthetic polymer, are used for adsorption. Some anion exchange resins are also used for the effective adsorption of fluoride ion(17). The high valent metal ions such as La(II), Ce(III) and Zr(IV) on suitable functional groups loaded biopolymers are also used as adsorbents for the removal of fluoride ions.

In this work we introduced a novel material, shellac and its iron loaded polymer, as adsorbent for the removal of heavy metal ions and dyes. Shellac is a natural resin obtained from lac trees in India and Thailand. It is a resin secreted by a small bug which used to live in the bark of lac tree. Shellac is a natural biodegradable resin. Shellac is a natural product consist of aleuritic acid and cyclic terpene acid both of which are connected through ester linkage using the carboxylic group of aleuritic acid. The carboxyl group of the cyclic terpene acid mainly contro the hydrophilicity of the molecule. Shellac is widely used in pharmaceutical applications and also used as food coating(18).

The availability of a number of hydroxyl as well as carboxylic groups in shellac make it a good adsorbent. Hydroxyl and carboxyl groups act as binding sites for chemisorptions of heavy metals ions and dyes. Since the number of hydroxyl and carboxyl groups are very high, shellac is superior over other adsorbents and is a better candidate for further modifications. After the heavy metal ions r dyes get adsorbed on shellac, it can be retained by hydrolysis or neutralisation and can be used again.

Materials and methods:

Materials.

Shellac flakes were collected from Krishna trading company Ahmedabad Gujarat. The shellac flakes(SH) were washed with deionised water and dried. The dried shellac (SH) was powdered and used for the preparation of iron loaded polyacrylamide grafted shellac(Fe-PGSH).

a)Preparation of Fe-loaded polycrylamide grafted shellac(Fe-PGSH).

About 20.0g of dried shellac flakes(SH) was added in 100.0ml solution containing 5.0g of methylene bisacrylamide(MBA), 5.0g glutaraldehyde(GA) and 7.5 g of acrylamide(AA). This solution was well stirred. Then 2.0g of potassium persulphate($K_2S_2O_8$) was added to it. The solution was made upto 400.0ml and was heated to 70°C and stirred well. The polyacrylamide grafted shellac was filtered , washed well with water , dried and powdered.

Polyacrylamide grafted shellac was then subjected to hydrolysis using the following procedure. To 10.0g of polyacrylamide grafted shellac, 1.0N NaOH (300ml) was added and the mixture was heated at 60°C for 3 hours. During hydrolysis ,the amide group in polyacrylamide grated shellac gets hydrolysed to carboxyl group. The hydrolysed polyacrylamide grafted shellac (PGSH) was filtered, washed with water ,dried and used for the iron loading.

For iron loading onto PGSH ,about 10.0g of PGSH was treated with 250.0 ml of 0.3 M sodium acetate/acetic acid buffer(pH 3) containing 6.8g of $FeCl_3.6H_2O$ for 10 hours at room temperature. Finally , te Fe(III) loaded

functionalised shellac (Fe-PGSH) was washed with water until all the non-chelated Fe(III) was removed. The dried sample was sieved to pass through 80+230 mesh sieve and stored in a desiccator for further use.

**b)Preparation of Vanadium(Cd) solution.**

Cadmium(Cd) stock solution was prepared by dissolving 1.168 g of cadmium nitrate in 100.0 ml distilled water. All other working solutions were prepared by diluting the stock solution using distilled water.

c)Characterization of SH, PGSH and Fe-PGSH.

The FTIR spectra of SH, PGSH and Fe-PGSH were obtained using the pressed disc technique in a Perkin Elmer spectrophotometer. XRD patterns of SH, PGSH and Fe-PGSH were obtained using X-ray powder diffractometer (Bruker AXS D8 model). A systronic pH meter calibrated with standard buffer solutions was used for pH measurements.

Figure.1. shows the FTIR spectra of SH, PGSH and Fe-PGSH. For SH, a peak at 3435 cm^{-1} shows –OH stretching vibration and 2920 cm^{-1} was caused by the aliphatic –CH stretching vibrations of lignocellulosic compounds. In PGSH, a band at 1033 cm^{-1}(P=O vibrating) onfirmed the successful introduction of phosphate groups during phosphorylation. Further, the adsorption of Cd onto PGSH made slight shift in the characteristic bands of Fe-PGSH.
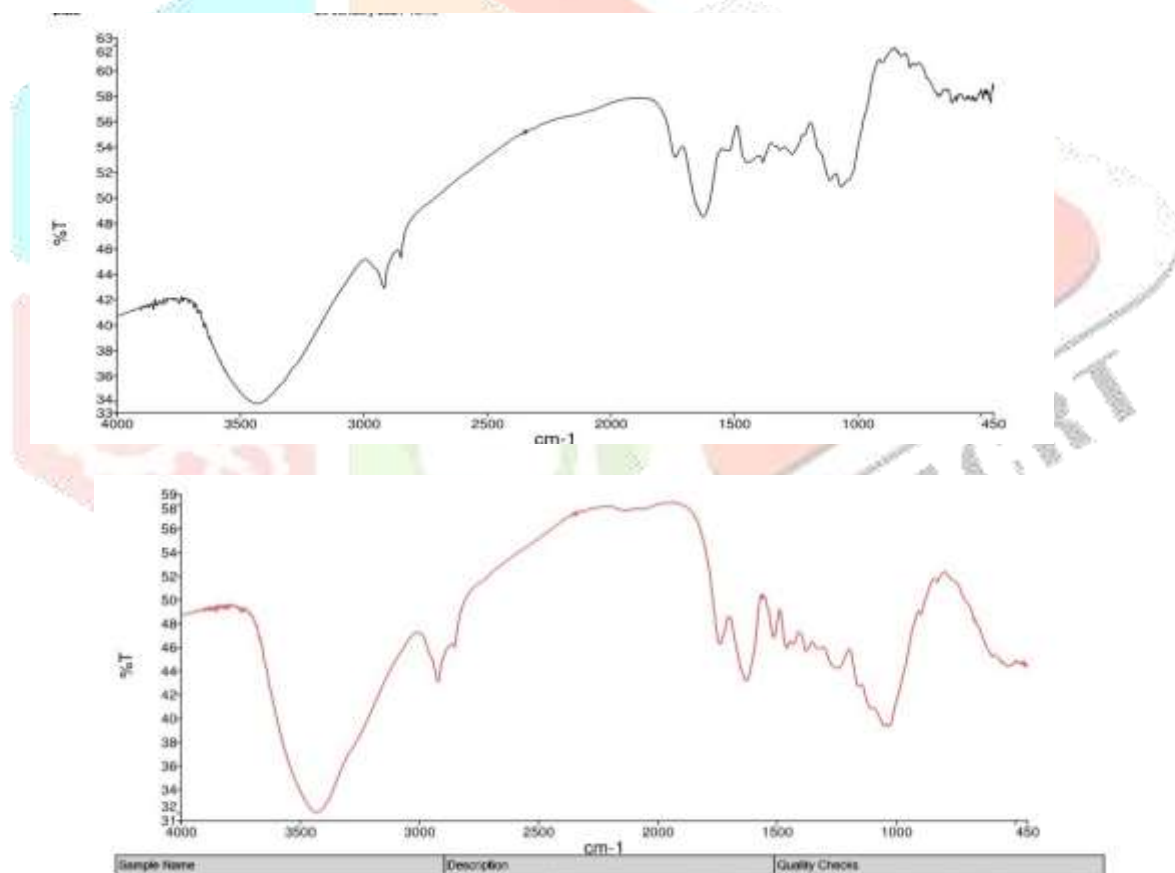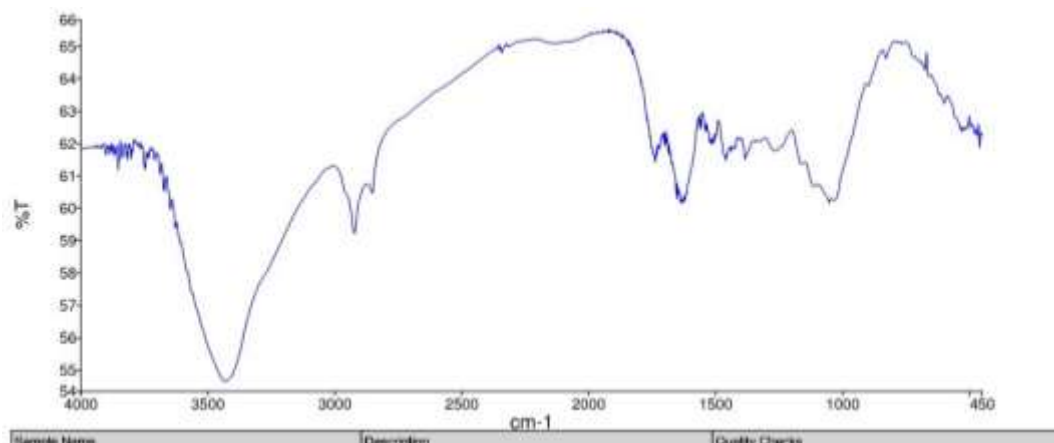
FTIR spectra of SH, PGSH ans Fe_PGSH

XRD patterns of SH, PGSH and Fe-PGSH

To examine the crystallinity of SH, PGSH and Fe-PGSH, XRD patterns was used. Fig. 2 represents the XRD patterns of SH, PGSH and Fe-PGSH. The diffraction patterns for TFS shows the appearance of peaks at 2θ values of 14.98°, 15.33°, 23.33°, 24.42°, 27.67°, 30.13° and 30.82°. The sharp XRD pattern shows the crystalline behavior of TFS. For PTFS, only three prominent peaks were observed at 2θ values of 14.89°, 24.31° and 29.44°. The intensity of the remaining peaks was lower and also a broadening takes place for the prominent peak in PGSH. This clearly confirms that, phosphorylation lowered the crystallinity of PTFS. Further in the case of Fe-PGSH, only a single peak is obtained at 2θ value of 24.37° and all other peaks disappeared. The Cd loading onto PGSH lowers the crystallinity substantially and PGSH begins to exhibit amorphous behavior.
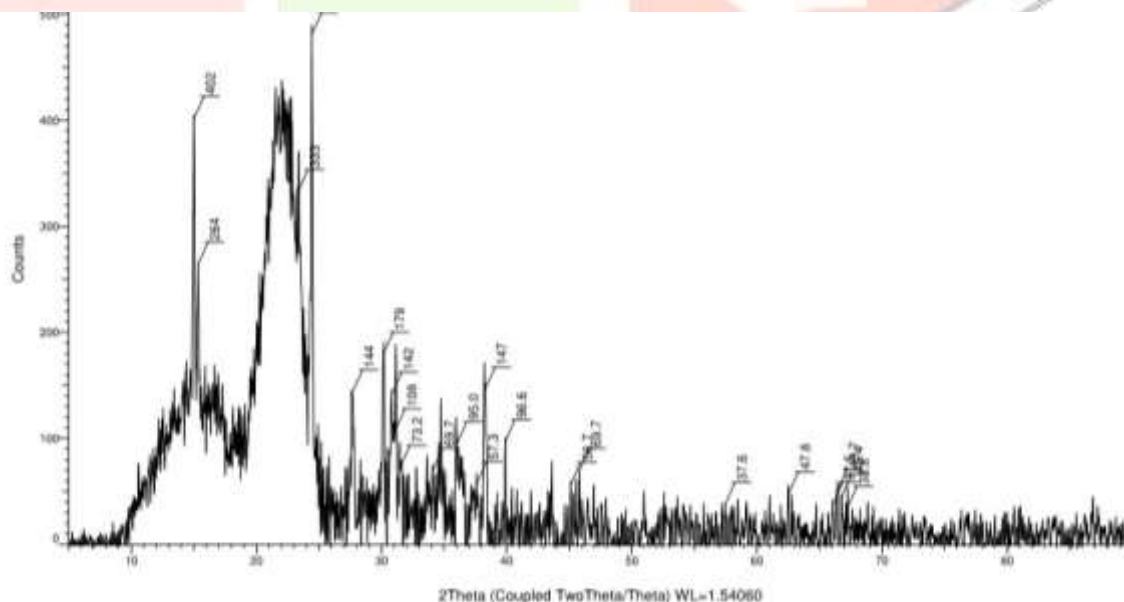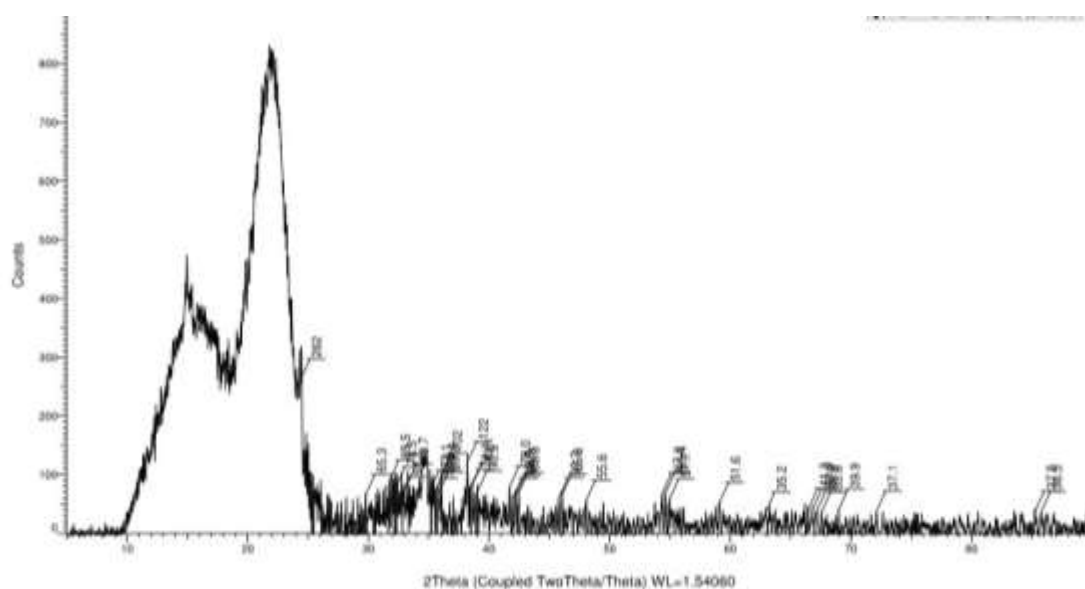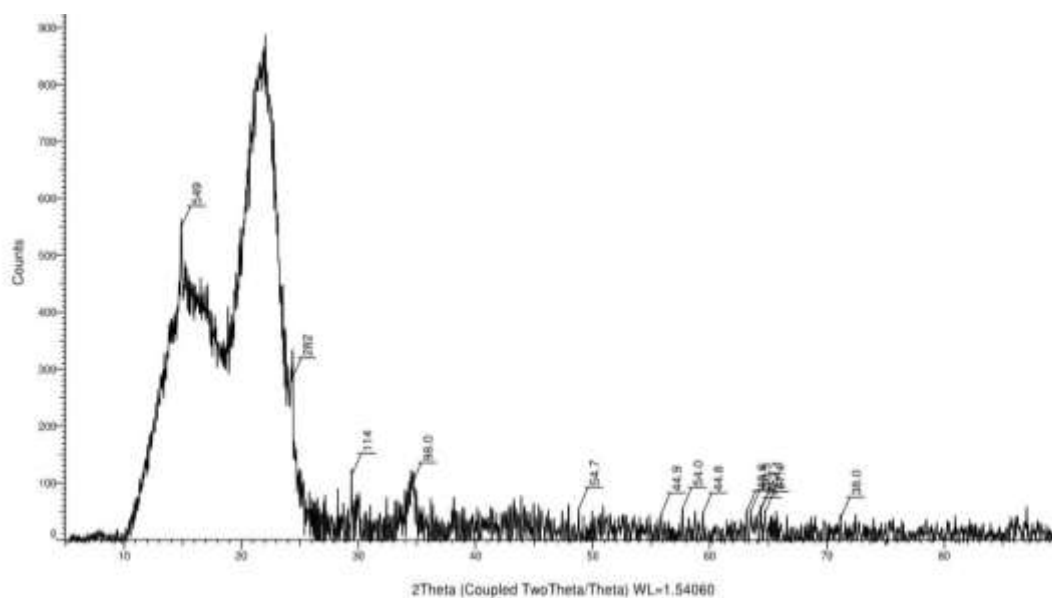
XRD patterns of SH, PGSH and Fe-PGSH

Methods.

Batch adsorption experiments were conducted by agitating 100.0 mg of adsorbent with 50.0 ml of Cd(II) solution of desired concentration in 100.0 ml stoppered conical flask using a temperature controlled water bath flask shaker(Labline,India) at a shaking speed of 200 rpm for 2 hours. Once the pre-set contact time (2H) reached, the samples were withdrawn and centrifuged and the supernatant solutions were analyzed for the residual Cd(II) concentration by titration against Mohr's salt solution. The amount of adsorption(Qe) was calculated using the following equation.

$$Qe \ = \ (\ C_0 - Ce)\ V/m$$

Where C_0 and Ce are the initial and equilibrium Cd(II) concentrations(mg/L) repectively, m is the mass of adsorbent Fe-PGSH(g) and V is the volume of the solution (mL). The amount of Cd(II) ions in soltuion was determined by volumetric method. The Cd(II) solutions of varying concentrations were pipette out into a clean conical flask. About 2 ml concentrated phosphoric acid solution and 5 drops of N-phenyl anthranilic acid indicator were added This solution is titrated against Mohr's salt solution from the burette and the end point is the appearance of colour change from green to purple.

Conclusion.

Fig. 1 represents the FTIR spectra of SH, PGSH and Fe-PGSH. The spectrum of SH, PGSH and Fe-PGSH shows an absorption band at 3418cm-1 which is attributable to the hydrogen bonded O-H stretching vibration. The spectra of SH, PGSH and Fe-PGSH respectively showed peaks at 2931,2930 and 2931 cm-1, indicative of the C-H stretching from the $-CH_2$ group. The appearance of peaks at 1694 cm-1 for SH and PGSH and1695 for Fe-PGSH indicate the presence of C=O stretching of amide group. The bands at 1543 and 1459 cm-1 are characteristic of –N-H groups which present in PGSH and Fe-PGSH.

The XRD patterns of the SH,PGSH and Fe-PGSH were displayed in Fig.2. With the grafting, the intensity of the peak at 30.83º increased in PGSH , resulting from the aggregation of the shellac molecules corresponding to polymer grafting. Additional peaks were observed at 26.5 and 28.4º in Fe-PGSH due to the occupancy of Fe in Fe-PGSH.

The present investigation showed that the Fe-PGSH was an effective and low cost adsorbent for the removal of Cd(II) ions from dilute aqueous solutions. Fe-PGSH gives a maximum monolayer adsorption capacity of 33.34 mg/g, which is the second highest reported for the removal of cadmium from aqueous solutions.

References.

1. H.Babich, M.A.Devanas, G.Stotzky. Environmental Research,1985,37(2) 253-286

2. A. Pagliuca, G.J. Mufti. British Medical Journl, 1990,300, 830

3. IARC(b) monographs on evolution of carcinogenic risks on human,1990, vol.49.

4. L.I Friberg, American Industrial Hygiene Association Journal, 1985, 46(11), 633-642

5.Lingfan hang, Xiu Liu, Wei Xia, Wenqing Zhang, International Journal of Biologicalmacromolecules,

   2013.

6. F.A.C Amorim, D.C Lima, J.Amaro, M.G.R. Vale and S.L.C.Ferreria, Journal of Brazilian chemical

   society,2007,18(8): 1566-1570.

7. Mathew S.b, G.Patiala, A.K.Gupta,Spectrochimica Act part A: Molecular and Biomolecular

   Spectoscopy,2011,81(1): 774-777.

8. Gil.R.A, S.N.Goyanes, G.Polla, P.Smichowski, R.A.Olsina and L.D.Martinez, Journal f Analytical

   Atomic Spectroscopy, 2007,22(10): 1290-1295.

9. S.L.C.Ferreria, F.A.C.Amorim,, D.C.Lima,J.Amaro and M.G.R. Vale, Journal of Brazilian chemical society, 2007,18(8): 1566-1570.

10. D.E.Nixo, K.R.Neuber, S.C.Eckdahl, J.A.Butz and M.F.Burritt, Spectrochica Acta Part B: Atomic

   Spectroscopy, 2002,57: 951-966.

11. F.Suzuki and A.Hirai, toxicological and environmental chemistry,2012, 19,713-727.

12. B.K.Priya, P.Subramanyan, J.D.Kumar and P.Chiranjeevi, Journa of chemistry,2006,3(4): 286-297.

13. K.S.Kumar, K.Suvardhan, L.Krishnaiah, D.Rekha, K.Kiran, K.Janardhanam, B.Jayaraj and P. Chiranjeevi, Talanta,2007,71(2):588-895.

14. Kumar.D.P, A.P.Kumar, I.Sreevani and P.R.Reddy, International journal of chemtech Research, 2012,4(2):686-690.

15. S.Mendoza,L.A.Godinez and J.E.H.Bechara, Journal of nanomaterials, 2012, 145380.

16. S. Sun and A. Wang, Separation and Purification technology,2006,51(3):409-415.

17. H.Paudyal,B.Pangeni,K.Inoue,H.Kawakita,K.Ohtoand S.Alam, Bioresource Tecnology, 2013,146,713-720.

18. Zhang et al, Physicochem.Eng.Aspets, 2009,346,34-38.