



Applicability of New Chitosan Coated Copolymer In Environmental Pollution Control

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Abstract

Environmental pollution due to toxic metals is topic of major concern related to pollution control. Arsenic, the heavy metal, is considered to be acute toxic, carcinogenic and mutagenic to living organisms and hence more hazardous, causing various diseases and disorders. For this reason, the treatment of arsenic polluted toxic water has received an extensive concern and become a hot topic in environmental research. Presence of arsenic in waste water and its various treatment methods are cited in the literature. Each method has its own advantages and limitations in terms of arsenic removal efficiency and economical effectiveness. The aim of the present investigation is to synthesize a new eco-friendly adsorbent i.e. Chitosan coated copolymer (CCRPHF-I) and to study its applicability in environmental pollution control with respect to arsenic removal efficacy from aqueous solution. Resorcinol, Phenyl Hydrazine and Formaldehyde were used as starting materials for synthesis of RPHF-I copolymer; which was later surface modified with chitosan. This chitosan coated copolymer, CCRPHF-I, was characterized using modern techniques like FTIR, SEM and TGA. The arsenic adsorption efficiency has been investigated using batch experiment method and the parameters like effect of pH, contact time, adsorbent dosage and initial arsenic concentration on its removal efficiency have also been studied and reported. The maximum removal of arsenic was observed to be 92.37 % under optimal condition. Thus the new chitosan coated copolymer under study can be successfully used as an efficient adsorbent material for removal of arsenic from contaminated water and can have variety of potential environmental applications with special reference to water pollution control.

Keywords: Arsenic toxicity, Copolymer, Batch experiments, Adsorption, Environmental application.

Introduction

Contamination of arsenic in drinking water is due to the untreated effluents discharged into water bodies from industries and agricultural fields. Arsenic is considered to be acute toxic, carcinogenic and mutagenic to living organisms and hence more hazardous, causing various diseases and disorders such as lung and urinary bladder cancer, muscular weakness, nerve tissue injuries, blackfoot disease etc. The arsenic concentration of 0.05 mg/L in drinking water has been set as permissible limit by World Health Organization (WHO).¹ Therefore, the treatment of polluted water due to toxic arsenic metal has received an extensive concern and become a hot topic in environmental research.²

This study is an attempt to synthesize a new copolymer using reacting monomers like resorcinol (R), Phenylhydrazine (PH) and Formaldehyde (F) followed by its surface modification with Chitosan (C). Characterization of the new self generated adsorbent material and its adsorptive property studies applying Langmuir model; where testing of parameters like effect of pH, contact time, adsorbent dosage and initial arsenic ion concentration is also involved; for uptake of arsenic from contaminated water are also under consideration. Thus the applicability of new adsorbent material in environmental pollution control can be established

Materials and Methods

All chemicals used were of analytical grade. The compounds like Resorcinol, Phenylhydrazine, Formaldehyde (37%) were procured from Merck, Mumbai, India. Double distilled water was used during all experiments.

Synthesis and Purification of RPHF-I Copolymer

The copolymer (RPHF-I) was synthesized employing the method published earlier.^{3,4} The purity of newly synthesized and purified copolymer sample has been tested and confirmed by TLC.⁵

Surface Modification of RPHF-I Copolymer by Chitosan Doping

5gm of chitosan powder was dissolved in 100 ml of 10% acetic acid, which from whitish viscous gel. It was heated to 40-50°C to facilitate the mixing. 50 gm of RPHF-I was slowly added to this viscous gel and mechanically agitated using rotary shaker at 150 rpm for 24 hrs. The gel coated RPHF-I was then washed with double distilled water and dried. The process was repeated for thrice until thick coating of chitosan was formed on the RPHF-I surface. The excess of acetic acid in Chitosan Coated RPHF-I (CCRPHF-I) was neutralized by treatment with 0.5% NaOH solution for 3 hrs. The resultant product was then filtered with Whatmann No. 41 filter paper, extensively rinsed with double distilled water,

dried in an oven at 55°C for 48 hrs and stored in air tight container.⁶

Characterization of copolymer

Characterization of surface modified copolymer was carried out by techniques like FTIR, NMR, SEM and TGA. The scanning was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh and SAIF Cochin

Batch Experiment

Batch equilibrium studies were conducted with different parameters such as pH, contact time, initial ion concentration and effect of adsorbent doses. The systems were agitated on rotary shaker at 29 rpm, filtered through Whatmman no.42 filter paper and filtrate was analyzed for trivalent arsenic concentration using UV-Visible Spectrophotometer. From experimental data, the applicability of Langmuir model was judged. Linear regression coefficient (R^2) and isotherm constant values i.e. adsorption efficiency (Q_m) and adsorption energy (b) were determined from the model.

Results and Discussions

The FTIR spectrum of the CCRPHF-I copolymer is shown in Fig.1. A broad band appeared in the range 3742.55 cm^{-1} which is attributed to O-H stretching vibration and the 3391.63 cm^{-1} which can be assigned to NH stretching vibration of chitosan molecules.⁷ The weak band at 2927 cm^{-1} may be due to methylene C-H stretching vibrations. The band appeared at 1390.06 cm^{-1} is a result of stretching vibration of $-\text{CH}_2\text{OH}$ (primary alcohol). Absorption peak at 1632 cm^{-1} corresponds to the NH bending. Absorption peak at 1685.64 cm^{-1} may be due to C = O stretching vibration of amide group. The sharp bands at 1474.45 cm^{-1} and 1547.89 cm^{-1} correspond to a symmetrical deformation of the C-H group and N-H deformation of amide respectively. The vibration bands at 1084.32 and 120.48 cm^{-1} are indicative of C-O-C vibration inside chitosan ring. The three weak peaks appeared in the region 824, 754.90 and 698 cm^{-1} are attributed to NH wagging of primary amine.⁸

Fig.2. represents the SEM image of CCRPHF-I obtained using an accelerating voltage of 15 KV at x3500 magnification. SEM image clearly revealed the presence of wide variety of globular microspheres. Microspheres were formed in the form of large beads with irregularity and polydispersity.^{9, 10} The sizes of microspheres are found to be 3.01 μm , 1.98 μm , 2.52 μm and 1.06 μm . The image indicates a transition state of material between the amorphous and crystalline. However, more predominantly, the material is

amorphous because of surface modification of copolymer by chitosan.^{11, 12}

The TGA curve of CCRPHF-I has shown in Fig.3. It can be seen from figure that three consecutive weight loss steps were observed in CCRPHF-I. The first weight loss stage is at 50 to 150°C. The derivative peak observed at temperature 67.23°C with a weight loss of 3 % which may be due to the removal of water molecules (moisture).¹³ The stage of second weight loss can be noticed at 250 to 529°C. The derivative peak observed at temperature 350.86°C with a weight loss of 13 % which may be due to the some volatile matter and scission of the ether linkage in the chitosan backbone. The third weight loss stage is observed in the temperature range of 500 to 700°C. The derivative peak observed at temperature 598.93°C with a weight loss of 37 % which may be due to the thermal decomposition of glucosamine residue present in chitosan.¹⁴ Beyond 700°C, the TGA curve is almost flattened due to remains of nondecomposable residue.¹⁵

Adsorption studies of As(III) on CCRPHF-I adsorbent

Effect of pH on As(III) ion removal

The influence of pH on the percentage sorption of As(III) has shown in Fig.4. The adsorption capacities of CCRPHF-I towards As(III) were determined using various pH values of the solution in the range 1.0 to 10. As the pH increased, there is little increase in the percentage of As(III) removal and it was maximum at pH 5 for the adsorbent i.e. CCRPHF-I with removal of 93.38 % of As(III) ion.

Effect of contact time on As(III) ion removal

The effect of contact time on percentage adsorption of arsenic (III) ion is shown in Fig.5. Figure indicate that the percentage of As(III) removal efficiency increased with an increase in contact time before equilibrium is reached. The optimum contact time for CCRPHF-I was found to be 120 min. Thus CCRPHF-I has required a shorter contact time to attain the equilibrium as compared to RPHF-I copolymer alone. This is due to the greater availability of various microspores on the surface of CCRPHF-I, which are required for strong interaction with metal ions which improves the binding capacity and rapid adsorption process.

Effect of adsorbent dosage on As(III) ion removal

The dependence of As(III) adsorption was studied by varying the amount of CCRPHF-I from 0.5 to 10 gm/lit. The influence of adsorbent dose on the percentage removal of As(III) has shown in Fig.6. It can be observed that the removal efficiency of As(III) ion increases by increasing the CCRPHF-I

dose up to a certain limit and then it becomes constant. When CCRPHF-I dosage were increased from 0.5 to 5 gm/lit, it resulted in increased rate for removal efficiency of As(III) from 20.42% to 93.38%. It can also be seen that further increase of CCRPHF-I dose(beyond 5.0 gm/lit) does not affect the percent removal of As(III); and hence 5.0g/L can be fixed as optimum adsorbent dose .

Effect of initial Arsenic (III) ion concentration

The percentage adsorption with different As(III) concentrations was studied by varying ionic concentration of arsenic from 10 to 100 mg/lit. The result has been presented in **Fig.7**. Experimental results proved that the percentage of As(III) removal was found to decrease from 98.13% to 63.50% as the initial concentration of As(III) ion increased from 10 to 100 mg/lit for the adsorbent under investigation.

Adsorption Isotherms

The experimental data are well fitted in Langmuir's linear plot of C_e/Q_e versus C_e and it suggests the applicability of the Langmuir isotherms. The values of adsorption efficiency ' Q_m ' and adsorption energy 'b' were determined from the slope and intercept of the plots as shown in **Fig.8**. The values of ' Q_m ' and 'b' for CCRPHF-I were respectively found to be 15.15 and 0.2727. Experimentally determined fractional(between 0 to 1) value of equilibrium parameter, that is, separation factor (R_L) confirmed the favorability of adsorption process for adsorbent-adsorbate pair under investigation.¹⁶

Conclusions

RPHF-I copolymer has been successfully synthesized using Resorcinol, Phenyl Hydrazine and Formaldehyde as starting materials with a good yield. Chitosan coating was successful on the surface of RPHF-I to get surface modified copolymer which has been abbreviated as CCRPHF-I. Characterization of CCRPHF-I adsorbent has been done employing the techniques like FTIR, SEM and TGA. CCRPHF-I was studied for testing its adsorption efficacy towards removal of As(III) ions from contaminated water. Results of batch experiment studies proved excellent efficiency of the newly obtained material for removal of As(III) from contaminated/waste water. The excellent capacity of the CCRPHF-I under present investigation is supported by correlation coefficient value(0.990) for Langmuir Isotherm. The values of adsorption efficiency (Q_m) and adsorption energy (b) calculated from linear Langmuir Isotherm are in good agreement for favorable adsorption process for the adsorbent - adsorbate pair reported in the this article. In this way adsorbent under consideration in the present research work is best suitable for the treatment of contaminated water/wastewater with special reference to abatement of toxic metal ion, that is, As(III) and thus can have potential applications in environmental/water pollution control.

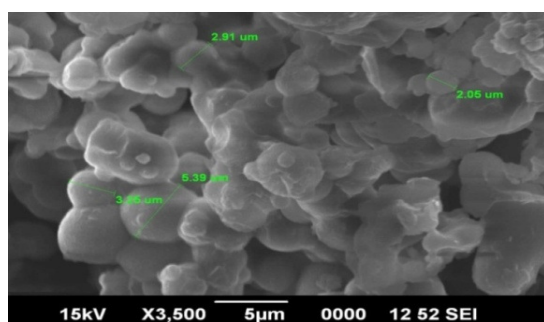


Figure 1:- FTIR Spectrum of CCRPHF-I

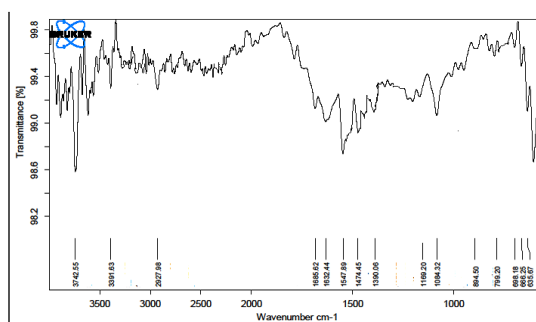


Figure 2:-SEM image of CCRPHF-I

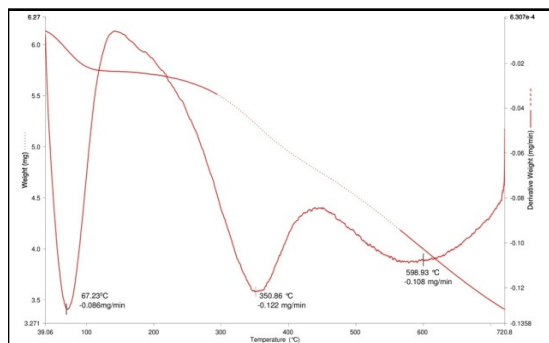


Figure 3:- TGA Curve of CCRPHF-I copolymer

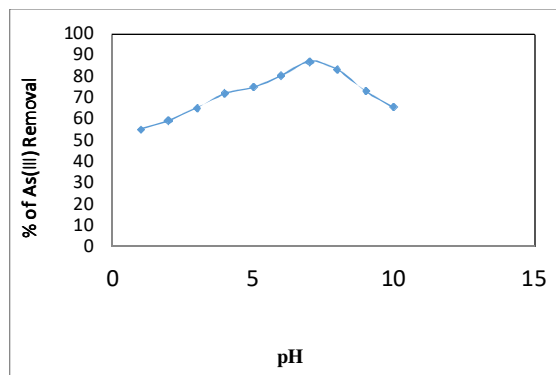


Figure 4. Effect of pH on As(III) ion removal by CCRPHF-I

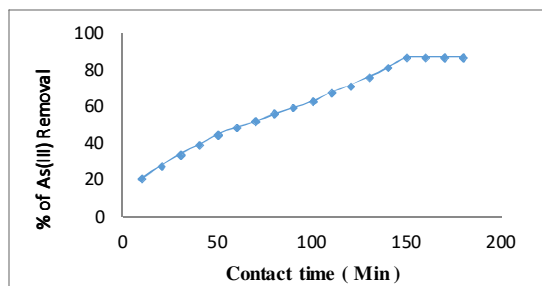


Figure 5.: Effect of Contact time on As(III) ion

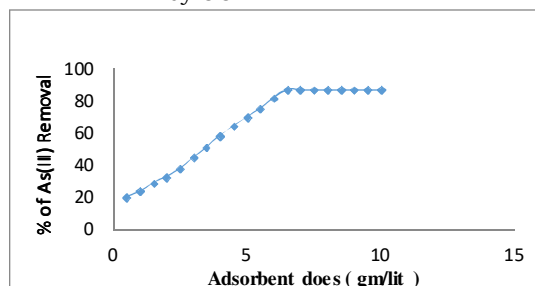


Figure 6: Effect of Adsorbent dose on As(III) ion removal by CCRPHF-I

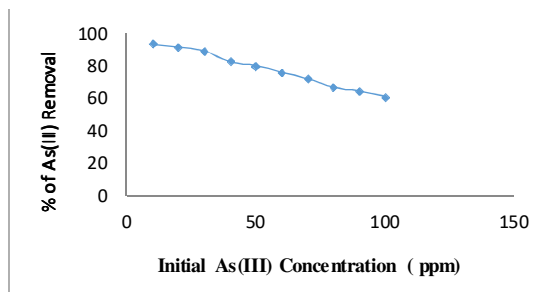


Fig. 7: Effect of initial concentration of As(III) removal by CCRPHF-I

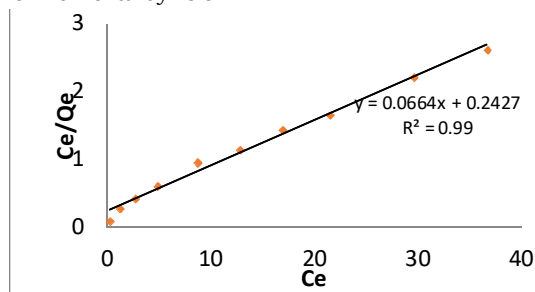


Figure 8 : Langmuir isotherm for the adsorption of As(III) on CCRPHF-I

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