

Removal of Toxic Cr(VI) from Contaminated Water Using Surface Modified Copolymer CCRSF-I

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Abstract

Synthesize super adsorbent copolymer RSF-I to remove toxic Cr(VI) from contaminated water. The Cr(VI) adsorption efficiency of RSF-I was enhanced, when surface modification of RSF-I copolymer by chitosan doping ie. CCRSF-I. This RSF-I and CCRSF-I copolymers was characterized using modern techniques like FTIR, TGA, XRD and SEM. The Cr(VI) adsorption of RSF-I and CCRSF-I was investigated using batch equilibrium method, while freundlich and Langmuir adsorption isotherm model was employed for detail adsorption studies including parameter effect of pH, contact time, adsorbent dosage and initial Cr(VI) ion concentrate on. CCRSF-I have maximum removal of Cr(VI) was obtained to be 91.22 % and optimal removal was favored at pH 5, contact time 120 min and adsorption dosage 5.5 gm/lit. The CCRSF-I can be successfully used as an efficient material for removal of Cr(VI) from water resources and can have a variety of potential environmental applications.

Keywords: -Copolymer, Toxic Cr(VI), Adsorption efficiency, Chitosan doping, Batch equilibrium, Adsorption isotherm.

1. Introduction

Recently Industrial, agricultural and domestic used wastewater directly through in water resources. These wastewaters mainly contain organic wastes, dyes and heavy metals pollutant. Heavy metals are non-biodegradable and they can be accumulated in living tissues, causing several diseases and disorders [1]. In the heavy metal specially Cr(VI) is highly soluble and reactive and considered to be acute, toxic, carcinogenic and mutagenic to living organisms and hence more hazardous than other heavy metals [2]. Cr(VI) is one of the world's most strategic, critical and highly soluble metal pollutants having wide range of uses in the metal and chemical industries. Chromium and its salts are used in the leather tanning industry, pigments and paints, manufacturing of catalysts, ceramic and glass industry, photography, chrome alloy and chromium metal production, chrome plating, pesticides, corrosion control and many more. The high risk of Cr(VI) is associated with its high reactivity and its potential carcinogenic properties. It is well known that Cr(VI) are very much toxic to human, animal microorganism and their environment [3]. Therefore, it is necessary to search for economical and efficient methods to remove heavy metal from water resources. Today many methods as such electrolysis,

electrodialysis, reverse osmosis and precipitation have been used to removed heavy metals from wastewaters [4]. However, these methods are high in cost and may also less efficient to remove toxic heavy metal in contaminated water. Adsorption with use of copolymers is non expensive and efficient method for removal of heavy metal from wastewater[5, 6] . Copolymer adsorption capacity have depends number of faction group present on the surface. However, copolymer surface from some drawbacks such as fixed structure and limited functional groups, as well as low elasticity, which decreases its efficiency for heavy metal adsorption[7] .The metal adsorption efficiency of copolymer was enhanced to require their surface modification. Surface modification of copolymer can be done with use of natural copolymer chitosan[8]. Among natural resources, chitosan have gained much attention due to their biodegradability, renewability and no toxicity, making them an ideal material for use adsorption of heavy metal in contaminated water[9]. In the present studies, copolymer RSF-I was synthesized by using resorcinol (R), semicarbazine (S) and Formaldehyde (F) in 1:1:2 molar ratios of the reacting monomer. Surface modification of RSF-I copolymer with chitosan (CCRSF-I) can be synthesize. This RSF-I and CCRSF-I has been characterized using modern techniques like $^1\text{H-NMR}$, FTIR and XRD. The new copolymer RSF-I and CCRSF-I can be successfully used as an efficient material for removal of Cr(VI) from aqueous environments such as domestic and industrial effluents and can have a variety of potential environmental applications.

2. Material and Method

2.1 Chemicals

All chemicals used were of analytical grade. Resorcinol, semicarbazine, Formaldehyde (37%) procured from Merck, India. Double distilled water was used for all the experiments.

2.2 Synthesis of (RSF-I) copolymer

The copolymer (RSF-I) was synthesized by condensing Resorcinol, Semicarbazine with formaldehyde in molar ratio (1:1:2) in the presence 2M HCl as a catalyst. The reaction mixture was taken in 500 ml round bottom flask fitted with water condenser and heated in an electrically operated oil bath at $120 \pm 2^\circ\text{C}$ for 6 hrs with occasional shaking. The temperature of the oil bath was controlled with the help of dimmerstat. The solid mass obtained was removed immediately as soon as the reaction period was over. The separated copolymer product (RPHF-I) was filtered and purified. The solid copolymer product was repeatedly washed with hot distilled water followed by methanol to remove unreacted monomers. The resinous product was air dried and powdered. The powder was washed several times with petroleum ether in order to remove resorcinol-formaldehyde copolymer which may be present with the copolymer. The product so obtained was further purified by reprecipitation technique. The copolymer was dissolved in 2N NaOH, filtered and reprecipitated by drop wise addition of 1:1(v/v) of conc. HCl / distilled water. The precipitated product was filtered off, washed with hot water until it was free from chloride ions, dried and powdered. The finely ground copolymer was passed through a 300 mesh size sieve. The yield of copolymer resin was found to be 87%. The proposed structure of RSF-I along with reaction scheme has shown in Fig.1.

2.3 Surface Modification of RSF-I Copolymer by Chitosan Doping

5gm of chitosan was dissolved in 100 ml of 10% acetic acid and was heated to 40-50°C to facilitate the mixing. The chitosan-acetic acid mixture formed a whitish viscous gel. 50 gm of RPHF-I was added to the viscous gel in small installments and finally agitated using rotary shaker at 150 rpm for 24 hrs. The gel coated RSF-I was then washed with double distilled water and dried. The coating process was repeated for three times until thick coating of chitosan was formed on the RSF-I surface. The amount of chitosan coated was about 25% by weight. The excess of acetic acid in chitosan coated RSF-I (CCRSF-I) was neutralized by treatment with 0.5% NaOH solution for 3 hrs. The resultant mixture was then filtered with Whatmann No. 41 filler paper. The CCRSF-I was then extensively rinsed with double distilled water and was dried in an oven at 55°C for about 48 hrs.

Table 1:- Reaction details of copolymer (RSF-I)

Copolymer	Reactants			Molar ratios	Catalyst (2M HCL)	Reflux Temp. (°C)	Time (hr)	Yield
	Resorcinol (R) (mol)	Semicarbazine (S) (mol)	Formaldehyde (F) (mol)					
RSF-I	0.5 mol	0.5 mol	1 mol	(1:1:2)	200 ml	120±2°C	5.15 hrs	80%

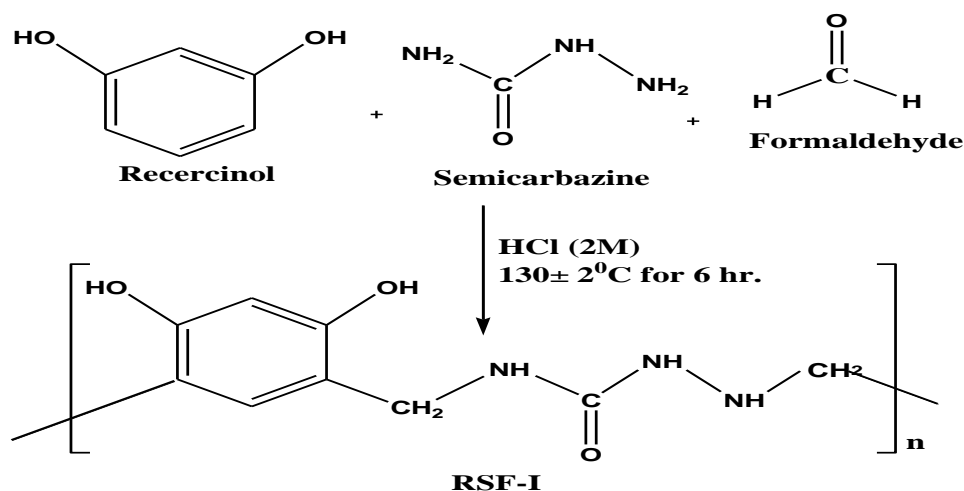


Fig. 1:- Structure and reaction of RSF-I copolymer

2.4 Batch Experiment

Batch equilibrium studies were conducted with different parameters such as pH, agitation time, initial concentration of Cr(VI) solution and effect of adsorbent doses. The systems were agitated

on rotary shaker at 200 rpm, filtered through Whatmman no.42 filter paper and filtrate was analyzed for Cr(VI) concentration using UV-Visible Spectrophotometer. From experimental data, the applicability of Freundlich and Langmuir model was judged.

2.5 Characterization of copolymer

Characterization of copolymer was carried out by techniques like FTIR, TGA, XRD and SEM analysis and the concerned spectra/image have been presented. FTIR, TGA, XRD and SEM was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh and SAIF Cochin

3. Results and Discussion

3.1 FTIR Analysis of RSF-I and CCRSF-I

The FTIR spectrum of the RSF-I is shown in Fig. 2. A sharp band appeared in the region 3748 cm^{-1} may be assigned to the phenolic hydroxyl group involved in intermolecular copolymeric association[10]. A weak band at 2305 cm^{-1} is due to (C–NH) stretching. Absorption peak at 638.83 and 1078.29 cm^{-1} are indicative of 1,2,3,4-substitution of aromatic benzene ring. The medium band appeared at 1526.41 cm^{-1} may be due to aromatic –C=C bending and stretching. The board band appeared at 1365.07 cm^{-1} may be due to phenolic –OH in plane bending [11]. Absorption peak at 1468.12 cm^{-1} may be due to –NH bending vibration of secondary amine. A sharp band at 1605.5 cm^{-1} may be due to C=O stretching of amide. The presence of –NH bridge in the copolymer is confirmed by the absorption band at 3474.71 cm^{-1} . Absorption peak at 2886.74 and 1192.33 cm^{-1} may be attributed to –CH₂ linkage present in the copolymer[12]. The FTIR spectrum of the CCRSF-I is shown in Fig. 3. A sharp band appeared in the range 3728.68 cm^{-1} is attributed to O-H stretching vibrations and weak band at 3392.07 cm^{-1} is attributed to NH stretching of chitosan molecule[13]. The stretching vibrations at 2927 cm^{-1} attributed to C-H methylene linkage. The weak band appeared at 1336 cm^{-1} may be due to stretching of –CH₂OH (primary alcohol). Absorption peak at 1548.6 cm^{-1} correspond to the NH bending. A board band at 1688.17 cm^{-1} correspond to stretching vibration C = O (amide group). The sharp band at 1451 cm^{-1} corresponds to a symmetrical deformation of the CH group and at 1511.10 cm^{-1} corresponds to the N-H deformation of amide[12]. The vibrations bands at 1077.60 cm^{-1} and 1166.55 cm^{-1} showed C-O-C vibration inside chitosan ring. Absorption peak at 832 , 752 and 695.77 cm^{-1} correspond to NH waging for primary amine[14].

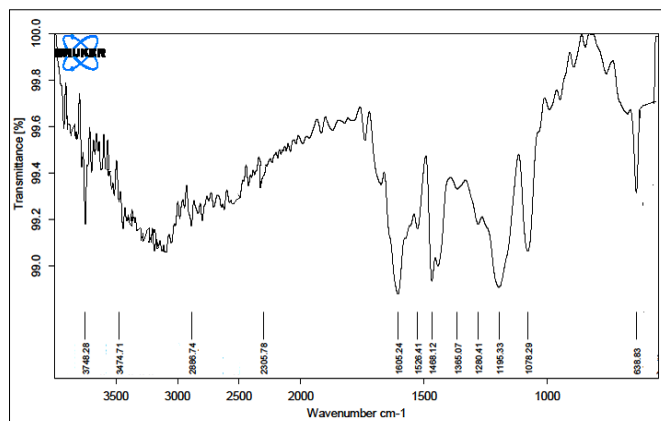


Fig. 2:- FTIR Spectrum of RSF-I

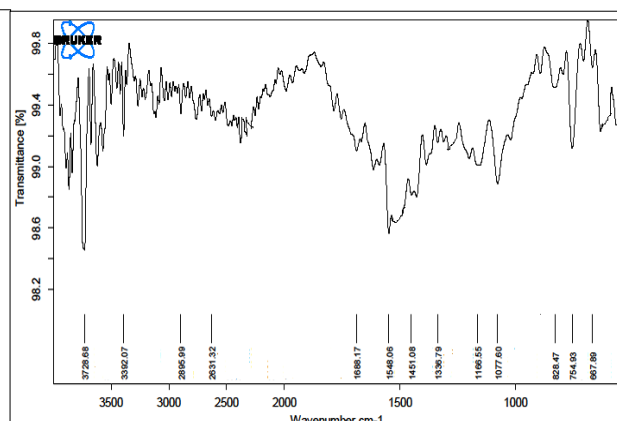


Fig. 3 :- FTIR Spectrum of CCRSF-I

3.2 SEM analysis of RSF-I and CCRSF-I

The surface morphology of RSF-I characterized by SEM indicates a porous and microsphere structure as shown in Fig.4. The SEM images of RSF-I obtained using an accelerating voltage of 20 KV at (x 1500, x10000) magnification. The microspheres are globular size with diameter 4.63 μ m, 4.15 μ m, 1.36 μ m and 980 nm.. The image also showed a transition state between the amorphous and crystalline states [15]. The surface was rough and folded due to the drying procedure. The microsphere arranged by a close packed array of column[16]. The SEM images of CCRSF-I obtained using an accelerating voltage of 15 KV at (x 1500, x3500) magnification are represents in Fig.5. SEM micrographs of CCRSF-I that clearly revealed that wide variety of microspheres and porous material are presents on the surface [15]. However, as the surface modification of copolymer by chitosan then microspheres are agglomerated shape changed from globular to irregular. Microspheres were formed in the form of large beads with irregularity and polydispersity. The size of microspheres are founds 5.39 μ m, 2.91 μ m, 2.05 μ m, and 3.25 μ m. The image also showed a transition state between the amorphous and crystalline states. Due to the porous material CCRSF-I thus possesses more amorphous nature and showing higher exchange capacity for metal ions. Such image is indicative that CCRSF-I may have very good adsorption efficiency than RSF-I [17].

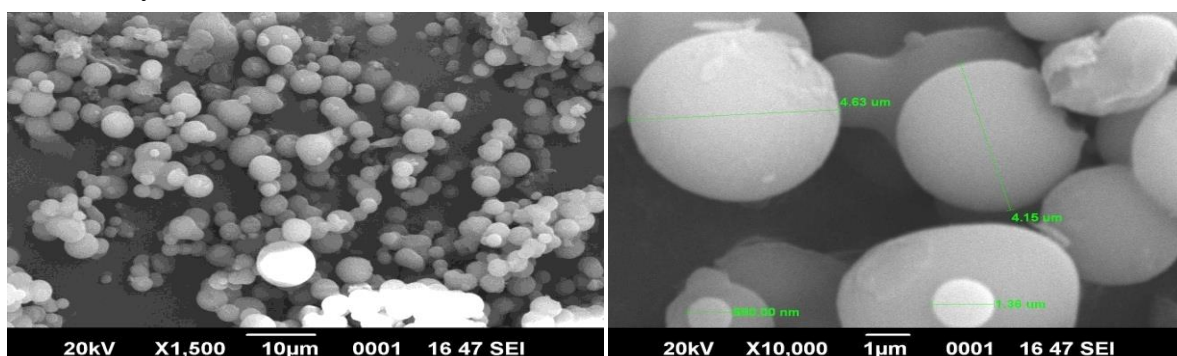


Fig.4:- SEM image of (RSF-I)

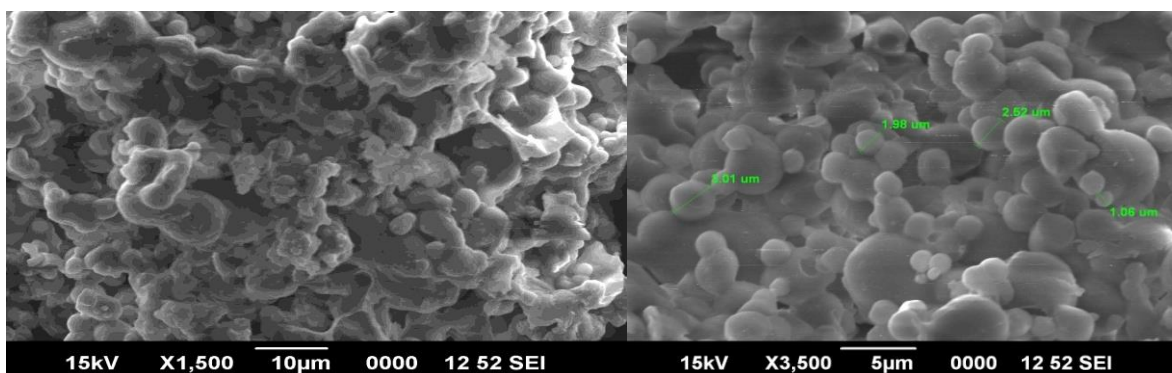


Fig.5: SEM image of (CCRSF-I)

3.3 TGA Analysis of RSF-I and CCRSF-I

The TGA curve of RSF-I shown in fig.6. It can be seen from figure that three consecutive weight loss steps were observed in RSF-I. The first weight loss was at about 50 to 150⁰C. The derivative peak observed at temperature 67.85⁰C with a weight loss of 3 % which may be due to the removal of water molecule [18]. When temperature was raised to the range 300-350⁰C, the second derivative peak appeared at 337.04⁰C with 14 % weight loss of material which may be due to the elimination of –OH groups attached to the aromatic nucleus of co polymeric sample. In the third stage, the weight loss was in the temperature range of 500 to 700⁰C. The third derivative peak was observed at temperature 582.75⁰C with a weight loss of 38% which may be due to the elimination of –CH₂ bridges and the aromatic nucleus. After 700⁰C, the TG curve was almost flat due conversion of material into stable as a result of action of heat[19]. The TGA curve of CCRSF-I has been shown in fig.7. It can be seen from figure that three consecutive weight loss steps were observed in CCRSF-I. The first weight loss was at about 50 to 150⁰C and the corresponding first derivative peak was observed at 71.92⁰C with a weight loss of 4 %, which may be due to the removal of water molecule [18]. The second weight loss was about 250 to 520⁰C. The second derivative peak observed at temperature 345.80⁰C 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. In the third stage, the weight loss in the temperature range of 500 to 700⁰C. The last derivative peak observed at temperature 603.91⁰C with a weight loss of 36 %, which may be due to the thermal decomposition of glucosamine residue (due to the degradation of the chitosan. After 700⁰C, the TG curve almost flattens due to the stable remains of the material[19].

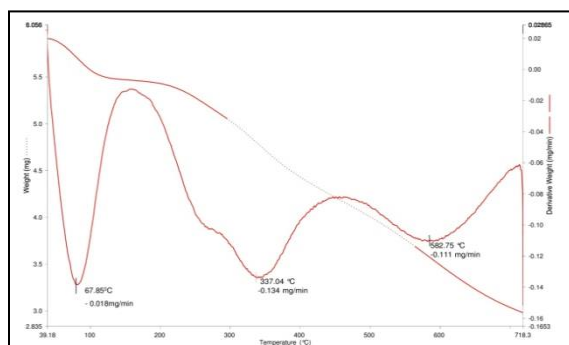


Fig. 6:- TGA Curve of RSF-I

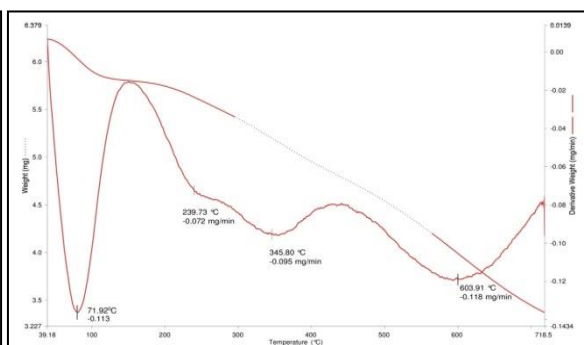


Fig. 7:- TGA Curve of CCRSF-I

XRD Analysis of RSF-I and CCRSF-I

The X-ray diffract to graph of RSF-I has shown in Fig. 8. In this spectrum a high intense sharp peaks at $2\theta = 23^\circ$ and 51° show crystalline nature of copolymer. The spectrum also contains low intense peaks at $2\theta = 73^\circ$ indicate semicrystalline nature. Thus it can be concluded that RSF-I copolymer exhibits crystalline and semicrystalline nature[20]. The X-ray diffract to graph of CCRSF-I has shown in Fig. 9. In this spectrum peak at $2\theta = 22^\circ$ and 51° show crystalline nature of the material. The spectrum also contains low intense peaks at $2\theta = 72^\circ$ again indicate semicrystalline nature[20]. In the CCRSF-I as compared to RSF-I have low intensity peak that mean chitosan has been successfully coated on the surface of RSF-I during the surface modification to get CCRSF-I. Thus it can be concluded that CCRSF-I material exhibits crystalline and semicrystalline nature [21].

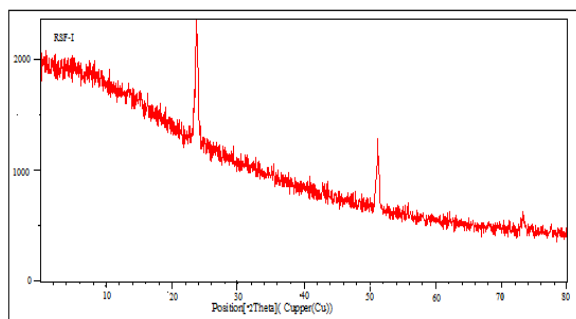


Fig. 8:- XRD spectrum of RSF-I

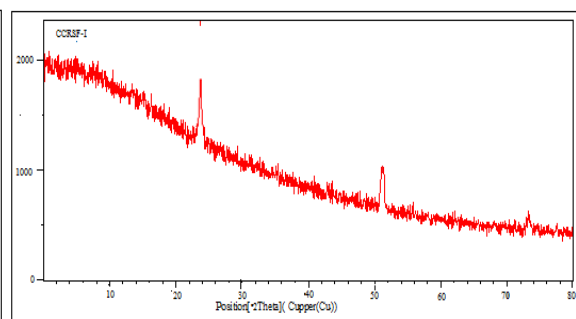


Fig. 9:- XRD spectrum of CCRSF-I

Adsorption of Cr(VI) ion on RSF-I and CCRSF-I

Effect of pH on Cr(VI) ion removal

The adsorption capacities of RSF-I and CCRSF-I towards Cr(VI) abatement were determined using various pH values of solution in the range of 1.0 to 10. From fig.10. It is observed that at pH 5.0 both the adsorbents i.e. RSF-I and CCRSF-I remove 85.28% and 91.22% of Cr(VI) ion respectively.

Effect of contact time on Cr(VI) ion removal

The effect of contact time on percentage of Cr(VI) ion removal have shown in Fig.11. Figure indicate that the percentage of Cr(VI) removal efficiency increase with an increased in contact time, before equilibrium is reached. It can be seen that Cr(VI) removal efficiency of RSF-I increased from 19.34% to 85.28% when contact time was increased up to 140 min. Thus optimum contact time for RSF-I was found to be 140 min. But in case of CCRSF-I removal efficiency increased from 24.48 to 91.22% when contact time increased up to 120 min that is optimum contact time. Thus, CCRSF-I required shorter optimum time as compared to RSF-I.

Effect of Adsorbent dose on Cr(VI) ion Removal

The dependence of Cr(VI) adsorption was studied by varying the amount of RSF-I and CCRSF-I from 0.5 to 10 gm/lit keeping other parameters are optimum. The influence of RSF-I and CCRSF-I concentration /dose on the percentage of removal of Cr(VI) has shown in Fig.12. From the figure, it is observed that there is increase in the removal efficiency of Cr(VI) ions increasing

the RSF-I and CCRSF-I dosage up to a certain limit and then it remains constant. On when RSF-I dose increased from 0.5 to 7.5 gm/lit, there was increase of removal efficiency of Cr(VI) from 20.33 % to 85.28 %. While in case of CCRSF-I, removal efficiency increased from 23.89 to 91.22% when dose of CCRSF-I increased from 0.5 to 5.5gm/lit. This indicates that the amount of CCRSF-I required is much lesser than the RSF-I.

Effect of initial Chromium (VI) ion Concentration

The percentage of adsorption with different Cr(VI) concentration was studied by varying Cr(VI) ion concentration from 10 to 100 mg/lit keeping other parameters such as pH of solution, adsorbents dose, contact time optimum, and it is shown in the Fig.13. It is observed that percentage of Cr(VI) removal was found to decrease from 93.38 % to 54.23% as initial concentration started from 10 to 100 mg/lit for RSF-I. The same trend was observed for CCRSF-I, that is the percentage of Cr(VI) removal was decreased from 97.12% to 56.12%.

Adsorption Isotherm

In order to establish the most appropriate correlation for the equilibrium data in the design of adsorption system, two common isotherm models were tested: Freundlich and Langmuir models. The applicability of the isotherm equations were compared by judging the values of square of correlation coefficient (R^2).

Freundlich isotherm

The Freundlich equation suggests multilayer adsorption. Sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. Therefore, the parameters of k_f and 'n' were be estimated from the intercept and slope of the plots between $\log Q_e$ against $\log C_e$. Freundlich isotherms have shown in **Fig.5.21** and **Fig.5.22**. The k_f values of both the adsorbents i.e. RSF-I and CCRSF-I were found to 1.9453 and 2.944 mg/g respectively, which indicate that dominance of adsorption capacity. The Freundlich exponent 'n' were 2.631 and 2.881 for RSF-I and CCRSF-I respectively which again reflects the favorable adsorption. The values of R^2 were found to 0.985 and 0.987 for both the adsorbents i.e. RSF-I and CCRSF-I respectively, showed the well fitting of Freundlich isotherm[22]. These findings indicate that probably the sorption of Cr(VI) on RSF-I and CCRSF-I was a multilayer coverage.

Langmuir isotherm

The Langmuir sorption isotherm suggests that when the adsorbate occupies sites, further sorption cannot take place at that site. All the sites are energetically equivalent and there is no interaction between the molecules adsorbed on the neighboring sites. The equilibrium data for Cr(VI) adsorption on RSF-I and CCRSF-I were fitted to Langmuir equation. The linear plots of C_e/Q_e versus C_e were shown in Fig.14 and Fig.15. The values of Q_m and 'b' were determined from the slope and intercept of the plots. The Langmuir monolayer adsorption capacity ' Q_m ' gives the amount of the adsorbate required to occupy all the available sites per unit mass of the sample. The Langmuir monolayer adsorption capacity of RSF-I and CCRSF-I was found to be 8.064 and

10.86 mg/g respectively and corresponding ‘b’ values were found to be 0.1651 and 0.2402. This lower value of ‘b’ indicates the affinity between solute and sorbent site which rules out the possibility of chemisorptions. The R^2 values were found to be 0.998 and 0.991 for RSF-I and CCRSF-I respectively, indicating the best fitting of Langmuir isotherm. One of the features of the Langmuir equation can be defined in terms of dimensionless constant known as separation factor (R_L) which are found in between 0 to 1 showing favourable adsorption on RSF-I and CCRSF-I[23].

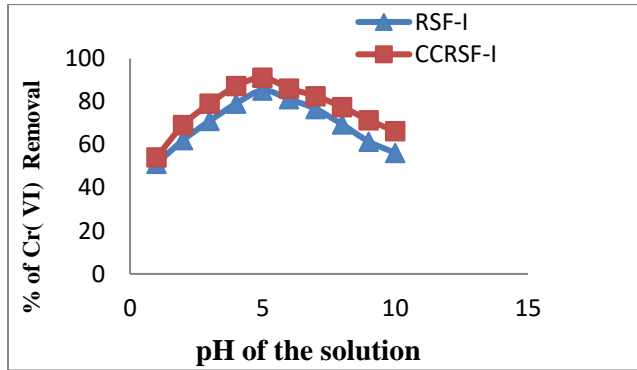


Fig.10 : Effect of pH on Cr(VI) ion removal

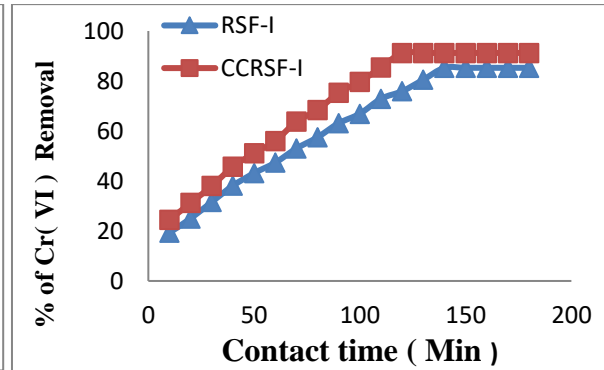


Fig.11 : Effect of Contact time

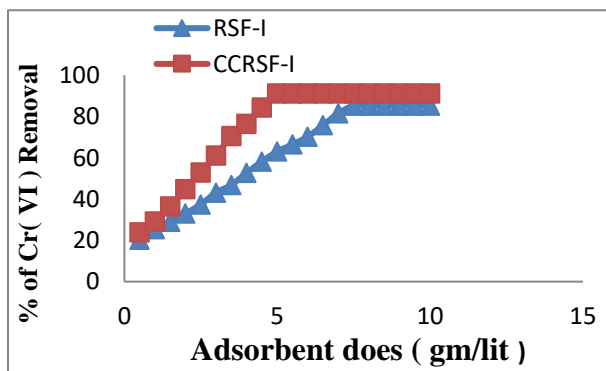


Fig.12: Effect of Adsorbent dose

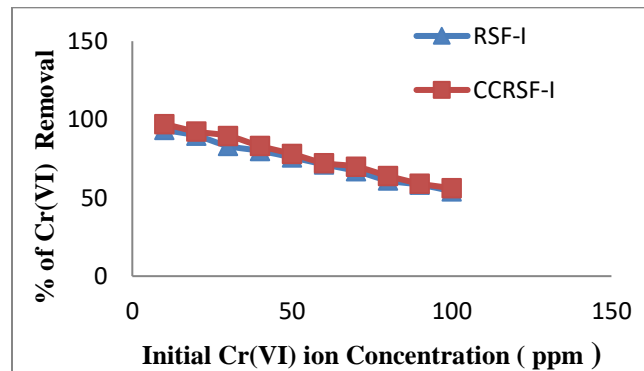


Fig. 13: Effect of initial concentration

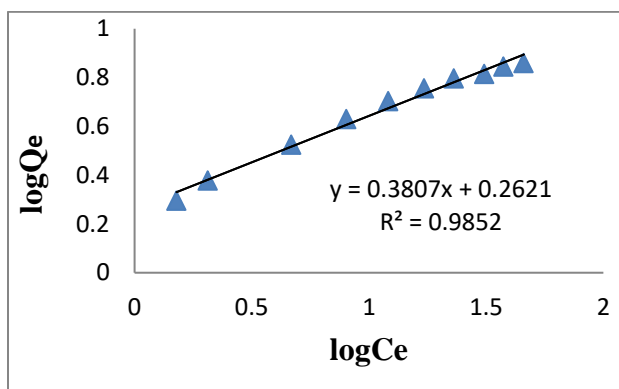


Fig.14 : Freundlich Isotherm for the adsorption of adsorptionCr(VI) on RSF-I

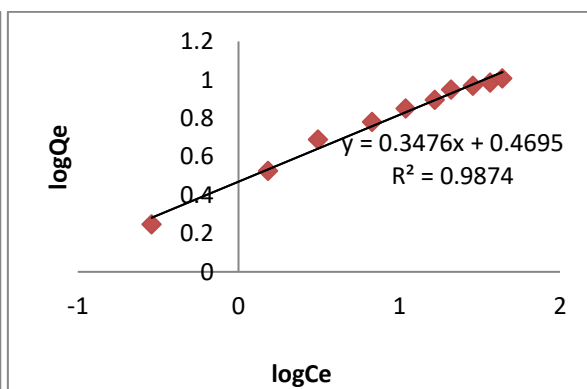


Fig. 15 : Freundlich Isotherm for the adsorption of Cr(VI) on CCRSF-I

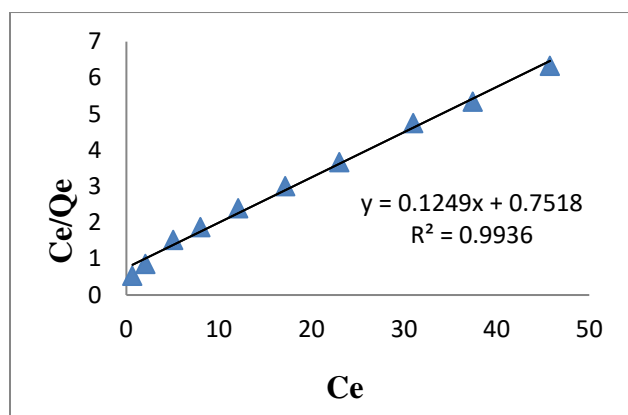


Fig.16 : Langmuir Isotherm for the adsorption of Cr(VI) on RSF-I

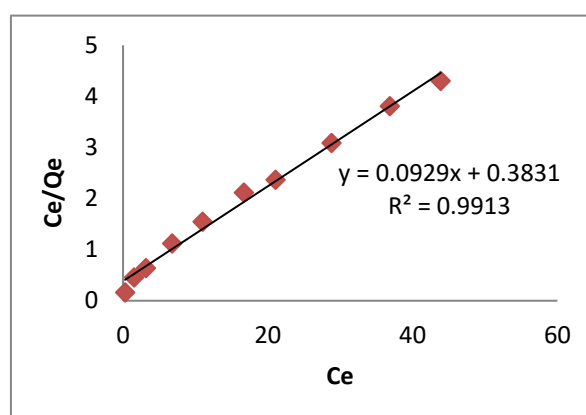


Fig.17 : Langmuir Isotherm for the adsorption of Cr(VI) on CCRSF-I

Conclusion

RSF-I copolymer is successfully synthesized with a good yield based on condensation reaction of resorcinol and phenyl hydrazine with Formaldehyde in the molar ratio of 1:1:2 in the presence of HCl as a catalyst, Surface modification of copolymer RSF-I can be done with use of natural copolymer chitosan ie CCRSF-I. RSF-I and CCRSF-I are characterized by FTIR, SEM, TGA and XRD studies.. RSF-I have maximum removal of Cr(VI) was obtained to be 85.28 % and optimal removal was favored at pH 5, contact time 140 min and adsorption dosage 7.5 gm/lit. CCRSF-I have maximum removal of Cr(VI) was obtained to be 91.22 % and optimal removal was favored at pH 5, contact time 120 min and adsorption dosage 5.5 gm/lit. The adsorption data satisfactorily explained by freundlich isotherms including k_f values of RSF-I and CCRSF-I were found to 1.9453 and 2.944 mg/g respectively. The Freundlich exponent 'n' were 2.631 and 2.881 for RSF-I and CCRSF-I respectively. The values of R^2 were found to 0.985 and 0.987 RSF-I and CCRSF-I respectively. Thus the newly generated RSF-I and CCRSF-I has been proved to be an excellent adsorbent which can employed for removal of Cr(IV) from polluted water. The adsorption data satisfactorily explained by langmuir isotherms including adsorption of Cr(IV) follows pseudo second order kinetics. The values of RL factor for both RSF-I and CCRSF-I ranging from 0 to 1 indicate the favorable adsorption situation. Comparison has been done amongst RSF-I and CCRSF-I for their Cr(VI) abatement efficacy from contaminated water. It is concluded that both RSF-I as well as CCRSF-I have good efficiency Cr(VI) removal. But CCRSF-I have shown adsorption efficiency to greater extent.

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