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Adsorption studies on toxic Cr (VI) removal using RSF-I Terpolymer

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ABSTRACT

The heavy metal, Cr (VI), is considered as one of the most toxic element to animals, plants, microorganisms and environment. Cr (VI) is non-biodegradable and accumulated in living tissues exerting its toxic effect thereby destabilizing ecosystems and even causing death of organisms. Therefore, it must be removed from contaminated water before discharge. The aim of the present study is an attempt to synthesize a new terpolymer with higher efficiency of Cr (VI) removal from aqueous solution. In the present study, a new terpolymer, RSF-I was synthesized using Resorcinol(R), Semicarbazine(S) and Formaldehyde(F). This terpolymer was characterized using modern techniques like ^{1}H-NMR, FTIR, XRD and SEM. The Cr(VI) adsorption was investigated using new terpolymer, RSF-I, and effect of pH, contact time, adsorbent dosage and initial Cr(VI) ion concentration was studied using batch experiments. The maximum removal of Cr (VI) was obtained to be 92% and optimal favored Ph was found to be 5. Thus new terpolymer, RSF-I, can be successfully used as an efficient adsorbent material for removal of Cr(VI) from aqueous media such as domestic and industrial effluents and can have a variety of potential environmental applications.

Key words: Heavy metals, Toxicology, Hexavalent Chromium, Environmental contamination.

INTRODUCTION

The pressure of increasing population, growth of industries, urbanization, energy intensive life style, loss of forest cover, lack of environmental awareness, lack of implementation of environmental rules and regulations and environment improvement plans, untreated effluent discharge from industries and municipalities are causing water pollution[1]. Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells). It has been suggested that it is the leading worldwide cause of deaths and diseases [2-3] and that it accounts for the deaths of more than 14,000 people daily[3]. Water is typically referred to as polluted in presence of pollutants, such as surfactants, pesticides, dyes, persistent organic chemicals and heavy metals. Among the pollutants, heavy metals are very common toxic pollutants and the presence of heavy metals in environment is a potential problem to water quality due to their high toxicity to plants, animals including human life[4-6]. Heavy metal is a general collective term applied to the group of metals and metalloids with an atomic density greater than 6 g cm^{-3} [7]. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, therefore they must be removed before their discharge[8].

Chromium (Cr) 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, manufacturing of catalysts, pesticides, ceramic and glass industry, photography, pigments and paints, chrome alloy and chromium metal production, chrome plating, corrosion control and many more[9-11]. The high risk of chromium (VI) is associated with its high reactivity and its potential carcinogenic properties[12].

This study is an attempt to synthesize and characterize new terpolymer with heavy metal adsorbent properties for their removal from environment, specifically Cr(VI), from contaminated water[13-14]. In the present investigation, terpolymer RSF-I was synthesized by using resorcinol (R), Semicarbazine (S) and Formaldehyde (F) in 1:1:2 molar ratios of the reacting monomers. The maximum removal of Cr (VI) was obtained to be 92% and optimal removal was favored at pH 5. The removal of Cr (VI) by terpolymer was found to be increasing with increase in contact time as well as with adsorption doses with stationary phase achieved at 160 min and 6 gm/lit respectively. This way the new terpolymer, RSF-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.

MATERIALS AND METHODS

Chemicals

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

Synthesis of RSF –I terpolymer

The terpolymer (RSF -I) was synthesized by condensing Resorcinol, Semicarbazine with formaldehyde in molar ratio (1:1:2) in the presence HCL (2M) used as catalyst. The reaction mixture was taken in 500ml round bottom flask with water condenser and heated in an electrically operated oil bath at 120 ± 2^0C with occasional stirring for 6hrs.The temperature of the oil bath was controlled with the help of dimmer stat. The solid mass obtained was removed immediately as reaction process was over. The solid terpolymer 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 terpolymer. The product so obtained was further purified by reprecipitation technique. The terpolymer was dissolved in 2.5N aqueous NaOH, filtered and reprecipitated by drop wise addition of 1:1 (v/v) conc. HCl / distilled water with constant stirring. The precipitated product was filtered off, washed with hot water until it was free from chloride ions, dried and powdered. The purified terpolymer sample was dried in vacuum at room temperature. The finely ground sample was passed through a 300 mesh size sieve. The purity of terpolymer was tested and confirmed by TLC. Dimethyl sulphoxide (DMSO) was used as solvant for developing chromatogram and was allowed to run for about 30 minute. When chromatogram was exposed to the iodine chamber then we got single colour spot for terpolymer sample. This indicates that the synthesized terpolymer has no impurities. The yield of terpolymer resin was found to be 81%. The synthesis summary has been given in Table1 while reaction scheme and proposed structure of RSF-I Terpolymer in Figure 1.

Table 1: Synthesis summary of RPHF-I Terpolymer

Terpolymer	Reactants			Molar ratios	Catalyst (2M HCL)	Reflux Temp. (^{0}C)	Time (hr)	Yield (%)
	Resorcinol (R) (mol)	Semicarbazine(S) (mol)	Formaldehyde (F) (mol)					
RSF-I	0.05	0.05	0.1	(1:1:2)	200ml	120± 2	5.15	81%

Preparation of Cr (VI) solution

A Cr(VI) stock solution having 1000 mgL^{-1}concentration was prepared by dissolving 2.8287 g of potassium dichromate in 1000ml of distilled water. This solution was diluted to proper proportions to obtain various standard solutions ranging their concentrations 10-100mgL^{-1}. Adjustment of pH was done using 0.5N HCl and 0.5N NaOH solution.

Batch Experiment

Batch equilibrium studies were conducted with variable 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 Langmuir model was judged. Linear regression coefficient (R^2) and isotherm constant values were determined from the model.

Characterization of terpolymer

Characterization of terpolymer was carried out by techniques like Fourier Transform Infra-Red (FTIR), Nuclear Magnetic Resonance (^{1}H-NMR) and X-Ray Diffraction (XRD) and SEM analysis which were carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh and SAIF Cochin University, Kerala

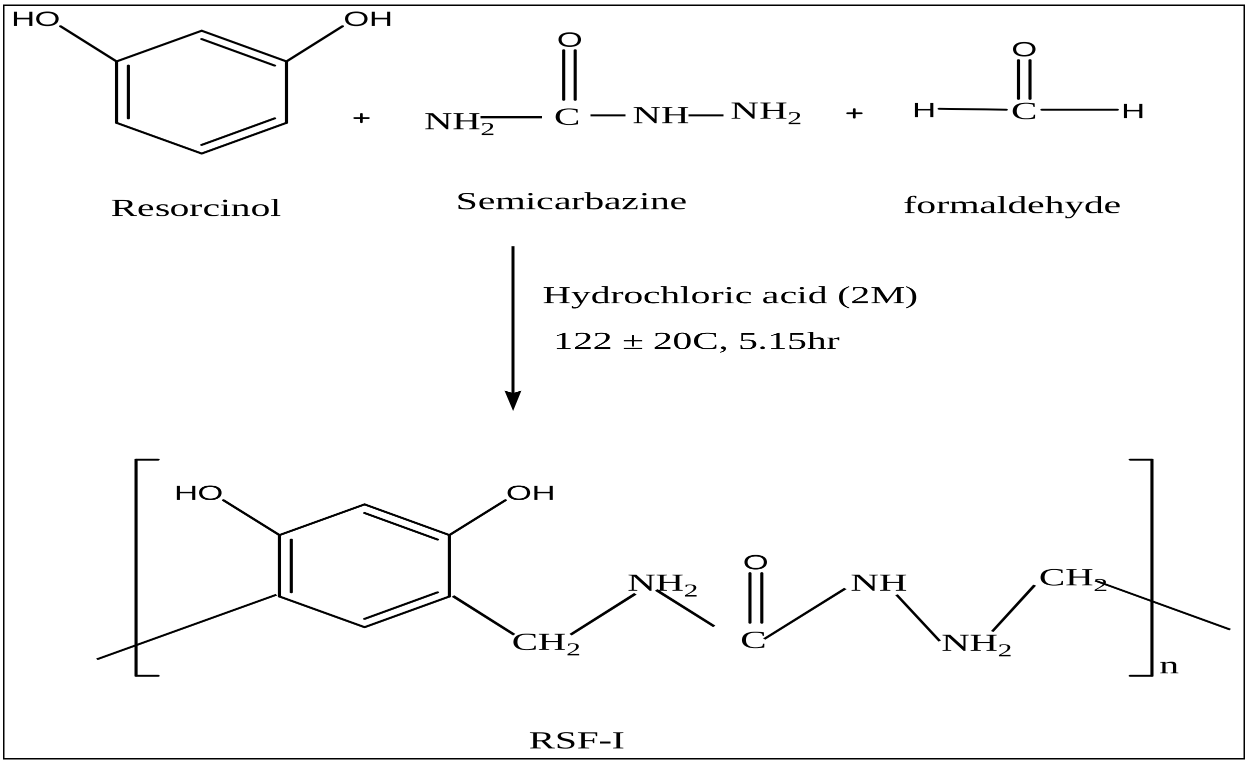


Fig1:Reaction scheme and proposed Structure of RSF-I Terpolymer

RESULTS AND DISCUSSION

The RSF-I terpolymer was found to be soluble in solvents like N,N-dimethylformamide, tetrahydrofuran, dimethylsulfoxide and aqueous NaOH/KOH solutions, whereas insoluble in common organic solvents. The FTIR spectrum of the RSF-I terpolymer has shown in Figure 2, and the spectral data have presented in Table 2[15-18].

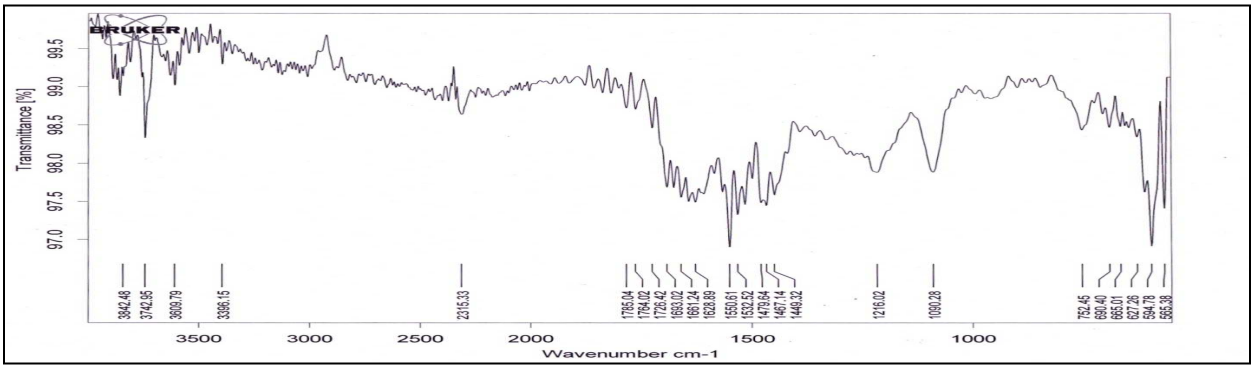


Fig 2: FTIR Spectra of RSF-I Terpolymer

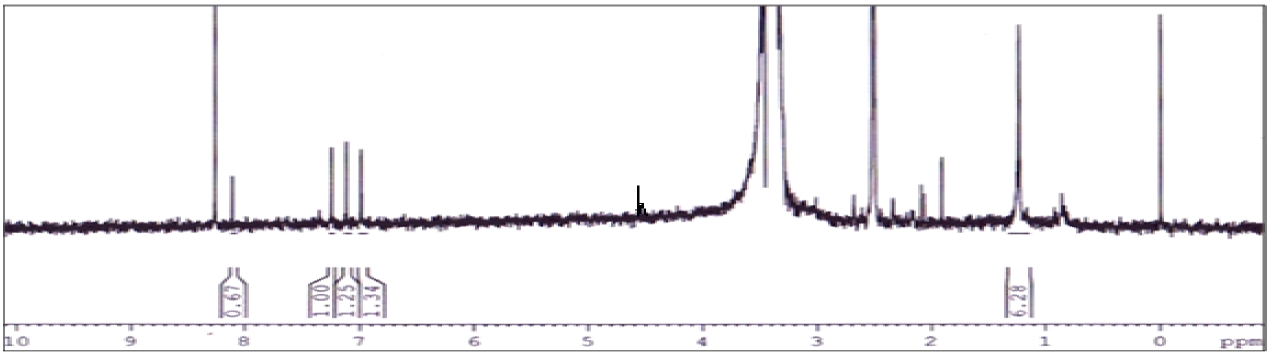


Fig.3: ^{1}H-NMRSpectra of RSF-I Terpolymer

Table 2: FTIR Spectral data of RSF-I

VIBRATION MODE	FREQUNCY (cm^{-1})	
	Reported	**Observed**
Phenolic (OH) group Intermolecular polymeric Association	3750-3150	3842.48,3742.95
-CH_2- Bridge	1460,1158-1180	1479.61
1,2,3,5-subtitude aromatic ring	1220,974	1216.02
-NH- bridge strong	3500-3200	3396.15
(C-N)Stretching	1250-1020	1090.28
N-H bending secondary amide	1500-1600	1550.61,1532
Isocyanides R-N=C	2270	2315.33

The ^{1}H NMR spectrum of RSF-I terpolymer is depicted in Figure 3, and the spectral data are presented in Table 3. The chemical shift (δ) ppm observed is assigned on the basis of the literature[17-20].

Table 3: ^{1}H NMR Spectral data of RSF-I

Nature of proton assigned Expected	Chemical shift (δ)ppm (Literature)	ChemicalShift (δ)ppm (Observed)
Methylene proton of Ar-C**H_2** moiety	2.35-2.99	2.5
Methylenic proton of Ar-C**H_2**-N moiety	3.91	3.8
Amido Poton of Ar–CH_2- N**H**-CO	4.54	4.4
Aromatic proton Ar-**H**	6.5-7.5	7.2
Proton of phenolic-O**H** involved intramolecular hydrogen bonding	8.45	8.2
Proton of amines -CH_2-N**H**-	1-2	1.2

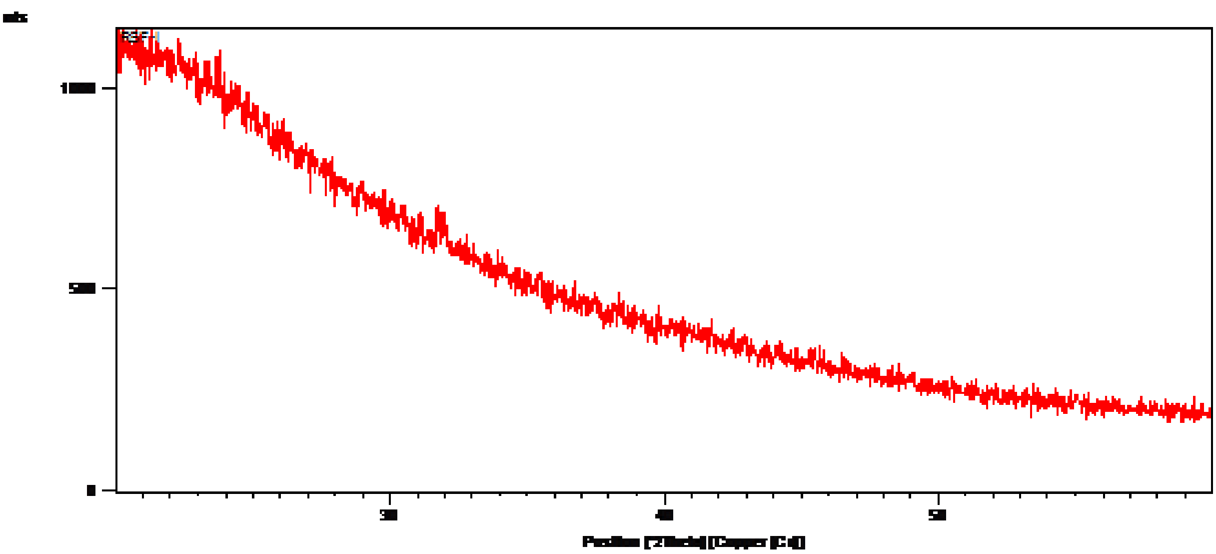
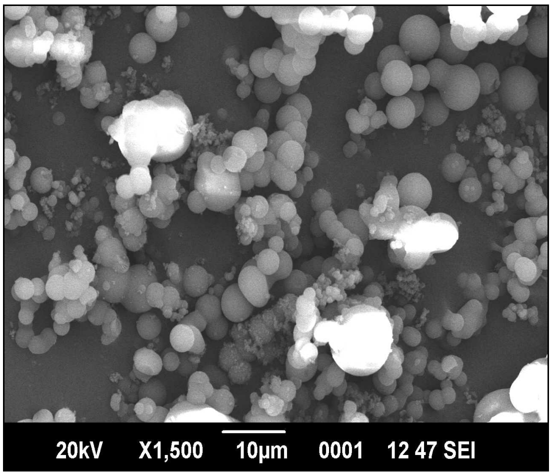


Fig. 4: XRD pattern of the 4-RSF-I terpolymer

The figure 4 depicts the XRD pattern of the 4-RSF-I terpolymer resin, a broad diffused peak and absence of well defined peak clearly pointed out the amorphous nature of the material under study[21].

The scanning electron microscopy (SEM) of RSF-I (Fig.5) indicates that the terpolymer has highly porous structure with smooth round ball shaped particles. There are very small but large number of cavities over the surface of the RSF-I. Due to the cavity like structure of the surface of the material it possessed high surface area and high adsorptive properties. Adsorption of any heavy metal depends upon the pore size of the terpolymer. Thus RSF-I shows high tendency to adsorb any heavy metals on its surface and can be proved to be an excellent adsorbent.



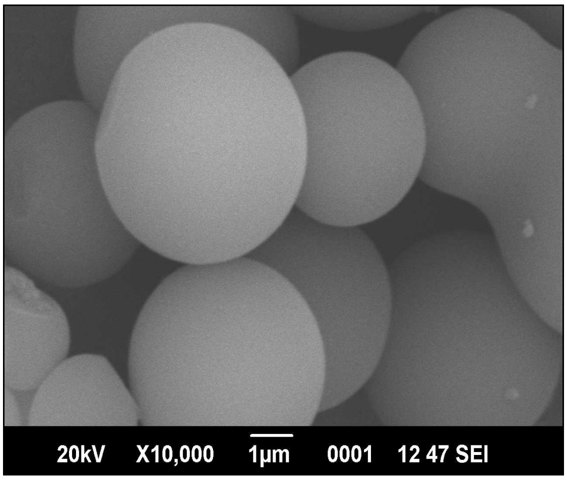
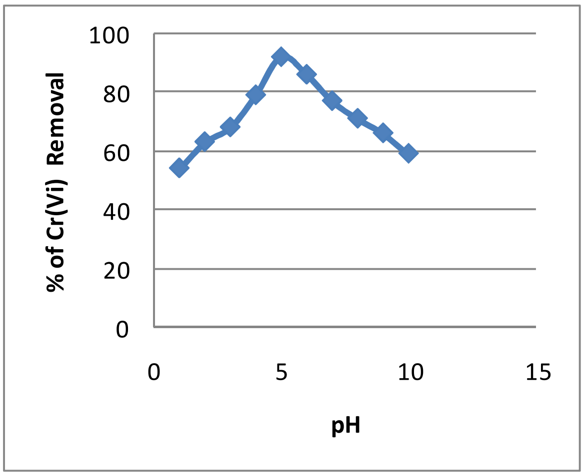


Fig.5: Scanning electron microscopy (SEM) images of RSF-I Terpolymer

Removal of Cr (VI) by RSF-I Terpolymer

Effect of pH: pH is an important parameter for adsorption of metal ions from the aqueous solution because it affects the solubility of the metal ions. Adsorbent has been studied in the pH range 1 to10. The effect of pH on the removal of Cr(VI) using RSF-I was studied (Fig.6). The maximum chromium removal efficiency (92%) was noticed at pH 5.

Effect of Contact Time: Efficient uptake of Cr(VI) ion with effect of contact time by RSF-I was studied and result are shown in(fig.7). Indicate that the Cr(VI) removal ability of RSF-I increased with increasing in contact time before equilibrium is reached. Other parameters such as dose of RSF-I, pH of solution and initial concentration was kept optimum. The percentage removal of Cr(VI) was studied within time range 10 to 200 min. After 160 minute negligible effect has been noticed on adsorption of Cr(VI). Thus 160 minute is the optimum time for these batch experiments.



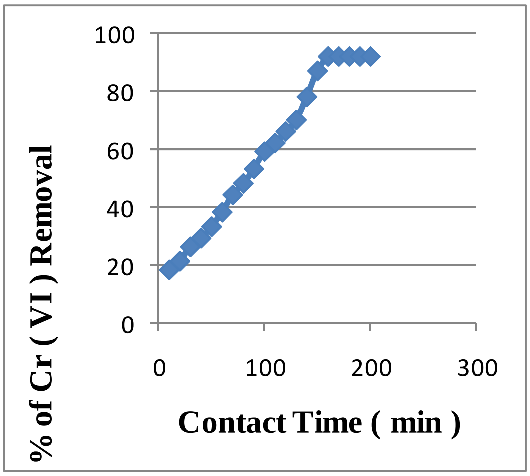
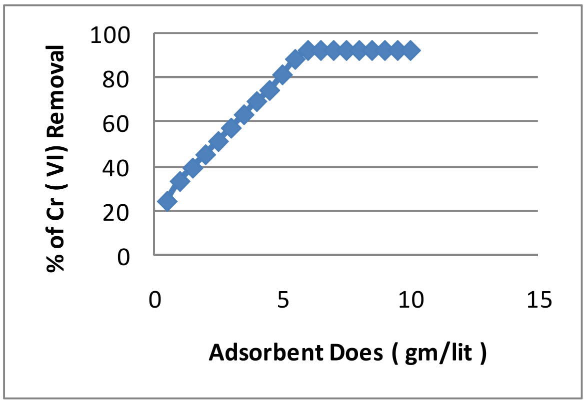


Fig.6. Effect of pH on Cr(VI) adsorption **Fig.7.Effect of Contact time on Cr (VI) adsorption**

Effect of Adsorbent Dosage: The effect of dosage on the removal of Cr(VI) was studied by varying the amount of RSF-I from 1 to 10 g/l while keeping other parameters (pH , contact time and initial concentration) constant as shown in (fig.8.) From the figure,The initial Cr(VI) concentration taken was 35 ppm. The percentage of Cr(VI) removal was found to increase from 24 to 92. The increase in Cr(VI) removal with increase in RSF-I doses is due to the increase in surface area and adsorption sites available for adsorption. However after certain dose it becomes constant and it is treated as an optimum adsorbent dose, which is found to be 6gm/lit. for the RSF-I adsorbent.

Effect of initial metal ion concentration: The effect of initial metal ion concentration on the percentage removal of Cr(VI) by RSF-I as shown in (fig.9.) In the present study adsorption experiments were performed to study the effect of initial Cr(VI) concentration by varying it from 10-100ppm solution while maintaining the Adsorbent dose 6gm/lit



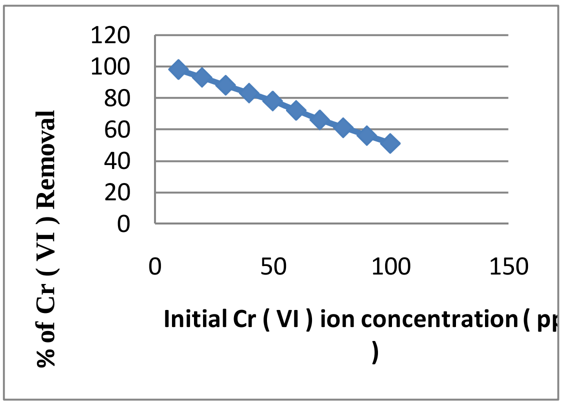


Fig.8. Effect of Adsorbent Does on Cr(VI) **Fig.9.Effect of initial ion concentration on adsorption Cr(VI) adsorption**

Adsorption Isotherm

The isotherm data have been linearized using the Langmuir equation and is plotted between Ce/Qe versus Ce. The Langmuir constant 'qm' which is measure of the monolayer adsorption capacity of RSF-I is obtained as 8.695. The Langmuir constant 'b' which denotes adsorption energy, is found to be 3.105.The high value (0.992) of regression correlation coefficient (R^2) indicates good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Cr(VI) onto the RSF-I. The dimensional parameter 'RL' which is a measure of adsorption favorability is found to be 0.091(0< RL < 1) which confirms the favorable adsorption process for Cr(VI) on RSF-I adsorbent.

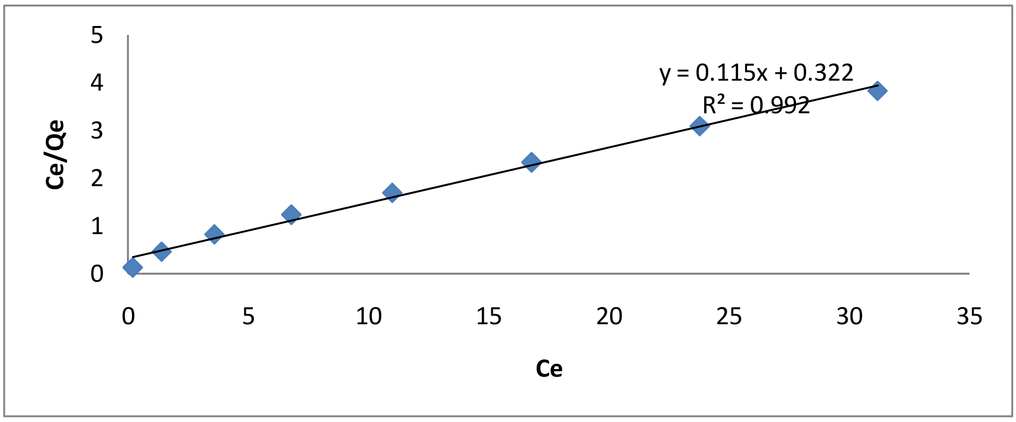


Fig.10: Langmuir isotherms for the adsorption of Cr(VI) on RSF-I

CONCLUSION

- Synthesis of RSF-I terpolymer is successful with a good yield based on condensation reaction of Resorcinol and Semicarbazine with Formaldehyde in the molar ratio of 1:1:2 in the presence of HCl as a catalyst
- Characterization and structure elucidation of RSF-I terpolymer is successful which is supported by FTIR, NMR, XRD and SEM studies.
- Removal of poisonous/carcinogenic Cr(VI) from aqueous solution is possible using RSF-I terpolymer which effectively removes more than 92 % of Cr(VI) at 308 K.
- Adsorbent dose=6.0gL^{-1}, pH=5.5 and contact time=160 min. were the optimum parameters during the adsorption studies.
- The adsorption data satisfactorily explained by Langmuir isotherms. The values of RL factor ranging from 0 to 1 indicate the favorable adsorption situation. Thus the newly generated RSF-I has been proved to be an excellent adsorbent which can employed for removal of Cr(IV) from polluted water.

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REFERENCES

[1] R.A.Horne'chemistry of Enviroment',wiley Interscince (**1978**)
[2] *Pink, Daniel* ."Investing in Tomorrow's Liquid Gold". *Yahoo. Archived from* the original *on (***2006***)*
[3] *West, Larry. About.com. (200***6)**
[4] Bowen H.J.M., The Environmental Chemistry of the Elements, Acdemic Press, London, **(1979).**
[5] A.S.Boughey' Man and Enviroment', 2nd Edition macmilliun Puplication Co.Inc.,New York **(1975**)
[6] S.M.Khopkar,'Enviromental pollution analysis', 2nd Edition., New Age International (p) Ltd.**(2012**)
[7] David. W. O, Colin.B, Thomas.F.O, *Bioresource Technology* 99, 6709–6724. **(2008)**
[8] Umar .F, Misbahul .A .K, Makshoof .A, Janusz A. Kozinski, *Chemical Engineering Journal,* Volume 171, Issue 2, 1 July 2011, Pages 400–410 **(2011)**
[9] Office of Drinking Water. Health advisory—chromium. Washington, DC, US Environmental Protection Agency, (**1987)**
[10] Chromium. Geneva, World Health Organization, (Environmental Health Criteria No.61). **(1988)**
[11] Slooff W et al. Integrated criteria document chromium. Bilthoven, Netherlands, NationalInstitute of Public Health and Environmental Protection, (Report no. 758701002). **(1989)**
[12] Waranusantigula,P, Pokethitiyook, P, Kruatrachue,M, Upatham, E.S, *Environmental Pollution* 125, 385–392. **(2003)**
[13] Rahangdale P. K., Gurnule W. B., Paliwal L. J. and Kharat, R. B. *J. Appl. Polym. Sci*.89 787. **(2003)**
[14] Duby R., Kandpal L. D., Mathur G. N. and Singh R. R. *J. Polym. Mater*. 17 33. **(2000)**
[15]Azarudeen RS, Riswan Ahamed MA, Jeyakumar D, Burkanudeen AR. *Iran Polym J*; 18:821–832. (**2009)**
[16] Riswan Ahamed M, Azarudeen R, Karunakaran M, Karikalan T, Manikandan R,Burkanudeen A. *Int J Chem Environ Eng;* 1:7–12. (**2010)**
[17] Silverstein RM, Webster FX. Spectrometric identification of organic compounds,6thedn. Wiley; New York. 9(**1998)**
[18] Azarudeen R, Riswan Ahamed M, Arunkumar P, Prabu N, Jeyakumar D, Burkanudeen A. *Int J Chem Environ Eng;*1:23–28. (**2010)**
[19] Burkanudeen A, Azarudeen R, Riswan Ahamed M, Ramesh P, Vijayan N. *Int J Chem Environ Eng*; 1:29–34.**(2010)**
[20] Pretsch E, Buhlmann P, Afflolter C. Structure determination of organic compounds.Springer,; New York (**2000**)
[21] M. Nawaz Tahir, M. Danish, Sqib Ali, Moazzam H. Bhatti and Dincer Ulka, *X-RayCrystal Analysis*, 23, 75 **(2007).**