



Removal of Chromium(III) Using Synthetic Polymers, Copolymers and their Sulfonated Derivatives as Adsorbents

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Abstract: This study is concerned with the development of some synthetic polymers, copolymers and their sulfonated derivatives as adsorbents. The effectiveness of these adsorbents in removing Cr(III) from aqueous solution was evaluated by batch technique. The influence of different experimental parameters on removal process such as solution pH, contact time, adsorbent dose, Cr(III) concentration and temperature were evaluated. Adsorption equilibrium was achieved in 20 to 30 min. at pH > 5. The Langmuir, Freundlich and Temkin adsorption isotherms were used to elucidate the observed sorption phenomena. The maximum Cr(III) 37.8mg/gram of PS(polystyrene) and 37.2 mg/g of SAN (styrene/acrylonitrile copolymer) was removed as evaluated from Langmuir isotherm while the heat of sorption was in the range 0.21–7.65 kJ/mol as evaluated from Temkin isotherm. It can be concluded that PS developed in this study exhibited considerable adsorption potential for application in removal of Cr(III) from aqueous media as compared to its copolymers and other derivatives used in this study.

Keywords: Chromium, Adsorption, Isotherm, Polymer.

Introduction

Chromium is considered as a priority pollutant among all the heavy metals. Various industrial effluents from pigments, electroplating, dying, canning, textile, leather tanning, paint, and steel industries contain substantial amounts of chromium. In general these industrial effluents contain both Cr(VI) and Cr(III) ions. Excessive buildup of Cr(III) ions can affect the ecological environment¹. The importance to minimize the amount of Cr(III) ions in industrial effluents and other resources has diverted the interest of scientists towards

selective adsorbents Cr(III) adsorption by different materials has been described elsewhere in the literature²⁻⁵. The commonly used methods for removing metal ion from aqueous waste include precipitation, lime coagulation, semisolidification, electrodialysis, chemical reaction, biological process, ion exchange, filtration, reverse osmosis, solvent extraction, and common adsorption. The latter process being a more useful method for the metal ion removal than all other processes and is a consequence of surface energy⁴.

Various chemical modifications have been made on solid adsorbents to improve their physical and chemical properties and also to increase their cation exchange capacity. Application of chemical modification to increase the adsorption capacities of Polystyrene⁶, Polyaniline⁷, Polypyrrole⁸, Polyacrylic ester⁹, Poly(MMA-MAGA)¹⁰, Poly(GMA-Co-EDGMA)-en¹¹, XAD-4NDA-701¹², Polystyrene-divinylbenzene¹³ has been reported in the past. Keeping in view the importance of these chemical modification as applied in surface chemistry, we have attempted the synthesis of adsorbents from polystyrene which were ultimately investigated as an adsorbents for the removal of Cr(III). This study was also further extended is to investigate the kinetic and equilibrium parameters of these synthesized materials for the removal of Cr(III) from aqueous solutions.

Experimental

All the chemicals used in this work were of analytical grade. All the monomers were redistilled under reduced pressure before polymerization except acrylic acid. Styrene and methylmethacrylate were washed first with 5% aqueous sodium hydroxide followed by distilled water until it was neutral¹⁴. Acrylonitrile was washed with dilute sulfuric acid (50% H₂SO₄) followed by dilute sodium carbonate solution (4% Na₂CO₃)¹⁵. Deionized water was used to prepare all the solution in the study. IR spectra of all the adsorbents were recorded with IR Prestige-21-Shimadzu FTIR spectrometer using Nujol method. HANNA digital pH-meter (Model-8417) was used for pH adjustment. Perkin Elmer Atomic absorption spectrometer (Model-AA100) was used for the determination of chromium concentrations in the solutions.

Adsorbents

All the adsorbents used for the removal of Cr(III) were prepared synthetically.

Preparation of PS, PAN, PMMA, PAA

Microspheres of these polymers [poly(styrene)(PS), poly(acrylonitrile) (PAN), poly(methylmethacrylate)(PMMA), and poly(acrylic acid)(PAA)] were prepared by taking monomer of each (23.0 g) by emulsifier-free emulsion polymerization using ammonium persulfate (APS) as the initiator. The reaction was carried out in the nitrogen atmosphere at 70 °C under mechanical stirring at 350 rpm. The resulting polymer microspheres were purified by repeating filtration of the latex.

Preparation of SAN, SMMA, SAA

Styrene/acrylonitrile copolymer (SAN) microsphere was prepared by copolymerization of styrene (20.0 g) with acrylonitrile (3.0 g) by emulsifier-free emulsion polymerization using ammonium persulfate (APS) as the initiator. The reaction was carried out in nitrogen atmosphere at 70 °C under mechanical stirring at 350 rpm. The resulting copolymer microspheres were purified by repeating filtration of the latex¹⁶.

Styrene/methylmethacrylate copolymer(SMMA) and styrene/acrylic acid copolymer (SAA) were prepared according to the same procedure.

Preparation of sulfonated adsorbents

Sulfonated polystyrene (SPS) was prepared using a homogeneous reaction of a polystyrene (PS) solution in chloroform with a mixture of concentrated sulfuric acid (H₂SO₄ 98%) and

phosphorous pentaoxide (P_2O_5). The reaction was carried out at about 40 °C for 30 min with agitation¹⁷. Sulfonatedpolyacrylonitrile (SPAN), sulfonated styrene/acrylonitrile (SSAN), sulfonatedpolymethylmethacrylate(SPMMA),sulfonated copolystyrene/ methyl-methacrylate (SSMMA), sulfonatedpolyacrylicacid(SPAA), sulfonated- copolystyrene/acryli-cacid (SSAA) were prepared in the same way by using their suitable solvent *i.e.* dimethylsulfoxide (DMSO) and chloroform respectively.

Particle size of adsorbents

All the synthetic adsorbents were grinded to their minimum size. The minimum attainable size by these adsorbents is as follow; PS, PAN, SAN, PMMA, SMMA, SSMMA, SAA (100-110 mesh), SPS, SSAN, PAA and SPAA (200-210 mesh) while for SPAN, SPMMA and SSAA it was (250-260 mesh).

Standard solutions

Stock solution of chromium (1000 ppm) was prepared with appropriate weighed quantity of chromium(III) nitrate. Standard solutions of the desired concentrations (200–500 ppm) were obtained by successive dilutions of this stock solution. Deionized water was used to prepare all the dilutions.

Effect of process parameters

A series of experiments were carried out to study the effects of three parameters *i.e.* amount of adsorbate, pH, and contact time on adsorption for the sample solution (200 ppm, 50 mL). To study the effect of certain parameter, that parameter has been varied gradually keeping the other two constant. Measuring flasks (100 mL) were washed with deionized water and then dried in an oven at 105 °C for 30 min. After adsorption under certain conditions, contents of the flasks were filtered and filtrate was subjected to Atomic Absorption Spectrophotometer for determination of chromium at 357.9 nm wavelength.

The effects of the pH was studied by varying the pH from 2 to 7 (2, 3, 4, 5, 6, and 7). Fourteen measuring flasks were taken for sample solution. Synthetic adsorbent (0.25g) was added to each and pH was adjusted by adding HCl (0.1 M) or NaOH (0.1 M) using pH meter. The flasks containing the adsorbent and solution were agitated on orbital shaker at 250 rpm for 30 min; solutions were filtered and analyzed to determine concentration of chromium. The effects of the contact time on Cr(III) adsorption was studied by varying the time of contact from 10 to 30 min (10, 20, and 30 min). Sample solution was taken in fourteen measuring flasks. 0.25g of synthetic adsorbent was added to each flask. pH of each sample was adjusted to 7 and agitated at 250 rpm for different time intervals. After filtration, absorption for chromium was taken on atomic adsorption. The effect of the initial concentration of Cr(III) ion on the uptake by synthetic adsorbents was carried out by placing 0.25 g of synthetic adsorbent in a series of flasks containing 50 mL of Cr(III) ion at definite concentrations (200-500 mg/L) and pH 7. The contents of the flasks were equilibrated on the shaker at 250 rpm for 30 min. After adsorption the residual concentration of the metal ion was determined. The data obtained from the adsorption experiments was used to calculate the adsorption capacity, q_t (mg/g) from Eq. (1):

$$q_t = [(C_0 - C_t) / W] \times V \quad (1)$$

Where C_0 and C_t are the concentrations of the Cr(III) in the solution before and after sorption respectively (mg/dm^3), V is the volume of the solution (dm^3) and W is the mass of the dry adsorbent (g).

Results and Discussion

Adsorbents characterization

The change in chemical structure of various polymers as a result of copolymerization and functionalization was monitored by using FTIR spectroscopy. The FT-IR spectra of PS, SPS, PAN, SPAN, SAN and SSAN (Figure 1, a-f); PMMA, SPMMA, SMMA and SSMMA (Figure 2, g-j) were taken from 4000 cm^{-1} to 400 cm^{-1} and can be explained as follow;

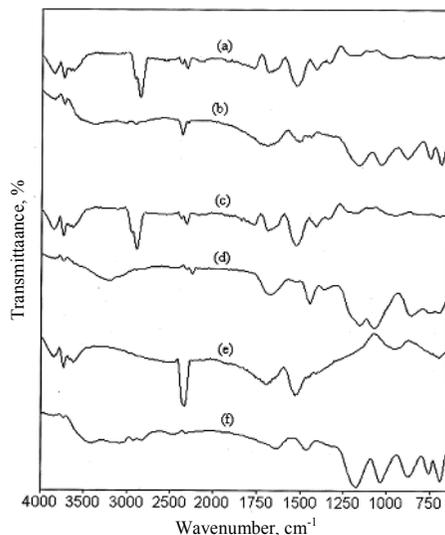


Figure 1. (a) PS (b) S-PS (c) PAN (d) S-PAN (e) SAN (f) S-SAN.

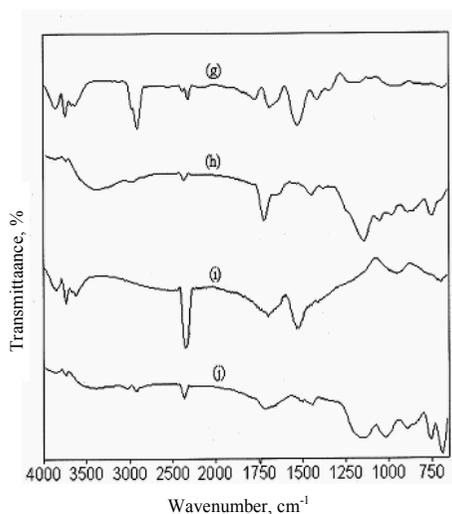


Figure 2. (g) PMMA (h) S-PMMA (i) SMMA (j) S-SMMA.

The FTIR spectrum of PS has characteristic peaks appearing at 3107 cm^{-1} , 2771 cm^{-1} , 1523 cm^{-1} and 1411 cm^{-1} and are attributable to C–H stretching vibrations, CH_2 bending vibration, aromatic C=C ring stretching vibration and (CH_2) group respectively¹⁸. The characteristic infrared absorbance's of SPS at 1033 cm^{-1} resulted from the symmetric

stretching vibration of $\text{-SO}_3\text{H}$ groups while at 1163 cm^{-1} can be attributed¹⁹ to sulfonate anion attached to a phenyl ring (Figure 1-b). The characteristic bands for C-H and $\text{C}\equiv\text{N}$ stretching vibrations of PAN were found at 2883 cm^{-1} , 2304 cm^{-1} respectively. Another band at 1413 cm^{-1} can be assigned to the C-H bending mode. All three bands (Figure 1-c) are strong and support the presence of PAN²⁰. Similarly the infrared spectrum of SPAN have been studied (Figure 1-d) which indicates the presence of sulfonic group at 1070 cm^{-1} while the absorption at 1155 cm^{-1} can be explained as resulted from a sulfonate anion attached to a -CH group. The IR spectrum of SAN (Figure 1-e) microspheres exhibited well-defined bands at about 947 cm^{-1} , 1529 cm^{-1} and 1691 cm^{-1} attributable to benzene ring of polystyrene while at 2347 cm^{-1} can be assigned to $\text{-C}\equiv\text{N}$ group²¹. The presence of these bands confirmed that the polymer microspheres are composed of styrene and acrylonitrile. For SSAN the absorption band at 1031 cm^{-1} can be assigned to symmetric stretching vibration of $\text{-SO}_3\text{H}$ groups and the absorption at 1172 cm^{-1} resulted from a sulfonate anion attached to a phenyl ring group (Figure 1-f).

Figure 2-g, shows the FTIR spectrum of PMMA with characteristic peaks at 2879 cm^{-1} (CH_3 stretching vibration), 2870 cm^{-1} (CH_2 stretching vibration), 1772 cm^{-1} (carboxyl - carbonyl stretching vibration) and 1687 cm^{-1} for carbonyl²² and suggest that the polymer microspheres are consisted of PMMA. The FTIR spectrum of SMMA microspheres revealed well-defined bands at about 947 cm^{-1} , 1529 cm^{-1} characteristic of the benzene ring of polystyrene and a characteristic peak of carbonyl group appearing at 1691 cm^{-1} . The data confirmed that the polymer microspheres consisted of SMMA in Figure 2-i. The formation of SPMMA and SSMMA can be confirmed by observing their respective spectrum (Figure 2-h&j) which indicates the presence of $\text{-SO}_3\text{H}$ groups at (1049 cm^{-1} & 1012 cm^{-1}) and a sulfonate anion attached to -CH group or a phenyl ring (1139 cm^{-1} & 1136 cm^{-1}). The FTIR spectrum of PAA has characteristic peaks appearing at 1710 cm^{-1} was caused by the stretching vibration of the vC=O in the carboxylic group of the PAA, a strong absorption band at 1523 cm^{-1} was observed which was assigned to the asymmetric vibration adsorption of the carboxylate group, 3606 cm^{-1} (OH stretching vibration), 2794 cm^{-1} (-CH stretching vibration). The data confirmed that the polymer microspheres consisted of PAA. The IR spectrum of SMMA microspheres revealed well-defined bands at about 947 cm^{-1} , 1529 cm^{-1} characteristic of the benzene ring of polystyrene and a characteristic peak of carbonyl group appearing at 1691 cm^{-1} . The data confirmed that the polymer microspheres consisted of SAA. The formation of SPAA and SSAA can be confirmed by observing their respective spectrum which indicates the presence of $\text{-SO}_3\text{H}$ groups at 1033 cm^{-1} and a sulfonate anion attached to a phenyl ring group or -CH group at 1157 cm^{-1} & 1136 cm^{-1} .

Effect of pH

Solution pH is an important factor controlling the surface charge of the adsorbent and the degree of ionization of the adsorbate in the solution²³. The effect of the pH on Cr(III) adsorption was studied by varying the pH from 2 to 7; the results are shown in Figure 3. Graph exhibits that pH significantly affects the adsorption and maximum adsorption occurs at $\text{pH}=7$. At $\text{pH} > 7$, insoluble chromium hydroxide starts precipitating from the solution, making true sorption studies impossible. So, it is concluded that pH of the solution should be acidic in order to get good results but should not exceed 7. The adsorption phenomenon exhibited by PS is might be due to physical adsorption and $\pi\text{-}\pi$ dispersion forces. These are due to the presence of aromatic ring of styrene^{24,25} while SPS shows the adsorption due to the presence of $\text{-SO}_3\text{H}$ as an additional group as compared to PS shown in Figure 3. PAN shows adsorption due to the presence of $\text{-C}\equiv\text{N}$ group. This functionality is responsible for the uptake of metal cations by a chelation mechanism. Indeed, nitrogen atoms hold free

electron doublets that can react with metal cations²⁶ while SPAN shows adsorption due to the presence of $-SO_3H$ as an additional group as compare to PAN as shown in Figure 3.

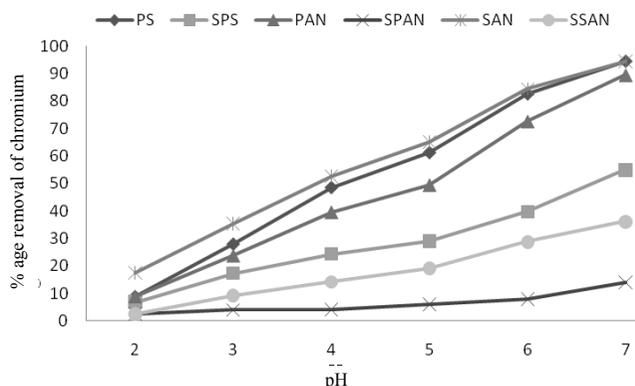


Figure 3. The effect of pH on adsorption of Cr(III) ions.

SAN shows adsorption due to the presence of aromatic ring of styrene (St) and nitrogen atoms of acrylonitrile (AN) present on the surface of the adsorbent while SSAN shows adsorption due to the presence of $-SO_3H$ as an additional group as compare to SAN as shown in Figure 3. Adsorption of Cr(III) increases with the increase of pH because at lower pH values competition exists between protons and metal ions for adsorption sites which decrease the adsorption capacity²⁷. PMMA shows adsorption due to the presence of both carboxylate group oxygen and also due to physical adsorption of the PMMA latex²⁸ while SPMMA shows adsorption due to the presence of $-SO_3H$ as an additional group as compare to PMMA shown in Figure 4.

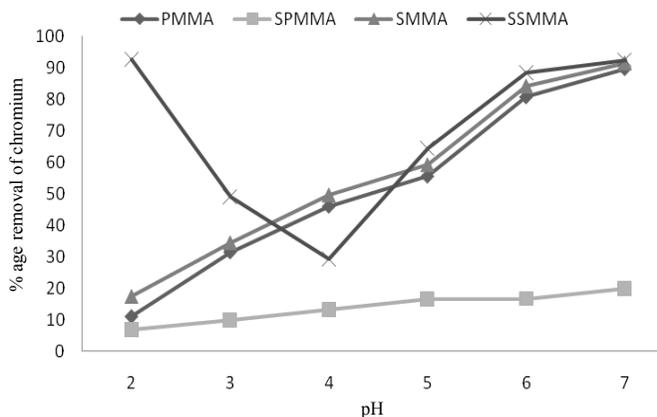


Figure 4. The effect of pH on adsorption of Cr(III) ions.

SMMA shows adsorption due to the presence of aromatic ring of styrene, carboxylate group oxygen of MMA present in the SMMA while SSMMA shows adsorption due to the presence of $-SO_3H$ group as an additional group as compare to SMMA. SSMMA shows maximum adsorption at pH 2 due to complex formation with oxygen and at pH 7 due to the $-SO_3H$ group because at lower pH competition exists between protons and metal ions for adsorption as shown in Figure 4. The carboxylate ($-COO^-$) group in the PAA is considered to be the active site for

metal ion adsorption. At lower pH values, carboxylate ion in PAA is protonated and competition exists between protons and metal ions for adsorption sites which decreases the adsorption capacity at lower pH values²⁹ while SPAA shows adsorption due to the presence of $-SO_3H$ group as an additional group present on the latex of adsorbent as shown in Figure 4. SAA shows adsorption due to the presence of carboxylate ($-COO^-$) group of AA and $\pi-\pi$ dispersion forces (due to the presence of aromatic ring) while SSAA shows adsorption due to the presence of $-SO_3H$ group as an additional group present on the latex of SAA. SSAA shows maximum adsorption at pH 2 due to the presence of carboxylate ($-COO^-$) ion complex formation and attraction of aromatic ring which decrease with increase in pH because there is internal interaction between ions carboxylate ($-COO^-$) and H^+ of $-SO_3H$ group as shown in Figure 5.

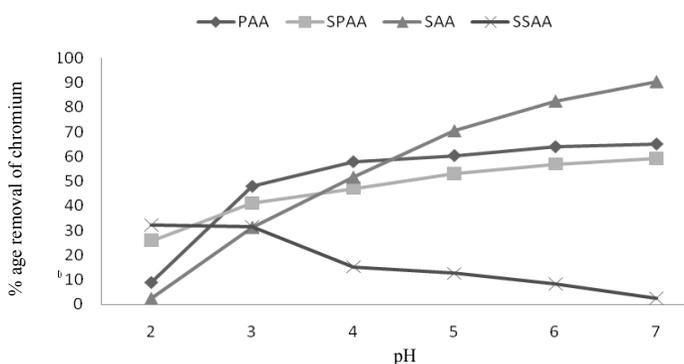


Figure 5. The effect of pH on adsorption of Cr(III) ions.

Effect of metal ion concentration

The effect of initial concentration of the metal ion uptake by adsorbents was conducted varying the metal ion concentration from 200-500ppm at pH 7. The flasks were agitated on orbital shaker at 250 rpm with the adsorbent dose of 5 g/L for 30 min. It was noticed that all these adsorbents show decrease in percentage removal of chromium because all the active sites are in limit and covered with Cr(III) as the concentration of Cr(III) is increased. All the adsorbent PS, SPS, PAN, SPAN, SAN, SSAN, PMMA, SPMMA, SMMA, SSMMA, PAA, SPAA, SAA and SSAA show maximum adsorption at 200 ppm.

Effect of contact time

The effect of the contact time on Cr(III) adsorption was studied by varying the time of contact from 10 to 30 min at pH 7. The flasks were agitated on orbital shaker at 250 rpm with the adsorbent dose of 5 g/L at concentration 200 ppm. Increase in removal efficiency with increase in time of contact is due to the fact that more time becomes available for metal ions to make a complex with adsorbents. Initial removal occurs immediately as soon as the metal and adsorbents came into contact, but after that when some of the easily available active sites become unavailable, metal needs time to find out more active sites for binding. It is concluded that metal and adsorbents *i.e.* SAN and SMMA should be in contact for at least 20min, while metal and adsorbents *i.e.* PS, SPS, PAN, SPAN, SSAN, PMMA, SSMMA, PAA, SPAA, SAA and SSAA should be in contact for at least 30 min in order to get good results. Adding more adsorbent will require less contact time to attain equilibrium.

Adsorption isotherms

The Langmuir, Freundlich and Temkin isotherms were plotted according to Eqs. (2) – (4):

$$q = [Q_{\max}b / (1 + bC_e)]C_e \quad (2)$$

$$q = K_f (C_e)^{1/n} \quad (3)$$

$$q = K_T \ln(C_e) + b_T \quad (4)$$

Where q (mg/g) is the amount of metal adsorbed per unit mass of adsorbent and C_e (mg/L) is the equilibrium concentration of adsorbate in solution after adsorption; Q_{\max} (mg Cr/g-adsorbent) and “ b ” (Langmuir adsorption coefficient, a constant) are Langmuir parameters. K_f is Freundlich adsorption coefficient, “ n ” is empirical constant reflecting the heterogeneity of the surface sites and dependent on the nature of sorbent and sorbate; b_T (kJ/mol) is Temkin adsorption potential of adsorbent and K_T is the Temkin adsorption coefficient. The Langmuir, Freundlich and Temkin isotherms are used to calculate above parameters and the corresponding parameters are given in Table 1.

Table 1. Langmuir, Freundlich and Temkin adsorption isotherm parameters.

Adsorbents	Langmuir parameters			Freundlich parameters			Temkin parameters		
	Q_{\max} , mgCr/g-adsorbent	b	R^2	$1/n$	K_f	R^2	b_T (KJ/mol)	K_T	R^2
PS	37.8	0.001	0.99	0.61	0.011	0.99	3.48	4.86	0.99
SPS	22	0.006	0.99	0.46	0.18	0.98	0.21	1.16	0.98
PAN	36.8	0.0013	0.98	1.44	0.034	0.99	0.51	1.25	0.99
SPAN	2.6	0.016	0.99	0.42	0.142	0.99	1.14	0.42	0.98
SAN	37.2	0.0011	0.97	0.23	63.14	0.98	6.31	6.79	0.96
SSAN	7.3	0.012	0.99	0.24	12.98	0.99	1.2	2.53	0.99
PMMA	29	0.004	0.98	0.67	0.044	0.97	1.10	0.10	0.97
SPMMA	9	0.01	0.99	0.17	2.83	0.99	7.65	13.51	0.99
SMMA	36.2	0.0014	0.98	1.05	0.69	0.98	1.63	2.86	0.99
SSMMA	37.1	0.0011	0.99	0.54	2.48	0.99	1.57	2.4	0.98
PAA	22.2	0.0058	0.96	0.43	11.37	0.99	0.98	1.63	0.99
SPAA	7.2	0.012	0.98	0.33	0.38	0.98	4.58	5.51	0.99
SAA	36.1	0.0015	0.99	0.18	1.64	0.99	0.53	0.96	0.96
SSAA	5	0.014	0.97	0.34	0.30	0.98	1.17	2.07	0.99

Q_{\max} value for all the synthetic adsorbent are in the following order: PS > SAN > SSMMA > PAN > SMMA > SAA > PMMA > PAA > SPS > SPMMA > SSAN > SPAA > SSAA > SPAN. PS has higher value of Q_{\max} and SPAN the least indicating PS has more active sites as compared to other adsorbents. Value of R^2 shows correlation or linear relationship. The Freundlich models indicate that SPMMA has more affinity towards Cr(III) than all other adsorbents. The smaller value of $1/n$ indicates formation of relatively stronger bonds between Cr on active sites of SAA. The affinity of all adsorbent towards Cr(III) are as follows: SPMMA > SAA > SAN > SSAN > SPAA > SSAA > SPAN > PAA > SPS > SSMMA > PS > PMMA > SMMA > PAN. The Temkin models indicate that SPMMA has

formed strongest bond with Cr(III) than all other adsorbents. Values of $b_T < 8$ indicate that bond formed between adsorbents and chromium is not very strong and is breakable in acidic conditions. High value of b_T for SPMMA indicates formation of relatively stronger bond between chromium and SPMMA than other adsorbents. The order of bond strength between chromium and adsorbents are as follow: SPMMA > SAN > SPAA > PS > SMMA > SMMA > SSAN > SPAN > PMMA > PAA > PAN > SAA > PAN > SPS.

Conclusion

The present study shows that PS, PAN, SAN, PMMA, SMMA, PAA and SAA were prepared by emulsifier-free emulsion polymerization and copolymerization and their sulfonated derivatives SPS, SPAN, SSAN, SPMMA, SSMMA, SPAA and SAA were prepared by homogeneous sulfonation. All the polymers, copolymers and their sulfonated derivatives were confirmed by FTIR analysis. All the synthetic products were used as an adsorbent for the removal of Cr(III). The amount of Cr(III) was found to vary with initial solution concentration, contact time and solution pH. The contact time necessary to reach the equilibrium using SAN and SMMA are 20min and for PS, SPS, PAN, SPAN, SSAN, PMMA, SPMMA, SSMMA, PAA, SPAA, SAA and SSAA is 30min. The adsorption is found to be highly dependent on pH. All the adsorbents show maximum adsorption at pH 7 except SSMMA and SSAA that shows at pH 2. Therefore maximum removal *i.e.* 95% is shown by PS at pH 7. Its found that physical adsorption, π - π dispersion forces, ion exchange and chelation reaction take place in the Cr(III) ion removal. The equilibrium data was well described by Langmuir adsorption isotherms. The maximum Cr(III) removal was 37.8mg/g of PS and 37.2mg/g of SAN. Relatively stronger bonds are formed between SPMMA and Cr(III) as evaluated from Temkin isotherm.

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