Synthesis of Polyaniline Nanoparticle Grafted Silica Gel and Study of Its Cr(VI) Binding Property

P. Chowdhury, P. Mondal, K. Roy

Synthetic Polymer Laboratory, Department of Chemistry, Visva-Bharati University, Santiniketan 731235, West Bengal, India

ABSTRACT: Polyaniline nanoparticles have been synthesized through simple micelle technique and then grafted it with silanized silica gel to develop a novel hybrid material. The nanoparticles are characterized by UV-Vis, TEM, CV, SEM, TGA, DTG, and DSC. Silanization and grafting reactions are evaluated by FTIR and chemical test. The Cr(VI) binding behavior of the composite is studied in various pH of the medium, and both competitive and noncompetitive conditions. The particle size, adsorption capacity, and surface area of the material are found to be 100 nm, 135 mg/g, and 720 m^2/g, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 823–829, 2011

Key words: Cr(VI); polyaniline nanoparticles; silanization; grafting; metal binding

INTRODUCTION

The surface modification of inorganic particles with polymeric chains to form functional core-shell hybrid structure has attracted much attention due to their potential applications in the biomedical field.[1–4] Recently, the hybrid materials find utility in the development of specific materials for metal ion adsorption,[5] catalysis,[6–8] and optoelectronic devices.[9] Silica particles are widely used to prepare the target inorganic–organic hybrids due to their chemical resistance, mechanical stability, relatively low costs, variables particle sizes, and high specific surface area.[10] So far silica particles coated with well-defined polymers have been achieved mainly by two polymerization techniques, such as 'grafting to'[11] (where functionalized polymer chains are reacting with silica surface) and 'grafting from' (where chains are growing from the silica surface). Some of the methods related to 'grafting to' techniques are coupling[12] and ultrasonic irradiation.[13] Among the 'grafting from' techniques, surface initiated radical polymerization,[14] controlled radical polymerization,[15] and ionic polymerization[16] are gaining importance recently. There are several reports of grafting polymer chain onto silica nanoparticles.[11–16] However, no report has been found for grafting polymer nanoparticles onto silica macroparticles, which are very much essential for metal ion extraction.

Recently variours polymeric materials,[17] such as poly(4-vinyl pyridine), poly(ethylene glycol dimethacrylate-1-vinyl-1,2,4-triazole), calixarens, polyacrylamied, polyamines, poly(2-methacryloloxyl trimethyl ammonium chloride), poly(acrylo nitrile), poly(ethyleneimine) have been reported to be good polymeric adsorbent for Cr(VI). Of the reported polymers, polyaniline (PANI) deserves special attention due to their suitable structures for selective chromate ion binding.[17,18] Grafting being a potential technique to prepare stable organic–inorganic hybrid materials[19] is expected to be useful for the preparation of polyaniline nanoparticle grafted silanized silica gel (PAN-INP-*g*-SSG). There is no report on the grafting of PANI nanoparticles onto silanized silica gel so far. Ruckenstein and coworkers[20] prepared luminescent silicon nano particles grafted by conducting polyaniline chains through the self-assemble method (SAM).[20] Polyaniline nanoparticles are prepared by various methods, such as chemical,[21] electrochemical,[22] and biocatalysis process.[23] In chemical process surfactant are generally used to control the size of polyaniline nanoparticles. However, recently surfactant free method has been developed to prepare polyaniline nanofibers.[24]

Cr(VI) is a powerful carcinogen and toxic to many plants and aquatic animals and bacteria.[25] Therefore, it is necessary to decrease the concentration of Cr(VI) below permissible levels,[25] which are less than 0.05 mg/L. Cr(VI) is a common waste product generated from industrial process. Several methods[17] such as chemical precipitation, reverse osmosis, ion

Correspondence to: P. Chowdhury (pranesh_02@yahoo.co.in).

exchange, foam flotation, electrolysis, solvent extraction, magnetic separation, liquid membrane isolation, biosorption, and surface adsorption has been reported for removal of Cr(VI). A varieties of adsorption materials studied for Cr(VI) removals, which include mainly biosorbents and natural materials.[17] However, the major drawback of the studied materials is their poor selectivity and low exchange capacity.

In this work an attempt has been made to synthesize (i) polyaniline nanoparticle (PANINP), (ii) silanized silica gel (SSG), and (iii) polyaniline nanoparticle grafted silanized silica gel (PANINP-g-SSG) with a view to study the grafted material as selective and effective Cr(VI) binder.

MATERIALS, INSTRUMENTS, AND METHODS

Materials

Aniline (Merck, Mumbai, India) was purified by distillation over zinc dust. The middle fraction of the distillate was collected and stored in a refrigerator. Potassium dichromate (Pfizer, Mumbai, India) was used for the preparation of stock solution of Cr(VI) (250 mg/L). All the working solutions were prepared by proper dilution of the stock solution with distilled water. 1,5 diphenyl carbazide used for the estimation of Cr(VI) was of analytical grade (Merck, Mumbai, India). Methylene blue stain (Merck, Mumbai, India) was used to determine the specific surface area of polyaniline nanoparticle grafted silanized silica gel (PANINP-g-SSG). Potassium peroxodisulfate (PPD, E. Merck, Bombay, India), sodium dodecyl sulfate (SDS, Glaxo, Mumbai, India), dimethyl dichloro silane (DDS, Merck, Mumbai, India) was used as received.

Instruments

UV-Vis-NIR spectrophotometer (Shimadzu Model UV-PC) was used for the analysis of Cr(VI) from aqueous solution. An ELICO made pH meter (Model LI120) was used for the pH measurement. The Fourier Trasform Infrared (FTIR) was recorded using KBr pellets by Shimadzu-8400S model. Thermogravimetric and differential thermal analysis were made using a Pyris Diamond TG/DTA (Perkin Elmer) thermal analyzer in nitrogen atmosphere at a heating rate of 10°C/min. Scanning Electronic Microscope (SEM) of the polymer was conducted by JEOL JSM 6700 FESEM. Sample for Transmission Electron microscopy (TEM) was prepared by drop coating the polyaniline nanoparticle of suspended solutions onto carbon coated copper grids. The film was allowed to dry prior to TEM measurement in a JEOL TEM-2010 instrument. Cyclic voltametry of the
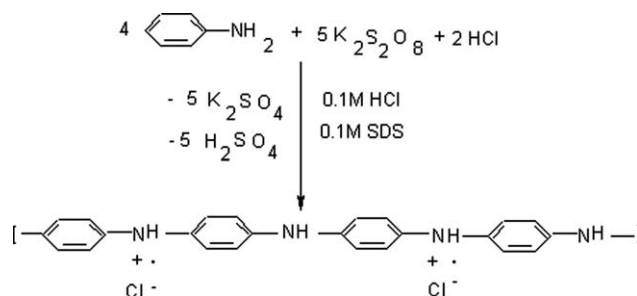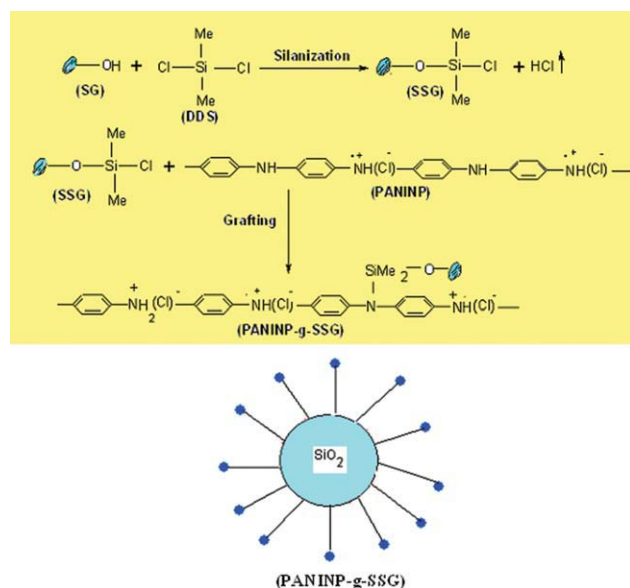
Scheme 1 Synthesis of PANINP.

materials were carried out in a Potentiostat-Galvanosat (PAR Versastat TM-II). The scan was done in the potential range 0.94 to −0.2 V vs. SCE at a scan rate 20 mV/s. Extraction and elution were studied in chromatographic column (internal diameter = 0.1 cm). The Sonicator (Branson 1510) was used for ultrasound irradiation in grafting.

Synthesis of polyaniline nanoparticles

The polyaniline nanoparticle (PANINP) was synthesized from aniline, ammonium peroxodisulfate, and hydrochloric acid, and characterized accordingly following the procedure as reported earlier.[26] The synthesis of nanoparticle of polyaniline was carried out in a three-necked round-bottom flask. Aniline (0.4 mL, 0.0044 mol) was taken in a round-bottom flask in 90 mL 0.1 (N) HCl. Sodium dodecyl sulfate (SDS) (2.88 g, 0.01 mol) was then mixed by stirring with magnetic stirrer for 2 h. Then potassium peroxodisulfate (1.485 g, 0.0055 mol) solution in 10 mL 0.1(N) HCl was added with a flow rate 1 mL/min. The suspended solution of polyaniline nanoparticles (Scheme 1) was obtained after constant stirring for half an hour at room temperature.

Silanization of silica gel and grafting

Silanization of silica gel was done following the procedure as mentioned earlier.[27] Silica gel (25 g) was mixed with 40 mL of 5% ether solution of dimethyl dichloro silane (DDS) and stirred for 20 min. The mixture was then dried in rotary vacuum evaporator to obtain silanized silica gel (SSG) (Scheme 2). SSG was then washed with methanol to remove excess DDS and dried again. The functionalized silica gel was then grafted with suspended polyaniline nanoparticle with constant stirring for 4 h at 50°C and sonicated for 2 h. The grafted silica gel was then washed with distilled water and methanol several times until the SDS was removed completely and dried to get polyaniline nanoparticle grafted silanized silica gel (PANINP-g-SSG) (Scheme 2). The percentage of grafting was found to be 8.89 (Table I).

Scheme 2 Chemical synthesis and physical representation of PANINP-*g*-SSG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Study of Cr(VI) binding

Cr(VI) binding ability of the synthesized novel material was studied by batch method. To determine the amount of Cr(VI) bound, 0.25 g sorbent (PANINP-*g*-SSG) was taken in a conical flask. Then 25 mL sorbate solution containing chromate ion at different pH was mixed and stirred. The initial concentration of Cr(VI) was kept to 4–70 mg/L. Amount of Cr(VI) extracted was calculated using the relationship: $q_t = (W_i - W_t) / M$---(1). Here q_t is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg/g). W_i and W_t are the initial and residual amount (mg) of Cr(VI), respectively in influent and effluent, respectively. M is the mass (g) of the adsorbent added.

TABLE I
Some Physicochemical Characteristics of PANINP-*g*-SSG

Parameters	Value	Method
Particle size (nm)	100	TEM
Surface area (m^2/g)	720	Methylene blue[5]
pH (Zero point charge)	8.0	Chromate titration[5]
Ion exchange capacity (meq.Cl$^-$/g)	2.11	Chloride titration[5]
Degree of grafting	0.089	Gravimetry[5]
Bulk density (g/mL)	1.23	Specific gravity[5]

RESULTS AND DISCUSSION

Evidence for grafting

The FTIR spectrum of the synthesized PANINP-*g*-SSG (Fig. 1) exhibited several characteristic peaks of PANI[28] (3458, 2588, 804 cm^{-1}) and SSG[27] (1338, 1060 cm^{-1}). A new peak appears at 594 cm^{-1}, which is absent in the spectrum of both PANI and SSG. The new peak is assigned for the Si—N linkage.[29] The presence of Si—N linkage is one of the strong evidence for the formation of grafted polymer. The insolubility of the composite material in NMP and concentrated sulfuric acid justifies the grafting of PANI onto SSG.

Polyaniline nanoparticles

A UV-Vis spectrum of the prepared polyaniline is shown in Figure 2. The spectrum exhibited sharp absorption peaks at 495 nm, which could be assigned to protonated polyaniline nanoparticles.[28] The size of the PANI remains within 100 nm as evident from TEM picture (Fig. 3). SEM photograph (Fig. 4) reveals the rod-like shape of polyaniline nanoparticles. The cyclic voltammogram of PANINP (Fig. 5) in 0.1(M) HCl solution exhibits two redox couples. The first one could be attributed to the leucoemaraldine to emaraldine salt transition and the
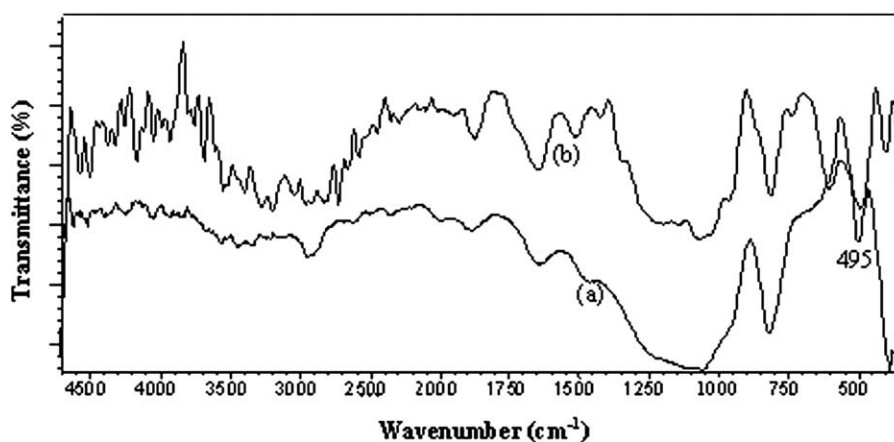

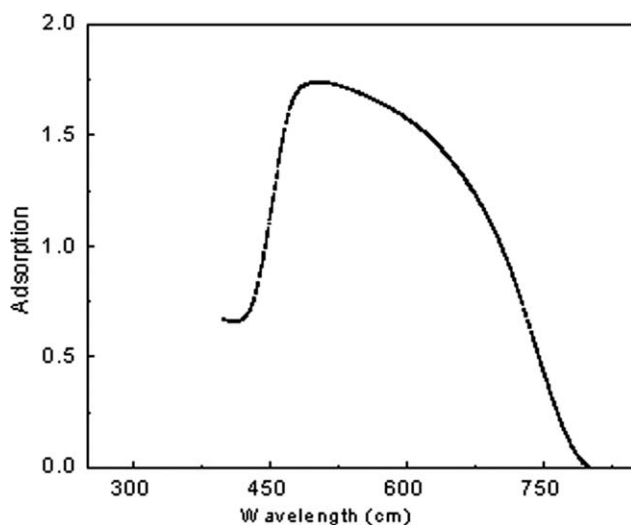**Figure 1** FTIR spectra of (a) PANINP-*g*-SSG and (b) Cr(VI) loaded PANINP-*g*-SSG.

Figure 2　UV-Vis spectrum of PANINP.

Figure 4　SEM photograph for PANINP.

second one is due to the transition from the emaraldine salt to pernigraniline salt.[24]

Physicochemical characterization

Surface area, exchange capacity, bulk density, particle size, percentage of grafting, and zero point charge of developed material are evaluated and the results are included in Table I. The values of surface area, zero point charge and bulk density of the grafted material are 720 m^2/g, 8.0, and 1.23 g/mL. The trace of thermo gravimetric analysis (TGA) of the sample PANINP-g-SSG (Fig. 6) indicates that mass loss of the samples occurs mainly through three stages (30–150, 150–275, and 275–375°C). First stage weight loss starts at 30°C and continued up to 150°C. The initial weight loss (10%) is probably due to loss of HCl. The second stage weight losses (81%)
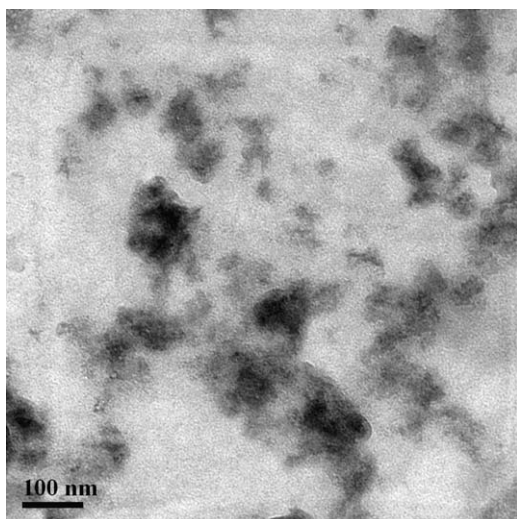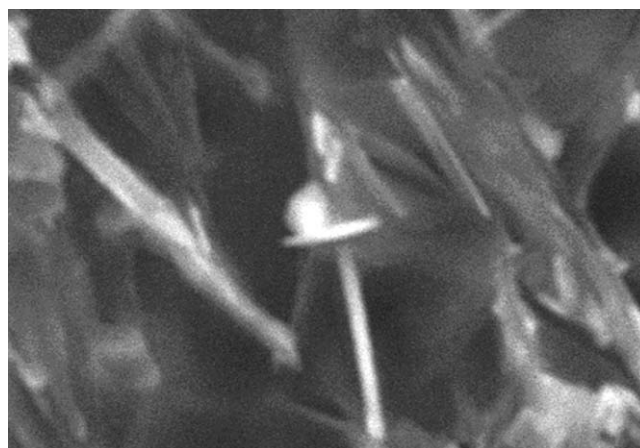
indicate the oxidative degradation of the polymer. The third stage weight loss may be attributed to loss of impurities present in the samples. TGA shows that PANINP-g-SSG is stable up to 150°C. Integral Procedure Decomposition Temperature (IPDT)[5] values (190°C) and activation energies (0.0087 KJ mol^{-1}) confirm the good thermal stability of the prepared materials. DTG traces (Fig. 6) shows three endothermic peaks at 80, 220, and 320°C for PANINP-g-SSG. The first endothermic peak is due to discharge of moisture. The second and third indicate the decomposition of polymer. The DSC trace supports the three stages degradation.

Effect of sorbate dose on Cr(VI) binding

The effect of sorbate dose on binding capacity was studied (Fig. 7) within the range 4–70 mg/L of Cr(VI), keeping other conditions (pH = 4.75, sorbent dose = 10g/L, time = 1 h) fixed. It was observed that binding capacity of the prepared material was increased with the increase of sorbate level. The
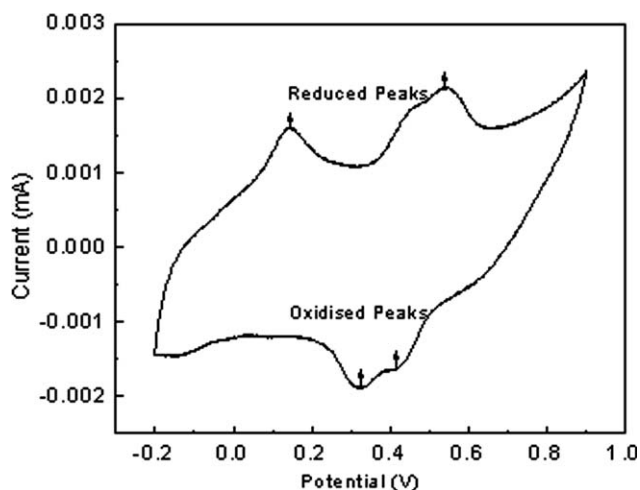

Figure 3　TEM image of PANINP.
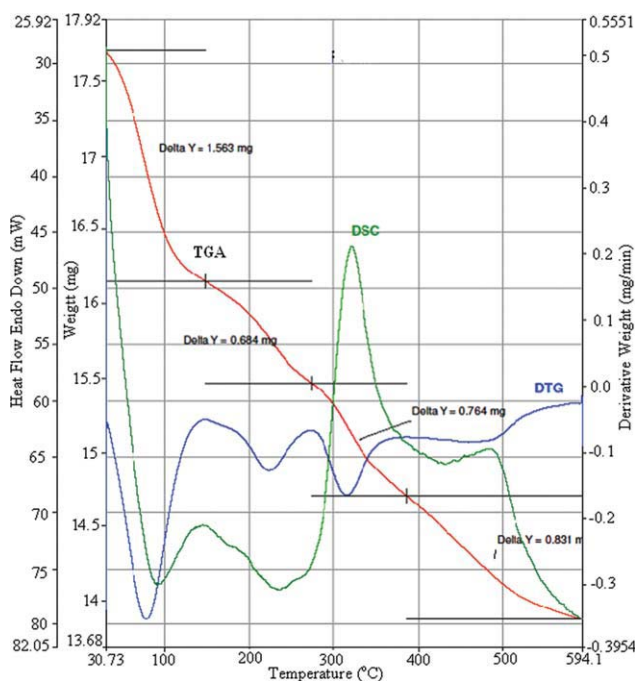

Figure 5　CV diagram of PANINP.

Figure 6 Simultaneous TGA-DTG traces of PANINP-*g*-SSG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

capacities of the developed materials are found to be 89.23, 102.73, and 135 mg/g at 5, 27, and 45°C, respectively with the 70 mg/L of Cr(VI) concentration. The values are higher compared to ungrafted polyaniline (PANI)[18] and the other commercial polymers,[17] such as quaternized polyvinyl pyridine, XFS-4195 (DOW Chemical), and IRA-900 (Rohm & Haas) at similar condition. The higher values were increased further with the increase of sorbate dose beyond 70 ppm. The higher binding capacity may be
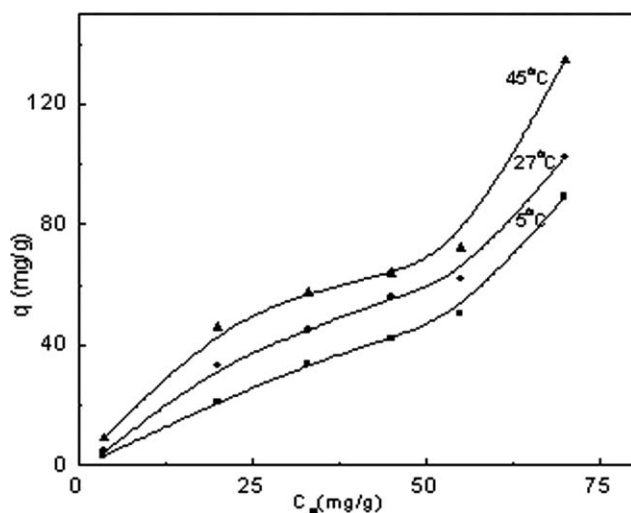

Figure 7 Variation of adsorption capacity with sorbate dose [pH = 4.75, Sorbent dose = 10g/L, Time = 1 h].
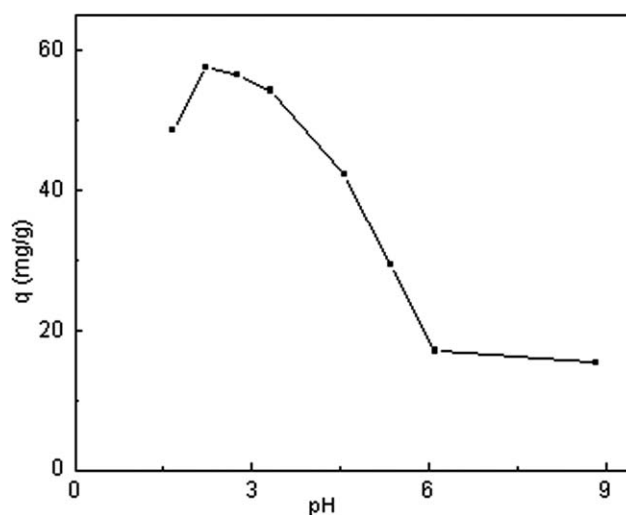

Figure 8 Variation of adsorption capacity with pH, [sorbent dose = 10 g /L, Sorbate = 45 mg /L, Temp = 27°C, Time = 1 h].

due to higher surface area (Table I) of the prepared PANINP-*g*-SSG.

Effect of pH on Cr(VI) binding

The results of Cr(VI) adsorption with increasing pH from 1 to 8 are shown in Figure 8. It was found that the adsorption capacity was increased with the increase of pH from 1 to 3 and then decreased gradually up to pH 8. The initial increase is probably due to autoionisation ($2H_2CrO_4 = Cr_2O_7^{2-} + 2H^+ + H_2O$) at relatively higher pH of the solution. The ionic species are bound by the polymer through ionic interaction (Scheme 3). The gradual decrease (beyond pH 3) may be explained by the gradual conversion of dichromate ion to chromate ion. Chromate being a monomeric form lacks the proper size to fit in the polymer sites. The sorption of Cr(VI) probably took place through ion exchange process (Scheme 3), particularly at pH less than 8. The presence of exchangeable chloride (Ion exchange capacity = 2.11 meq Cl$^-$ /g) favors the ion exchange
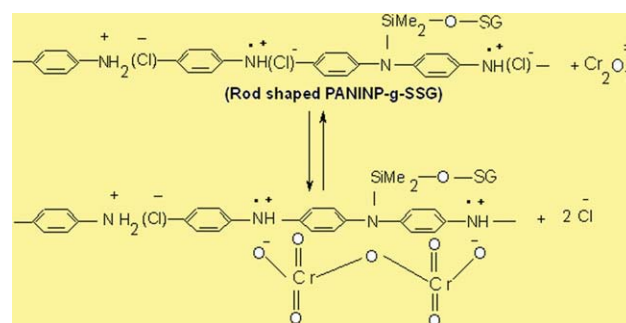
Scheme 3 Illustration of binding mechanisms of Cr(VI) onto PANINP-*g*-SSG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanism. The release of chloride ion in the aqueous media is tested by chemical test.[30] The ion exchange nature of the reaction is further confirmed through elution of the adsorbed dichromate by NaCl and NaOH of more than 10 times higher concentrations compared to dichromate (Table II).

The effect of time and temperature on Cr(VI) binding

Figure 9 shows that the amount of Cr(VI) adsorbed (q_t, mg/g) at different contact time and temperature. Almost 90% adsorption took place within 20 min and the time required to reach the equilibrium is 30 min. The adsorption capacity increases with the increases of temperature. The rapid adsorption probably due to the availability of the positive charged surface of the sorbent (PH_{zpc} = 8.0).

Selective binding of Cr(VI) in competitive condition

In this group of experiments, the competitive binding of sulfate, chloride, nitrate, phosphate, and bicarbonate with the polymer were investigated. These experiments were performed at a constant pH (4.75), temperature (27°C), sorbent dose (10 g/L), and time (1 h) with the solution containing 0.0001 mole of each metal ion. The selectivity[31] (S) of the polymer for the metal (M$_1$) ion with respect to the competitive metal (M$_2$) ions was determined according to the relationship: S = log K_d(M$_1$) − log K_d(M$_2$); where the distribution coefficients (K_d) of metal ions between the sorbent phase and sorption medium at equilibrium was calculated by using the expression: $K_d = W_1/W_2$; (W_1 = metal ion (mg) adsorbed per g of polymer and W_2 = metal ion (g) present per mL of solution). The selectivity of the polymer for chromate ion with respect to sulfate, chloride, nitrate, phosphate, and bicarbonate are 0.19, 0.39, 0.31, 0.24, and 0.28, respectively. The positive values of selectivity indicate that the prepared material binds chromate ion preferably in presence of the studied anions. The polymeric nature of both sorbent and sorbate in the reaction conditions probably makes
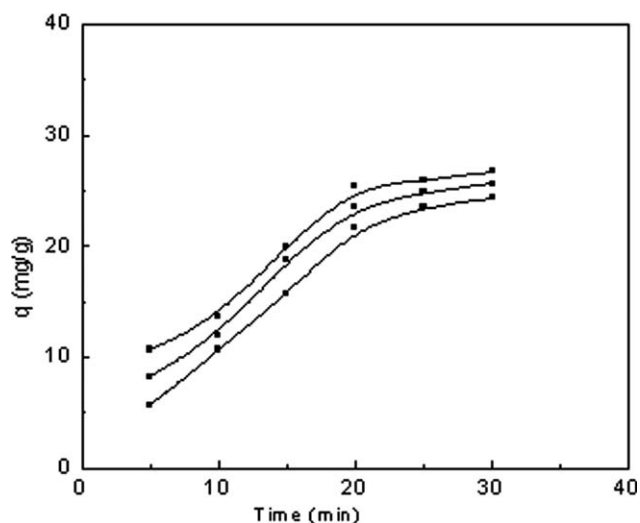

Figure 9 Variation of adsorption capacity with time and temperature, [pH = 4.75, sorbent dose = 10 g/L, sorbate dose = 45 mg/L].

the system selective toward chromate. Commercial anion exchangers are unable to remove dissolve chromate anion[32] selectively. The ion exchange nature and selectivity of the grafted material is further confirmed through elution of the adsorbed dichromate by NaCl, Na$_2$SO$_4$, NaNO$_3$, Na$_3$PO$_4$, and bicarbonate in a chromatographic column. It is found that eluents having more than hundred times higher concentrations (compared to dichromate) is required for effective elution (Table II). The table shows that sodium hydroxide is the most effective eluent.

CONCLUSION

Polyaniline nanoparticle of desired shape and size (rod like, 100 nm diameter) has been synthesized through micelle technique. Polyaniline nanoparticles grafted silanized silica gel (organic–inorganic hybrid material) with 8.9% grafting and high surface area (720 m^2/g) have been prepared successfully by 'grafting to' method. The hybrid material is stable up to 150°C and posses high ion exchange capacity. The material was found to be a potential and selective binder for Cr(VI). It has metal binding capacity of 135 mg/g even at very low level of Cr(VI) (70 mg/L). The value is higher compared to the many commercial polymers, such as quaternized polyvinyl pyridine, XFS-4195 (DOW Chemical), and IRA-900 (Rohm & Haas) at similar condition. The synthesized polymer has exceptional selectivity toward chromate ion. The adsorption–desorption of chromate ion occurs through ion exchange mechanism and the process may be controlled by pH switching.

TABLE II
Elution of Extracted Cr(VI)

Eluents	Concentration (M)	V$_t$ (mL)[a]	Recovery (%)[b]
NaOH	0.10	25	95.67
NaCl	0.10	25	81.76
Na$_2$SO$_4$	0.10	25	90.35
Na$_2$NO$_3$	0.10	25	76.01
Na$_3$PO$_4$	0.10	25	56.90
NaHCO$_3$	0.10	25	45.23

[a] Total volume of eluent (ml).
[b] (Metal ion eluted/Metal ion loaded) × 100.

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