Talanta 83 (2011) 1482–1486

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Synthesis of polypyrrole nanoparticles and its grafting with silica gel for selective binding of chromium(VI)

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A R T I C L E I N F O

Article history:
Received 15 September 2010
Received in revised form
13 November 2010
Accepted 15 November 2010
Available online 23 November 2010

Keywords:
Cr(VI)
Polypyrrole nanoparticles
Functionalizing
Grafting
Metal ion binding

A B S T R A C T

Polypyrrole nanoparticles of desired structure have been synthesized through simple micelle technique. It is then grafted with functionalized silica gel to develop a novel organic–inorganic hybrid material. The role of dimethyl dichloro silane (coupling agent) in grafting is demonstrated. The nanoparticles are characterized by TEM, SEM and TGA. Grafting reactions are evaluated by spectral (FTIR) analysis and chemical test. The Cr(VI) binding behavior of the composite is studied in various pH of the medium. The selectivity in binding Cr(VI) is monitored. The metal ion adsorption capacity and surface area of the material are found to be 38 mg/g and 235 m^2/g, respectively.

1. Introduction

Inherent conducting polymers (polypyrrole, polyaniline and polythiophene) have attracted a great deal of interest owing to their remarkable properties, such as redox [1], acid–base [2], ion-exchange [3] and chemical sensing [4] in addition to its high conductivity [5]. Bulk polypyrrole is infusible, intractable and insoluble in common solvents due to partial cross-linking [6] through hydrogen bonding. As a result the polymer has poor process ability and inferior mechanical properties [7]. Various approaches [8] have been utilized to improve the process ability of polypyrrole [9–11], including (i) chemical modification of polymer backbone; (ii) copolymerization of appropriate functional co-monomers; (iii) use of polymeric or surfactant-type doping anion; and (iv) preparation of stable colloidal dispersion. Formation of later through hybridization of polypyrrole with silica deserves special attention due to its composite nature. The benefit of such composite is the synergistic combination of properties of both the components. Thus one can achieve required mechanical strength of silica as well as high ion exchange properties of polypyrrole [3] in their composite (organic–inorganic hybrid material based on polypyrrole and silica). The composite may be helpful in selective binding of chromate through ion exchange process [12,13]. Two types of polypyrrole silica composites (PPY–SiO_2) such as (a) silica rich PPY–SiO_2 nano composite [8] and (b) polypyrrole rich PPY–SiO_2 hybrid materials [7] are gaining importance now-a-days due to their various applications. We have focused on the latter approach in the present study.

Various authors reported on the preparation of PPY–SiO_2 composites. Armes and co-workers [14–17] have shown that the polymerization of pyrrole in the presence of ultra fine aqueous silica sols lead to the formation of unusual "raspberry-shaped" PPY–SiO_2 nano composite which exhibit silica-rich surfaces. Wallace et al. [18,19] used porous silica gel particles for the preparation of novel silica rich PPY–SiO_2 composite for chromatographic use. Faverolle and fellow researchers [20,21] demonstrated that polypyrrole could be deposited onto E-glass fibers with the help of silane coupling agent. The resulted composite leads to polypyrrole rich over layers (20–50 nm thickness). Chehimi and his group [7,22] describe the use of aminopropyl triethoxysilanes (APTS) in the preparation of polypyrrole-coated silica gel (PPY–APTS–SiO_2) with the aim of obtaining a polypyrrole-rich hybrid particles with surface area in the range162–184 m^2/g.

In the present work, we demonstrate the role of dimethyl dichloro silane (DDS) in the preparation of polypyrrole-grafted silica gel (PPY–DDS–SiO_2) with a view to obtain polypyrrole-rich silica particles with surface area greater than 200 m^2/g. The process will be compared to the method published by Chehimi et al. [7,22] and it will be different from Armes et al. [14–17]. We have synthesized polypyrrole nanoparticles for grafting onto functionalized silica gel and studied its chromium(VI) binding ability. A

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doi:10.1016/j.talanta.2010.11.037

polypyrrole-rich surface having higher specific surface area lead to conductive as well as better ion exchanger. Silica particles coated with well-defined polymers have been achieved mainly by two polymerization techniques such as “grafting to” [23] (where functionalized chains are reacting with silica surface) and “grafting from” [24,25] (where chain are growing from the silica surface). In the present study “grafting to” technique has been used for getting higher surface area. However, Chehimi et al. [7,22] utilized ‘grafting from’ approach.

2. Materials, instruments and methods

2.1. Materials

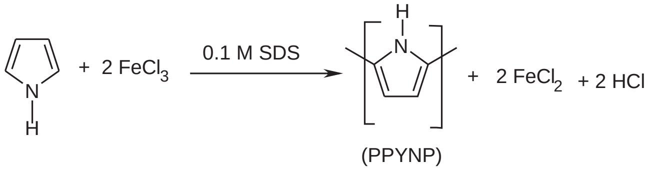
Pyrrole (Spectrochem, Mumbai, India) was purified by distillation. The middle fraction of the distillate was collected and stored in a refrigerator. Potassium dichromate (Pfizer Ltd., Mumbai, India) was used for the preparation of stock solution of Cr(VI) (300 mg/l). All the working solutions were prepared 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. Silica gel (60–120 mesh, Merck, Mumbai, India), ferric chloride (Ranbaxy Laboratory Ltd., Punjab India), sodium dodecyl sulfate (SDS, Glaxo, Mumbai, India), dimethyl dichloro silane (DDS, Merck, Mumbai, India) was used as received.

2.2. 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 Transform Infrared (FTIR) was recorded using KBr pellets by Shimadzu-8400S spectrometer. Thermo-gravimetric 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 polypyrrole 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. Extraction and elution were studied in chromatographic column (internal diameter = 0.8 cm). The Sonicator (Branson 1510) was used for ultra-sound irradiation in grafting.

2.3. Synthesis of polypyrrole nanoparticles

The polypyrrole nanoparticle (PPYNP) of desired shape and size was synthesized from pyrrole using suitable surfactant and maintaining proper oxidant to pyrrole mole ratio. Pyrrole (0.4 ml, 0.0057 moles) was dissolved with 100 ml 0.01 (N) HCl in a round bottom flask. Sodium dodecyl sulfate (SDS) (2.88 g, 0.01 mol) was then mixed by stirring with magnetic stirrer for 2 h. Ferric chloride (0.0114 moles, dissolved in 10 ml 0.01 N HCl) was added dropwise in the mixture maintaining oxidant-to-pyrrole mole ratio 2:1, which is close to the work of Omastova et al. [26]. However, Evseeva [24], Armes [17] and Chehimi [2] used higher mole ratios (2.33:1, 2.5:1 and 2.5:1, respectively). The suspended solution of polypyrrole nanoparticles (Scheme 1) was obtained after constant stirring for half an hour at room temperature. The suspended solution were centrifuged for 5 min to settle polypyrrole nanoparticles (PPYNP) and it was then washed with distilled water to remove impurities. The purified PPYNP was re-dispersed with 100 ml distilled water and used for grafting functionalized silica gel.



Scheme 1. Preparation of polypyrrole nanoparticles.

2.4. Functionalizing of silica gel

Functionalizing of silica gel and its characterization was done following the procedure as mentioned earlier [13]. Silica gel (25 g) was mixed with 40 ml 5% ether solution of dimethyl dichloro silane (DDS) and stirred for 20 min. The mixture was then dried in rotary vacuum evaporator to obtain functionalized silica gel (FSG). It was then washed with methanol to remove excess DDS and dried again. The reaction path and the structure of FSG (Scheme 2) were evaluated as reported earlier [13].

2.5. Grafting of polypyrrole

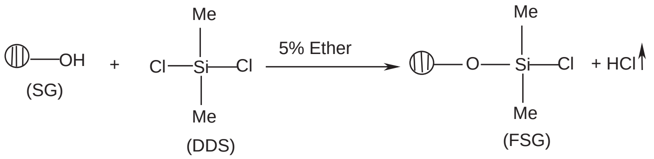
The functionalized silica gel (FSG) was mixed with the re-dispersed polypyrrole nanoparticle (100 ml solution) with constant stirring for 2 h at room temperature and sonicated for an hour. The product was then washed with distilled water several times until the impurities were removed completely and dried to get polypyrrole nanoparticle grafted functionalized silica gel (PPYNP-g-FSG).

2.6. Study of Cr(VI) binding

Cr(VI) binding ability of the synthesized novel material was studied by batch method [13]. To determine the amount of Cr(VI) bound, 0.20 g sorbent (PPYNP-g-FSG) was taken in a conical flask. Then 25 ml Cr(VI) solution was mixed and stirred. The initial concentration of Cr(VI) was kept to 5–90 mg/l. Amount of Cr(VI) bound was calculated using the relationship: $q_t = (W_i - W_t)/M$. 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 sorbent added.

2.7. Kinetic study

Batch adsorption tests were carried out by mechanical agitation (agitation speed: 90–100 rpm) at temperature from 8 to 55 °C. To determine the amount of Cr(VI) adsorption, 0.20 g sorbent, (PPYNH$^+$) was taken in a 100 ml beaker with 25 mL sorbate solution. The concentration of Cr(VI) in aqueous solution was kept to 5–90 mg/L. The pH of the solution was maintained to 5.25. One ml sample solution was withdrawn each time from the reaction mixture by a syringe at a gap of fixed interval and analyzed. Amount of Cr(VI) adsorbed was calculated using the relationship: $q_t = (W_i - W_t)/M$. Here q_t is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg/g) at time ‘t’. W_i and W_t are the initial and residual amount (mg) of Cr(VI) respectively in solution. M is the mass (g) of the sorbent added.



Scheme 2. Functionalizing of silica gel.

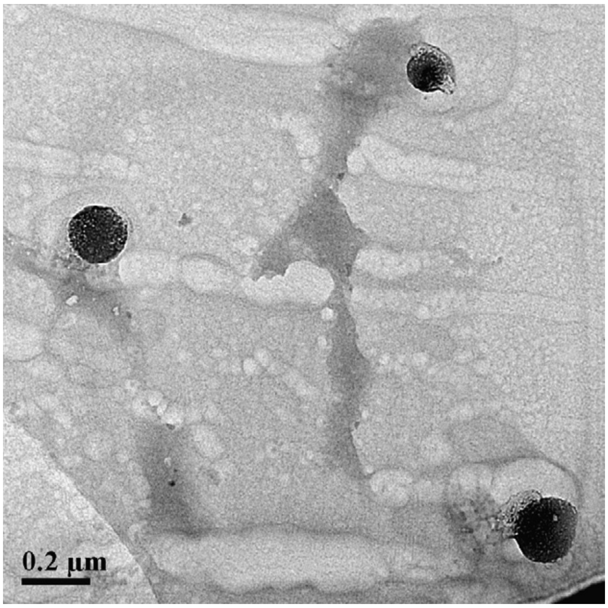


Fig. 1. TEM image of PPYNP.

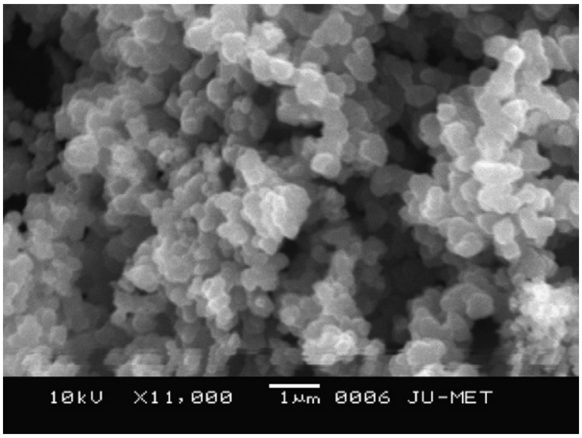


Fig. 2. SEM photograph of PPYNP.

3. Results and discussion

3.1. Characteristics of polypyrrole nanoparticles

A typical transmission electron micrograph (TEM) of diluted polypyrrole nanoparticles is shown in Fig. 1. The sample has a number average particle diameter of 100 nm and it looks like opal shaped. It is also seen that some of the PPYNP agglomerated in the colloidal solution.

The scanning electron micrograph (SEM) depicted in Fig. 2 is of a polypyrrole bulk powder precipitated by centrifugation. This polypyrrole bulk powder sample had a fused globular morphology with particular diameter in the range 0.2–0.5 μm (200–500 nm). Hence precipitated particles are larger than the dimension of polymer in colloid state (100 nm). The results are in line with the work of Boukerma et al. [27].

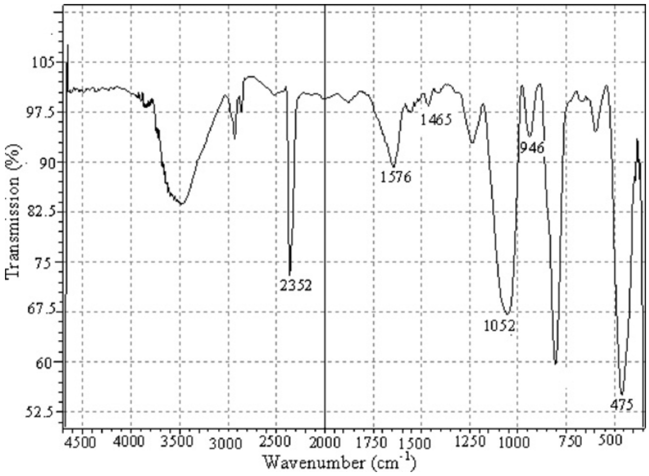


Fig. 3. FTIR spectra of PPYNP-g-FSG.

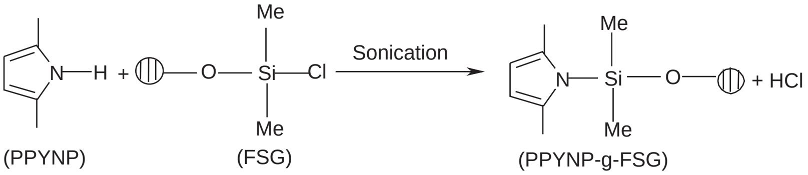
3.2. Evidence for grafting

The percentage of grafting was found to be 6.59, which indicates the polypyrrole-rich surface of the composite. The color of the white silica gel turned into black, which was not discharged with repeated washing with water and acids. The result suggests the formation of chemical linkage between polymer and silica. The formation of covalent linkage was confirmed by FTIR spectra (Section 3.2) and pH measurement (Section 3.5). It is noteworthy to mention here that PPYNP did not react with silica gel in the absence of DDS coupling agent. The probable grafting mechanism has been evaluated and suggested (Scheme 3).

The FTIR spectrum of the synthesized PPYNP-g-FSG (Fig. 3) exhibited several characteristic peaks of PPY [26] (2352, 1576, 1465 and 946) and FSG [13] (1338, 1052 cm^{-1}). A new peak appears at 475 cm^{-1}, which is absent in the spectrum of both PPY and FSG. The new peak may be assigned to the Si–N linkage [28]. The presence of Si–N linkage is one of the strong evidence for the formation of grafted polymer. Other evidences are discussed in Section 3.3.

3.3. Physico-chemical characteristic of PPYNP-g-FSG

Surface area, exchange capacity, bulk density, particle size, percentage of grafting and zero point charge of the developed material were evaluated following the procedure as described earlier [12] and the results are 235 m^2/g, 1.78 meq. Cl$^-$/g, 1.17 g/ml, 100–145 μm, 6.59 and 8.0, respectively. The surface area and size of the purchased silica gel were found to be 430 m^2/g and 60–120 μm, respectively. The surface area of the grafted product is larger than that reported by Chehimi group [7,22]. Thus the polypyrrole



Scheme 3. Grafting of polypyrrole nanoparticles by functionalized silica gel.

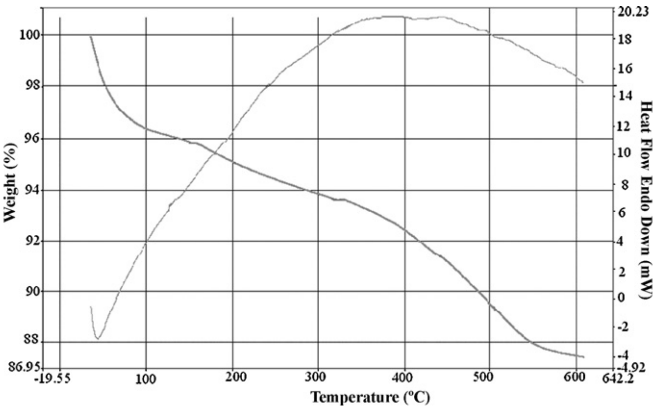


Fig. 4. Simultaneous TGA-DTG traces of PPYNP-g-FSG.

nanoparticles are more effective for the preparation of polypyrrole-rich PPY-SiO_2 composite and DDS plays an effective role in binding PPYNP with silica gel.

The trace of thermo-gravimetric analysis (TGA) of the sample PPYNP-g-FSG (Fig. 4) indicates that mass loss of the samples occurs mainly through three stages (40–100, 100–250 and 250–375 °C). First stage weight loss starts at 40 °C and continued up to 100 °C. The initial weight loss (9%) is probably due to loss of water. The second stage weight loss (71%) indicates 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 PPYNP-g-FSG is stable up to 100 °C. Integral procedure decomposition temperature (IPDT) [12] value (160 °C) and activation energies (0.0067 KJ mol^{-1}) confirm the good thermal stability of the prepared materials. DTG traces show one sharp endothermic peak at 45 °C, which indicates the evolution of water from the sample.

3.4. Effect of sorbate dose on Cr(VI) binding

The effect of sorbate dose on binding capacity was studied (Fig. 5) within the range 5–90 mg/l of Cr(VI), keeping other conditions (pH = 5.25, sorbent dose = 8 g/l, time = 1 h) fixed. It was observed that binding capacity of the prepared material was increased with the increase of Cr(VI) level. The materials probably undergo oxidation with the increase of hexavalent chromium. As a result, the sorbent binds chromate ion more as a counter anion. The capacities of the developed materials are found to be 28.45, 34.36 and 37.89 mg/g at 8, 27 and 55 °C, respectively. The values are higher compared to un-grafted polypyrrole (PPY) [29] and commercial polymers such as quaternized polyvinyl pyridine [30], XFS-4195 (DOW Chemical) and IRA-900 (Rohm & Haas) at similar condition. It is noteworthy to mention that Cr(VI) uptake capacity of pure silica is negligibly small.

The adsorption of chromium is favored at higher temperature meaning that the process is endothermic. The endothermic nature indicates the sorption process is entropially driven as evidence from Eq. (2) (Section 3.6).

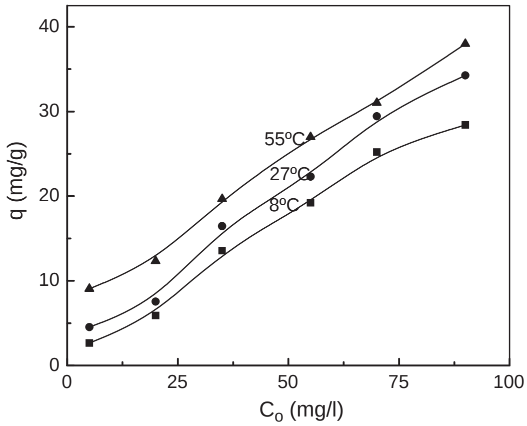


Fig. 5. Variation of adsorption capacity with sorbate dose [pH 5.25, sorbent dose = 8 g/l, time = 1 h].

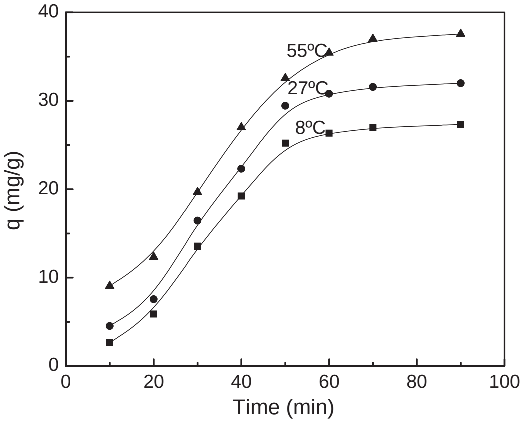


Fig. 6. Variation of Cr(VI) uptake capacity with time and temperature [pH 5.25, sorbent dose = 8 g/l, sorbate dose = 45 mg/l].

3.5. Effect of contact time: kinetic measurement

Fig. 6 shows that the amount of Cr(VI) adsorbed (q, mg/g) at different contact time. Almost 90% adsorption took place within 1 h, which indicates the optimum incubation time of the system. The time required to reach the equilibrium is 1.5 h. The initial rapid adsorption may be attributed to the availability of the positive charged surface of the sorbent (pH_{zpc} = 8.0). Similar type of observation was made at the temperatures 8, 27 and 55 °C. The contact time required for maximum Cr(VI) adsorption was found to be nearly 1.5 h. This equilibrium time is much less than commercially available exchangers [12].

3.6. Effect of pH on Cr(VI) binding

It was found (Fig. 7) that adsorption capacity of PPYNP-g-FSG was increased from pH 1 to 2 and then decreases gradually up to pH 8. At very low pH (<2), the Cr(VI) remains mainly as non-ionic form (H_2CrO_4), which accounts for its low adsorption. At pH 2–6 both

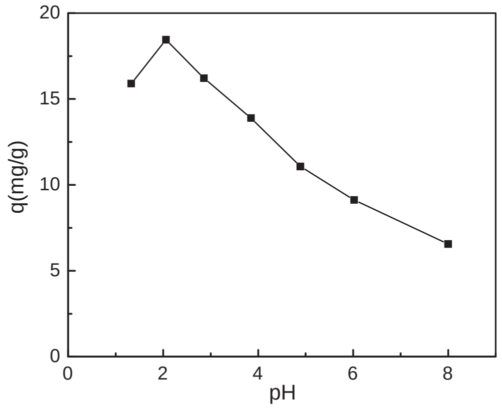


Fig. 7. Variation of adsorption capacity with pH [sorbent dose = 8 g/l, sorbate = 45 mg/l, temp. = 27 °C, time = 1 h].

Table 1
Elution of extracted Cr(VI).

Eluents	Concentration (M)	V_t (ml)[a]	Recovery (%)[b]
NaOH	0.10	25	97.56
NaCl	0.10	25	79.16
Na_2SO_4	0.10	25	89.22
Na_2NO_3	0.10	25	66.32
Na_3PO_4	0.10	25	47.25
$NaHCO_3$	0.10	25	39.33

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

the sorbate and sorbent exists as ionic species of the type $Cr_2O_7{}^{2-}$ and $PPYNPH^+$ (protonated grafted polymer). So the electrostatic interaction between sorbate and sorbent is mainly responsible for the adsorption of chromate onto PPYNP-g-FSG surface. High ion exchange capacity (1.78 meq Cl^-/g) favors the ion exchange mechanism (Eq. (1–2)). The appearance of chloride and disappearance of chromate ($Cr_2O_7{}^{2-}$) in the aqueous phase was tested by qualitative test [31]. The results are in line with the work of Saoudi et al. [3].

$$\text{PPYNP-g-FSG} + \text{HCl} = \text{PPYNPH}^+\text{Cl}^-\text{-g-FSG(atpH2–6)} \quad (1)$$

$$2\text{PPYNPH}^+\text{Cl}^-\text{-g-FSG(solid)} + \text{Cr}_2\text{O}_7{}^{2-}\text{(aq.)} = (\text{PPYNPH}^+)_2\text{Cr}_2\text{O}_7{}^{2-}\text{(solid)} + 2\text{Cl}^- \quad (2)$$

3.7. 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 grafted polymer were investigated. These experiments were performed at a constant pH (5.25), temperature (27 °C), sorbent dose (8 g/l), and time (1 h) with the solution containing 0.00018 moles of each metal ion. The selectivity [27] (S) of the grafted 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 0.2, 0.36, 0.29, 0.22 and 0.26, 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 the system selective towards chromate. Commercial anion exchangers are unable to remove chromate anion [13] selectively.

3.8. Elution of adsorbed Cr(VI)

The adsorbed chromate was eluted by NaCl, Na_2SO_4, $NaNO_3$, Na_3PO_4 and bicarbonate in a chromatographic column (Table 1). It was found that eluents having more than hundred times higher concentrations (compared to chromate) is required for effective elution. The table shows that sodium hydroxide is the most effective eluent.

4. Conclusion

Polypyrrole nanoparticle of desired shape (opal like) and size (100 nm diameter) has been synthesized through micelle technique. Polypyrrole nanoparticles grafted silanized silica gel (organic–inorganic hybrid material) with 6.59% grafting and high surface area (235 m^2/g) have been prepared successfully by 'grafting to' method. Dimethyl dichloro silane plays an effective role in coupling polypyrrole with silica gel through covalent linkage. Polypyrrole nanoparticles increase the surface area of the hybrid material more compared to its bulk form. The hybrid material is stable up to 100 °C and possesses high ion exchange capacity. The material was found to be a potential and selective binder for Cr(VI). It has high metal binding capacity (38 mg/g) even at very low level of Cr(VI) (90 mg/l) and the capacity increases with the further increase of chromium(VI) concentration. The observed capacity is higher compared to the many commercially available polymers. The adsorption–desorption of chromate ion occurs mainly through ion-exchange mechanism and the process may be controlled by pH switching. The developed material has significant chromium binding capacity even at pH greater than 7, which may be treated as its special quality.

Acknowledgements

The authors gratefully acknowledge the financial supports provided by UGC (F. No. 37-569/2009 (SR) dated 23.12.2009) and CSIR (No. 01/2392/10/EMR-II dated 7.6.10).

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