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Feasibility study of novel sorbent for chromium sequestration and enhanced immobilization

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ABSTRACT

The present solid phase sorption studied for the treatment of water containing mainly chromium by "In-house" synthesized specific amphoteric chelator have been evaluated w.r.t. basic parameters like concentration, time, and elution etc. High uptake values of the metal ions proves its selectivity, whereas negligible elution or high immobilization factor (0.97) confirm further decontamination of run-off water during natural calamities. This polymeric ligand exchanger displayed minimum and maximum level sorption of 41.2% and 99.6% at the feed concentration of 50 and 500 ppm respectively.

Keywords: Decontamination; Ligand; Exchanger; Chromium; Immobilization; Elution

1. Introduction

Concerns about the hazardous effects caused by the presence of heavy metals in aquatic environments in concentrations exceeding the permissible limit have induced the search for effective solutions to mitigate water pollution. Several processes have been developed among which the use of polymeric resins have shown significant potential. Heavy metals are defined as those metals having a density greater than 5 g/cc. Toxic metals are those which even in extremely minute amounts can interfere with the life processes of the human body. Almost all heavy metals are toxic. Elements of highest concern are As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Sn; the emissions of which are regulated even in waste incinerators within European countries.

In this case, main concern is about chromium (Cr). Waste streams from chrome plating industries and processing units, steel industries, tanneries, textile industry (mordants), pigment and electronic device manufacturing facilities contain significant amounts of chromium. Cr (VI) is highly poisonous, extremely mobile in groundwater at wide ranges of pH and has been identified as a potent carcinogenic. Cr (VI) has been reported to be responsible for lung cancer, chrome ulcer, perforation of nasal septum, brain and kidney damage. Hence, it is essential to decontaminate chromium containing effluent, at aquifer's or from industrial effluent. The WHO permissible limits for Chromium in drinking water are 50 ppb. The potentiality of chromium toxicity w.r.t. our body is main concern for selection of sorbent for treatment of chromium along with other cations by the same resin.

Chromium occurs in the environment primarily in two valence states, trivalent chromium (Cr III) and hexavalent

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chromium (Cr VI). The metal chromium is used mainly for making steel and other alloys. Chromium compounds, in either the chromium (III) or chromium (VI) forms, are used for chrome plating, the manufacture of dyes and pigments, leather and wood preservation, and treatment of cooling tower water. Exposure may occur from natural or industrial sources of chromium. Chromium (III) is much less toxic than chromium (VI). Acute animal tests have shown chromium (VI) to have extreme toxicity from inhalation and oral exposure. The respiratory tract is the major target organ for chromium (VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure. Human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in an increased risk of lung cancer. Animal studies have shown chromium (VI) to cause lung tumors via inhalation exposure.

The main reason why Cr (VI) is so toxic is that one of the reduction products of Cr (VI) is Cr (V). In human body, the acidity and action of enzymes on Cr (VI) will promote the formation in small quantities of Cr (V). Chrome (V) is a known carcinogen and will lodge in any tissue to form cancerous growths. The size of this is normally too large to be adopted by a tissue and hence is likely to lodge is in some of the fine capillaries in the kidneys, intestines or lungs. Genotoxicity of chromium (V) has also been studied wherein Cr (VI) reduces to Cr(V) and it binds to DNA thus bring mutations.

Chromium (III) is an essential element in humans, with a daily intake of 50–200 μg/d recommended for adults. The body can detoxify some amount of chromium (VI) to chromium (III). Cr (III) is a very stable oxidation state for chromium and in this state, the chrome is labile and kinetically very slow to react or form complexes. It is not a strong oxidiser and the human's natural body acidity is enough for the chrome to keep to this Cr (III) state.

A variety of techniques are available for water treatments of which chemical precipitation, electrolysis, membrane processes, reverse osmosis, sorption and ion exchange techniques are worth mentioning. In chemical precipitation technique, other chemicals are required and significant amount of sludge is generated. Electrolysis and membrane processes require high capital and maintenance. Low cost bio-sorbent can be used but without effective immobilization under adverse condition. Different types of bio-sorbents have been tried [5–13] for the removal of chromium from waste effluent on soya cake, Tamarindus indica seeds, Lentinus sajor-caju, activated cow dung carbon, powder of green coconut shell, rice bran, sugar beet pulp, red pine sawdust, Untreated coffee husks, eucalyptus bark, Grainless modified biosorbent like agricultural by-products modified with dimethyloldihydroxylethylene etc. Beside these, chitosan biopolymer, Trialkylamine impregnated macroporous polymeric sorbent, Dowex M 4195 chelating resin, novel regenerable *p-tert*-butylcalix[8]areneoctamide, impregnated Amberlite resin, amino-modified polyacrylamide-grafted coconut coir pith, *N*-methylimidazolium functionalized strongly basic anion exchange resins, Amberlite XAD-7 resin impregnated with Aliquat 336, D301, D314 and D354 anion-exchange resins, Lewatit-anion exchange resins, quaternary amine anion exchange resins [14–19] are also widely used. Therefore, selective sorption can be performed by organic materials preferably embedded in macromolecular chain. Rosângela et al. found that aniline moiety. Poly(ethylenimine), chitosan coated perlite beads etc. respectively were covalently bonded to the matrix and treated for chromium containing effluents.

In this study, oxodonar attached to nitrogen and one to carbon within the same ligand acting as caution exchanger and protonated amines of amide group act as anion exchanger (Sangita Pal et al. 2006, 2010) in polyacrylamidehydroxamate (PHOA) sorbent embedded as a hydrophilic exchanger or chelate moiety with aliphatic backbone containing matrix for parametric study for the decontamination/removal of chromium from industrial run-off.

2. Experimental

2.1. Materials and preparation

Materials such as acrylamide, *N*,*N*′–methylene-*bis*-acrylamide, hydroxylamine hydrochloride, methanol, acetone, sodium hydroxide were procured from different sources. Preparation of the polyacryamide-hydroxamic acid based sorbent has been described. The reaction outlines are (Fig. 1) as follows:

1. *Polymerisation*—Acrylamide to polyacrylamide (PAAm)
2. *Conversion*—Polyacrylamide to polyhydroxamic acid (PHOA)

2.1.1. Preparation of PAAM

Synthesis of crosslinked polyacrylamide (PAAM). Crosslinked polyacrylamides were prepared by polymerizing a solution of acrylamide and *N*,N_0-methylenebisacrylamide in a different ratio with a fixed amount of initiator at 60°C. Gel formed after 20 min of reaction. After achieving room temperature, acetone was poured in the gel for phase inversion. After 24 h, the gel was

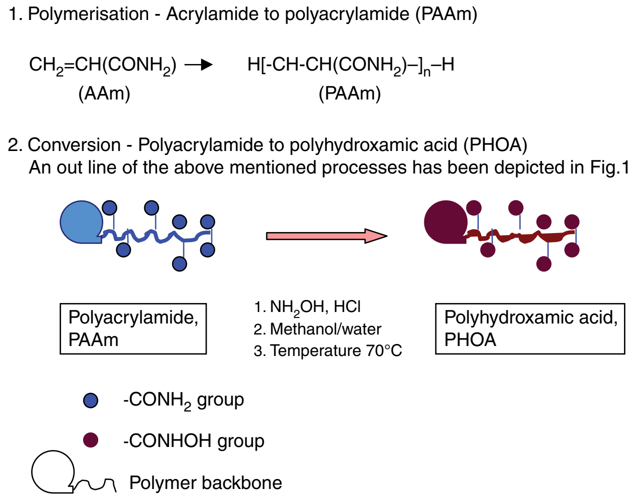

Fig. 1. Conversion of polyacrylamide to polyhydroxamic acid.

crumpled and washed with water. After drying, it was crushed to reduce the particle size.

2.1.2. Conversion to PHOA

Conversion of PAAM to polyacrylhydroxamic acid chelating resin (PHOA). A solution of a calculated amount of hydroxylamine hydrochloride and sodium hydroxide was added to a suspension of dry crosslinked PAAM. The resulting mixture was stirred for 5 min at room temperature. The reaction was continued for 6 h at 70°C. The resulting polymer was washed with water, thoroughly.

An out line of the above mentioned processes has been depicted in Fig. 1.

The uptake performance has been evaluated by equilibrating a known weight of dry sorbent with feed and calculated according to the mass balance on the metal ions as

$$q = \left[\left(C_0 - C_e \right) V \right] / m \tag{1}$$

Here, q is the amount of metal ions sorbed on to the dry sorbent (µg/g), C_0 and C_e are the concentrations of the metal ions in the initial solutions and in the aqueous phase at equilibrium, respectively (µg/l); V is the volume of the aqueous phase and m is the mass of the dry sorbent used (g).

2.2. Distribution coefficient

The sorption equilibrium expressed by the distribution coefficient K_d (ml/g) is given by

$$K_d = \left[\left(C_0 - C_e \right) V \right] / C_e m \tag{2}$$

where, C_0 and C_e are the concentrations of element (µg/ml) initially (t = 0) and at equilibrium (t = 24 h), in solution. V is the volume of the liquid phase in ml and m is the weight of the sorbent (polymer) in gram.

2.3. Elution

The metal ion loaded sorbent was placed in the elution medium of certain volume and stirred for 3 h at room temperature. For all the experiments around 0.5 g dried sorbent was taken, in 50 ml solution, kept for 1 d and extracted with 15ml 0.1 (N) HCl.

Extraction procedure—The metal ion loaded sorbent was placed in the elution medium of certain volume and stirred for 3 h at room temperature.

$$\text{Elution ratio} = \frac{\text{Amount of metal ion eluted to the elution medium} \times 100}{\text{Amount of metal ions sorbed onto the elution medium}} \tag{3}$$

2.4. Sample analysis

Samples for calibration were prepared in the laboratory in the ppm range using stoichiometric solutions. No specific preparation of samples is required before testing the solutions were directly introduced into AAS.

2.4.1. Sample preparation and analysis

Preparation of samples:

A salt of potassium dichromate of Merck was used as obtained without purification to prepare Cr(VI) ion solution.

Analysis:

Analysis of the samples of chromium ions (Cr(VI)) was carried out with flame ionized Chemito AA 203 Atomic Absorption Spectrophotometer (AAS).

Various parameters of the instrument for analysis:

Parameter	For chromium
Current	5.0 mA
Wavelength	357.9 nm
Working range (ppm)	2–8 ppm
PMT	409.5
Air acetylene ratio	1.6
Slit width	0.2 nm

3. Results and discussion

3.1. Effect of initial concentration on chromium uptake

Concentration of a solution always has a profound effect on uptake (Eq. 1) of any sorbent due to the basic reason of occupancy of the available functional moiety onto which sorption followed by chelation affect. Uptake of $Cr_2O_7^{2-}$ ions with varying feed concentration (ppm), viz., 50, 100, 200, 300, 400 and 500 increased sharply as shown in Fig. 2 and the trend indicates a gradual approach towards saturation at higher concentration. A maximum amount of 26.48 mg of chromium/g of sorbent was observed for 500 ppm feed solution. The tendency towards saturation at high concentration is attributed to the huge number of dichromate ions compared to the fixed number of sorption sites.

3.2. Distribution co-efficient

Distribution co-efficient and its trend reflect the saturation tendency of the sorbent more prominently compared to uptake curve. A trade-off relationship results from calculated distribution co-efficient (Eq. 2) values with the same experiment and uptake studies mentioned above. Distribution co-efficient (K_d) showed (Fig. 3) that K_d (ml/g) falls sharply from 1,000 to 200 with increase of chromium concentration in feed solution and after that reaches almost a steady state value of about 100 for higher concentration (300–500) ppm.

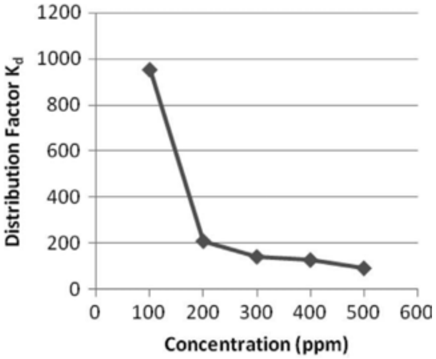

Fig. 3. Effect on distribution coefficient with variation in concentration of initial feed solution of chromium.

3.3. Kinetics study of chromium sequestration

According to the nature of sorbent when it is in contact with ions, the kinetic effect become quite prominent specially, for hydrophilic sorbent. The imbibing power of water into the stack of dry sorbent encourages it to swell and thus facilitated the diffusion of metal ions through the pores. Fig. 4 reflected the same phenomenon in uptake of $Cr_2O_7^{2}$ions with time for 100 ppm solution. Sorption of $Cr_2O_7^{2-}$ ions are comparatively slow. The curve shows 60% uptake within 1 h and 72% in 4 h is similar to the parametric study [29].

In this regard, the experimental data such as effect of kinetics can be illustrated. Even, the time dependent chromium uptake data can be used to predict the order of kinetics. In order to investigate the adsorption processes of metal ions on the sorbent, the pseudo-first order and pseudo second order kinetic models were experimented.

Pseudo first-order equation

$$\ln\left(q_o - q_t\right) = \ln q_o - k_1 t \qquad (4)$$

where q_e is the adsorption capacity in equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at time t (mg/g), k_1 is the pseudo first-order rate constant (min^{-1}), t is the time of contact between the adsorbent and adsorbate (min). Pseudo second-order equation:

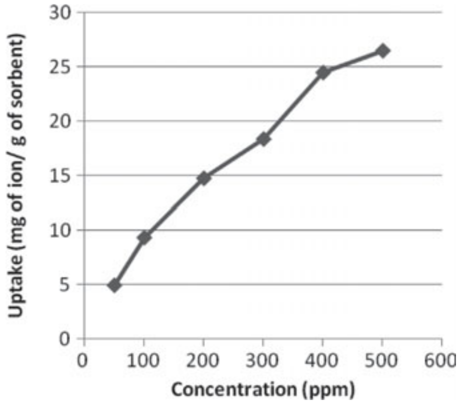

Fig. 2. Effect of chromium concentration on uptake of the sorbent.

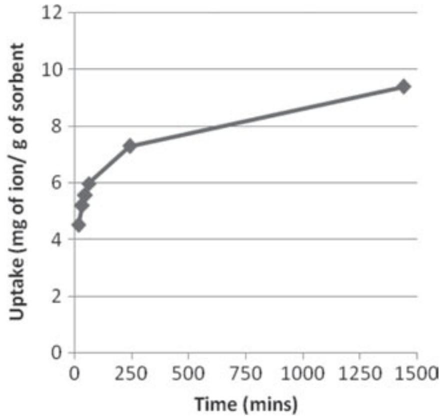

Fig. 4. Uptake (mg/g of sorbent) as a function of time (minutes) for $Cr_2O_7^{2-}$ ions.

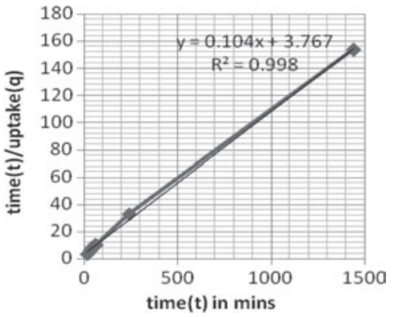

Fig. 5. Second order equation for uptake of $Cr_2O_7^{2-}$ ions.

$$t/q_e = t/q_o + 1/\left(k_2 q_o^2\right) \qquad (5)$$

where k_2 is the pseudo second-order rate constant (g/mg min).

Fig. 5 shows that the uptake of $Cr_2O_7^{2-}$ ions with time is well represented by pseudo second-order kinetics. The numerical inverse of slope of the line indicates that the max uptake is 9.615 mg/g of sorbent for the given 100 ppm solution and value of k_2 is 0.00287 g/mg min. However, the correlation co-efficient was much more closer to 1 for second order equation compared to first order rate equation.

3.4. Effect of pH

Batch uptake of chromium by sorbent was studied by changing various parameters, e.g., concentration, time, mesh size, pH changes etc. and pH variation indicated.

In the above data the experiments have been conducted by changing pH regarding $Cr_2O_7^{2-}$ ions of 100 ppm concentration. The variation in pH from 4.5 to 6.5 indicated very low filtrate concentration due to high uptake of sorbent in the acidic medium supports the schematic diagram in Fig. 6 The above data also reflected an indication on immobilization effect. However, specific complex formation of chromium with ligand is being studied by EPR (electro parameter resonance) spectroscopy which is indicating the presence of chromium and its valance state.

Schematic drawing regarding chemical description and explanation has been shown in Fig. 6 below.

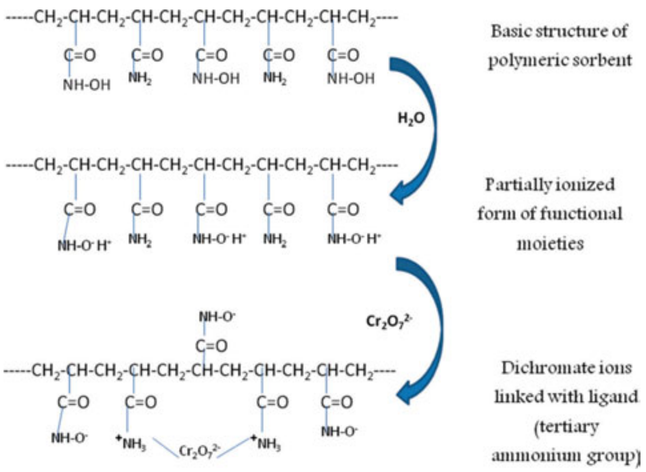

Fig. 6. A probable sortion of $Cr_2O_7^{2-}$ with the $+NH_3$ form of the ligand.

Table 1
Effect of pH variation in feed solution

pH Variation (initial feed concentration: 100ppm)				
pH	Filtrate concentration (ppm)	Filtrate volume (ml)	Leach concentration	Leach volume (ml)
4.5	8.00	36	3.39 ppm	19
6.5	9.82	35	5.64 ppm	23
8.5	32.8	36	1.17 ppm	22
13	76.6	37	BDL	17

Table 2
Effect of elution with feed concentration variation

Feed concentration (ppm)	Percentage elution	Immobilization factor (100-elution ratio)
50	3.22	96.78
100	2.76	97.24
200	2.86	97.14
300	2.48	97.52
400	2.72	97.28
500	2.8	97.20

3.5. Elution behavior

Sequestration or chelation is one of the prime aspect for immobilization of multivalent metal ions with polydentate conjoining ligand. Metal ion immobilisation of a resin is the act of limiting movement or making incapable of movement if the metal ions by trapping or rather chelating it with the functional groups of resin. For tratment of outlet effluent i.e., to inhibit percolation to ground level aquifer's it is always advisable to remove toxic-heavy metal much before. In this aspect, the experiment was carried out to study the elution behavior of the sorbent containing $Cr_2O_7^{2-}$ ions with 0.1 M HCl concentration of eluant. Analysis of the leached filtrate indicated that substantial amount of the chromium ions remain immobilized when experimented for concentration varying from 50 to 500 ppm. Table 2 indicates immobilization of 97% chromium while only 3% of the ions were leached out.

4. Conclusions

All uptake studies were conducted in water and therefore can be extended to water bodies that contaminated with chromium of different concentration, pH etc. However, performance in soil was not considered. In water, the sorbent swells during which, the entangled polymer chains disentangled and gradually hydrated. Due to hydration hydroxamic acid group can dissociate and liberated proton converts the amide group to positively charged species. This positively charged moiety can attract chromate ions and get sorbed on the sorbent. Gradually, with time and increasing concentration of chromium more and more di-chromate ions linked with functional moiety of the protonated amines of amide group. The most aesthetic part of the resin is that it acts as amphoteric resin, therefore can take care of both cations and anions.

In this study, results showed that this novel sorbent has a great tendency to uptake chromium. It is useful for the treatment of chromium bearing effluent even from significantly high concentration. Experimental results indicated that the synthesized sorbent has a kinetic dependence on the sorption effect pertaining to chromium removal. This kinetic effect and subsequent pH changes reflects a new mechanism towards chromate affinity. Further elution study (Table 2) ensures high immobilization factor which reflects feasibility for the treatment of chromium containing waste or industrial run-off preferable for electroplating, tannery and battery industries and fulfills non-percolating character of chromate species under adverse acidic condition.

Symbols

q — amount of metal ions sorbed on to the dry sorbent (μg/g)
C_0 — concentrations of the metal ions in the initial solution (μg/l)
C_e — concentrations of the metal ions in the aqueous phase at equilibrium (μg/l)
V — volume of the aqueous phase
m — mass of the dry sorbent used (g)
K_d — distribution co-efficient (ml/g)

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