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# Composite sorbent for attrition minimization

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ABSTRACT

Attrition is erosion by friction, i.e., wearing down of particles by friction due to water. Powdery materials such as titanium dioxide ($TiO_2$), a well known sorbent, suffers from attrition loss during metal ion recovery, mainly during regeneration of $TiO_2$ for reuse. To minimize the inorganic sorbent ($TiO_2$) loss, inorganic–organic composite (hybrid) sorbent was prepared from a radical initiated solution polymerization of acrylamide and freshly prepared titanium dioxide. Uranium uptake has been compared with titanium dioxide (freshly prepared), $TiO_2$–polymer composite and virgin polymer. The potential of this composite sorbents for the uranium recovery was ascertained.

*Keywords:* Composite sorbent; Titanium dioxide ($TiO_2$); Polyacrylamide (PAAm); Attrition loss; Reusability desalination; Column treatment

## 1. Introduction

During sorption, $TiO_2$ attrition creates [1,2] several problems. It forms (i) very fine particles that lower the quality of treated water, (ii) introduce a new titanium based contamination [11], (iii) that further increase number of unit steps to purify and (iv) decreasing the cost effectiveness of the process. Attrition changes (v) the shape of the beads, (vi) causing an increase in pressure drop [12,13] across the bed of the resin [3–10] and (vii) deteriorate column properties. Softer beads with low degree of cross-linking are more susceptible to attrition but smoothen the access of active sorbent, whereas high cross-linking introduce degradation stability but may increase brittleness of the resin. Therefore, an optimization in resistivity towards osmotic shock by balancing structural features preferably in column operation is essential for attrition resistivity. Inorganic potential sorbents, especially titanium dioxide [14,15], zinc oxides, etc. are well known for their use in removal and recovery of metal ions from contaminated substances, but suffer from limitations of sorption rate and insufficient mechanical stability compared to modern organic polymeric sorbents. Our purpose is to improve the re-usability of inorganic sorbent by reducing attrition loss. One method to approach such problem is by enveloping core oxide with polymer matrix in a core–shell structure. Many papers reported the use of freshly prepared titanium dioxide for its very high selectivity. Enveloped hydrophilic polymer appends the property of (i) rapid loading kinetics (in order to minimize contact time and to achieve maximum uptake), (ii) higher reusability, (iii) low cost (due to inexpensive polymer and insignificant loss of sorbent), and (iv) rapid elution kinetics ensures process efficiency.

In this study, preparation methodology [4,16–18] of polymeric coating and its potentiality w.r.t. attrition loss has been discussed. However, recovery of spiked uranium from seawater has been carried out in both batch and column condition to realize the importance of negligible attrition loss for uranium uptake of the sorbents from the brine.

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## 2. Preparation methodology

Hydrous titanium oxide is one of the earliest adsorbent explored [19–21] for uranium extraction from seawater. Neutralization (by alkali) methodology for preparation titanium dioxide was adopted in the present study.

From the literature survey it is confirmed that freshly prepared titanium hydroxide or oxide based sorbents are good for sorbing heavy metals. To prepare fresh sorbent by an easy and instantaneous or less time consuming method, titanium-tetrachloride ($TiCl_4$) was used as precursor for the preparation of titanium based (freshly prepared) sorbent. $TiCl_4$ is highly hydroscopic stuff. It reacts with water to form $Ti(OH)_x$, $TiO_2$ and HCl. While pouring $TiCl_4$ in water, the system was kept in an ice bath so that the vapors of $TiCl_4$ could condense and react properly. The reaction was performed in fuming hood and glass delivery tube was used for transferring it. The acid produced during reaction was neutralized with water to get maximum precipitation and converted to irreversible reaction where, alkali (NaOH solution) eats away the chloride produced during hydrolysis of $TiCl_4$.

After precipitation it was poured into a homogenized mixture of acrylamide and its cross-linker in (weight) the ratio of 98:2. The mixing was performed at 150 rpm at 30°C. In this well stirred solution freshly prepared precipitate of titanium dioxide was poured in the weight ratio of 3:1. The solution temperature was increased to 60°C and water soluble initiator (of 0.01% concentration) was added. Within 15 min the temperature reached 70°C and the whole mass converted into a gel. Total mixture was cooled down and crumbled to reduce the size around 25 mesh sizes. The gel was washed dried and stored.

A schematic feature (Fig. 1) has been given to understand the process further.

### 2.1. Purification of composite

After radical polymerization (as described above), the product was thoroughly washed with organic solvent (co-solvent of water and acetone in 9:1 volume ratio, and 100 ml co-solvent used for 25 g of resin) to remove un-reacted monomers, and again washed with water and dried. The prepared composite sorbent was white in colour and irregular shapes (Fig. 2). The initial weight and weight after polymerization implies the polymer matrix attachment in the composite. Titanium content in the hybrid was 22%. The kinetics of sorption on the absorbers is very fast, because the finely divided particles of the active component are embedded into macro-pores of the binding matrix.

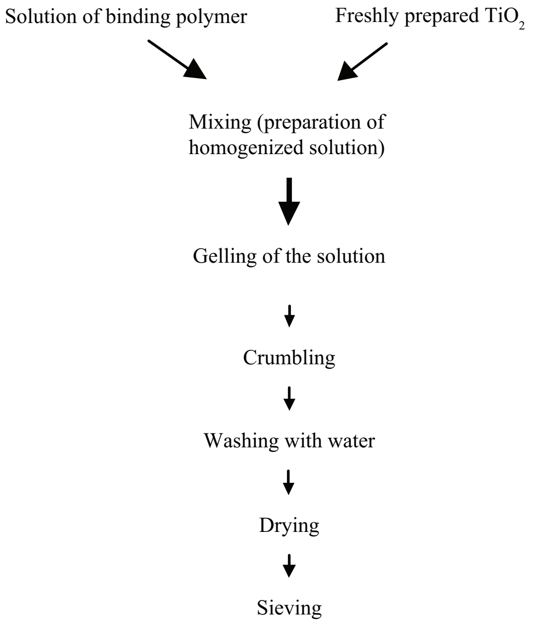

Fig. 1. A schematic flow sheet of preparation methodology for composite sorbent.

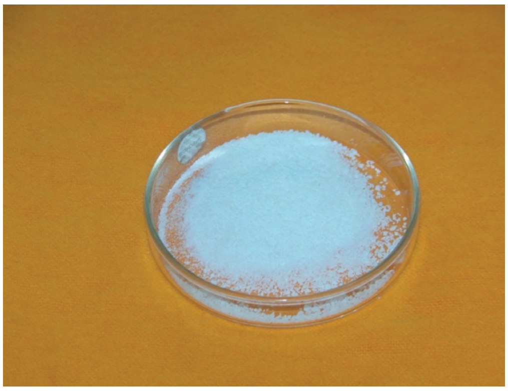

Fig. 2. Irregular beads of composite sorbent.

## 3. Characterization and experimentation

### 3.1. Composite sorbent characterization

FT-IR study has been carried out by pelletizing individual materials like (i) $TiO_2$, (ii) polyacryamide (PAAm) and (iii) composite sorbent with potassium bromide. Besides these, a resistance in swelling kinetics (Fig. 3) of $TiO_2$–PAAm composite sorbent (swelling ratio 5 achieved after 120 s) compared to virgin PAAm (swelling ratio 5 within 10 s) determined by microscopic views.

### 3.2. Sorption procedure

The uptake performance has been evaluated by equilibrating a known weight of dry sorbent in contact

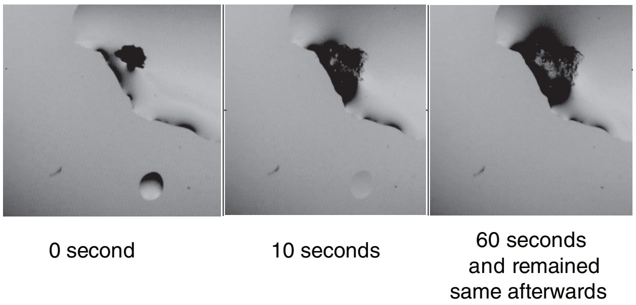
0 second
10 seconds
60 seconds and remained same afterwards

Fig. 3. A microscopic view on the kinetic swelling effect of composite sorbent in aquatic medium.

with particular concentration. The uptake of metal ions by the sorbent was calculated according to the mass balance on the metal ions expressed as

$$q = [(C_0 - C_e)V]/m$$

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 solution and in the aqueous phase at equilibrium, respectively (µg/ml); $V$ is the volume of the aqueous phase (ml) and $m$ is the mass of the dry sorbent used (g).

### 3.3. Extraction procedure

The metal ion loaded sorbent was placed in the elution medium (alkaline solution of NaOH, pH 10) of certain volume and stirred for 3 h at room temperature.

### 3.4. Uranium sorption studies

For batch reaction study uranyl nitrate was spiked in seawater to prepare a concentration of 12 ppm. The aliquot was used to study the extent of uranium uptake with virgin polyacrylamide, freshly prepared $TiO_2$ and $TiO_2$–polymer composite. In a conical, 4.5 g sorbent in 100 ml solution was equilibrated for 24 h and after that filtrate was analyzed. One column has been prepared having 1 in. I.D. and filled with 9 g of composite sorbent. The feed solution was passed through the column at 2 ml/min flow rate. The sorbent after a specified period of contact, were eluted with 1 N NaOH solution. The same sorbent washed with water and dried under IR lamp, and reused in the same way as explained for the composite sorbent only. The estimation of uranium in the original feed sample (i.e., before the sorption experiment), the filtrate and eluent were carried out by ICP–MS analyzer.

## 4. Results and discussion

Freshly prepared inorganic clays are always more interactive [19] because of the presence of opening and accessible layers of crystallites. The main purpose of the study is to reduce/minimize the attrition loss. A plausible mechanism and schematic drawing has been pictured in Fig. 4 to understand the effect of forces acting on the freshly prepared layers. Initially loose powder may form aggregate and even further break into more numbers of particle, but at the cost of energy during operation, as well as titanium concentration may increase in the outlet effluent. This incidence increases desorption probability of the sorbed materials. Even during column operation different forces especially longitudinal stress and torsional stress leads to further mobilization of loose layers of inorganic layers and exists in the product outlet. The separation of this titanium dioxide from product effluent again increases number of unit operations/separations. One more practical problem (as depicted in Fig. 4) is pressure drop and chocking of porous sintered disk during column study. If this freshly prepared structures are intact in hydrophilic binder as shown in Fig. 5, then polymer chains helps in the expansion of the distance between the clay galleries thus facilitates diffusion of metal ions and implies a

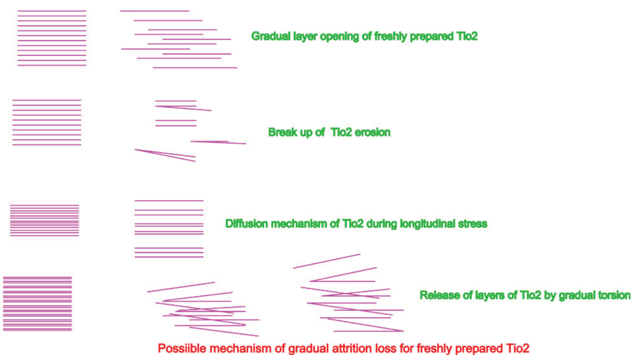

Fig. 4. Plausible mechanism of attrition loss of freshly prepared $TiO_2$.

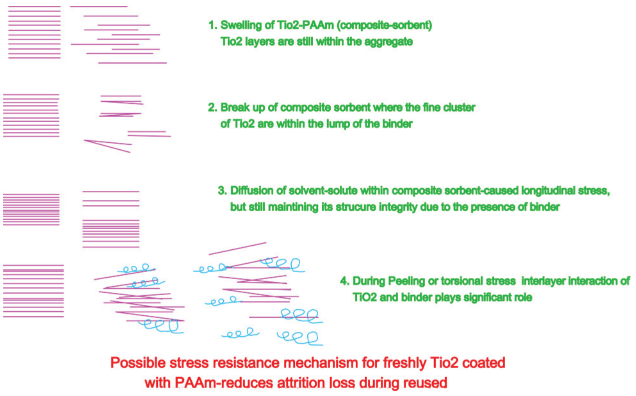

Fig. 5. Plausible mechanism of attrition resistance of composite sorbent.

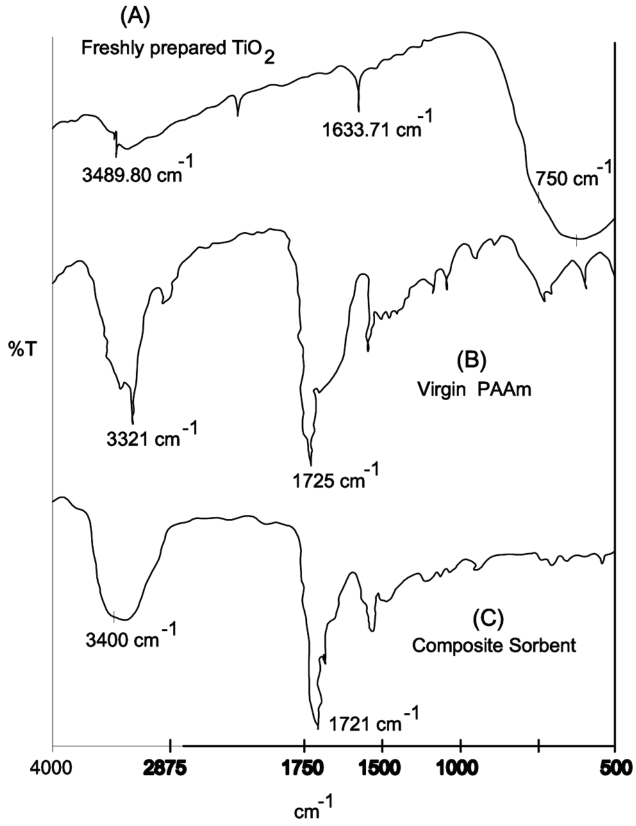

Fig. 6. FT-IR spectra of (a) Tio2 - Freshly prepared (b) polyacrylamide (virgin PAAm) (c) composite sorbent.

better interaction and accommodation of metal ions within the opened layer. The FT-IR spectrum (Fig. 6) of freshly prepared $TiO_2$ precipitate is exhibited. The strong and wide peak at 3439.08 $cm^{-1}$ and peak at 1633.71 $cm^{-1}$ are due to the hydroxyl groups of Ti–OH with which water molecules are bound by weak hydrogen bonds and Ti–O stretching at 700 $cm^{-1}$. In PAAm contains an N–H band at 3321 $cm^{-1}$ which showed a hypershift at 3400 $cm^{-1}$, indicating interaction of titanium complex with amide N–H groups. As, there is virtually no corresponding change in the carbonyl region (at 1725 $cm^{-1}$ present also in the virgin polymer), we conclude that this is a result of hydrogen bonding between the N–H groups in the polymer and Ti–OH groups in the inorganic domains. All these features expected to contribute in availability of sorbent matrix to the sorbate (Fig. 7), prevents high attrition loss and increase reusability.

### 4.1. Calculations and explanations of the design parameters

For all of batch experiment previously carried out, the dose rate of the resin at 1 g of resin/100 ml of feed effluent was optimized. Based on this observation 1 g of inorganic freshly prepared sorbent is expected to be in a fixed amount of composite sorbent sorbent. The calculation is as follows: [4.5 g of composite sorbent and 22% titanium present (4.5 × 0.22 = 0.999 g or approximately 1 g)]. We have taken 24 h to equilibrate the sorbent with inlet effluent during batch studies.

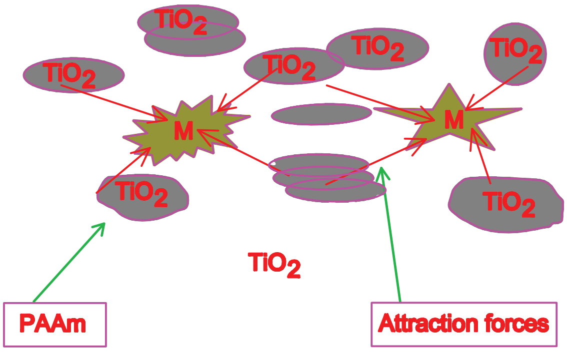

Fig. 7. Diagram depicting the trapped metal ions within the composite sorbent.

Column studies were also performed in the same way i.e. by putting 4.5 g resin in column and checked the data after passing different volume of effluent, there we have seen due to less bed volume packing was not proper and leaking of effluent (uranium) was taking place and producing erroneous result. Then the sorbent amount was increased to twice and the leakage was eliminated. Then the flow rate (2 ml/min) with time (16 h 40 min) was optimized and uranium uptake values were found accordingly. (2 ml/min × 60 min = 120 ml/h, at this rate 2000 ml will be passed taking 16 h and 40 min approximately 17 h.)

The theoretical concept has proved in desirable attributes during experimentation (Table 1). In the batch experiments hybrid composite has been tried with brine solution with spiked uranium to prepare 12 ppm solution and contacted with dose rate of 4.5 g dry sorbent (1 g of $TiO_2$)/100 ml spiked solution. Virgin PAAm does not contribute (Table 1) to the uptake of metal ions (2.3 µg/g of dry PAAm). When maintained the similar condition with composite sorbent it reflected an uptake of 31.45 µg/g of dry hybrid resin, compared to the virgin freshly prepared $TiO_2$, which is 34.02 µg/g of resin. Initial results of batch operation for uranium uptake with this composite are encouraging and further encourage us for further study in column mode.

During column study, 9 g dry composite sorbent was taken in 1 in. I.D glass column. In each cycle 2 l of effluent was passed at a flow rate of 2 ml/min in the 1st cycle uranium uptake values are substantially high, e.g., which is 31.45 µg/g of dry sorbent, for the 2nd cycle 28.12 µg/g of dry sorbent, whereas in 8th cycle the value came down to 15.48 µg/g of dry resin. Table 2 showed that, for composite sorbent the titanium loss (from 1.98 g in the 1st cycle to 1.55 g in the 8th cycle) was not so

Table 1
Initial results of uranium uptake of sorbents

| Sl. no. | Parameters studied | Values | % RSD |
|---|---|---|---|
| 1 | Conc. of uranium in desalination plant brine (μg/ml) | 12 | 3.66 |
| 2 | Sorption of U (μg/g) with virgin PAAm | 2.3 | 4.12 |
| 3 | Uptake of U (μg/g) with freshly prepared/virgin $TiO_2$ | 34.02 | 3.87 |
| 4 | Uranium uptake (μg/g) with equivalent amount ($TiO_2$ present in composite) | 31.45 | 4.58 |

*Standard deviation calculation*

| Inst. values | Mean value | Variance | Variance$^2$ | Average of variance square | Sqrt of variance$^2$ | % RSD |
|---|---|---|---|---|---|---|
| 11.65 | 11.975 Approx. | 0.375 | 0.105625 | 0.1925 | 0.4387 | 3.66 |
| 11.9 | 12 | 0.075 | 0.005625 | | | |
| 12.2 | | −0.225 | 0.050625 | | | |
| 12.15 | | −0.175 | 0.030625 | | | |

Table 2
The gravimetric loss and uranium uptake encountered during column experiments

| No. of Cycles | Uranium uptake (μg/g) $TiO_2$–PAAm composite | Weight of Ti (g) in $TiO_2$–PAAm in hybrid/composite (after use in the respective cycle) | Weight (g) of virgin/freshly prepared $TiO_2$ (without binder) |
|---|---|---|---|
| 1st | 31.45 | 1.98 | 1.64 |
| 2nd | 28.12 | – | – |
| 3rd | 25.04 | – | – |
| 8th | 15.48 | 1.55 | 0.29 |

significant; whereas for uncoated $TiO_2$, titanium loss (from 1.64 g in the 1st cycle to 0.29 g in the 8th cycle) is substantial. The result indicates that attrition loss of titanium can be minimized by coating the freshly prepared slurry with the solvent friendly polymeric binder.

### *4.2. Economic assessment*

Economic assessment of the reduction of titanium lost can be considered based on some facts, e.g., (i) less number of ingredients, (ii) an easy preparation methodology, i.e., precipitation of inorganic components, (iii) homogeneous mixing of water based solution and temperature raised up to 70°C and then air cooling of the gel mass and normal crumbing/shredding of the soft mass to reduce the size and drying.

Already freshly preparation steps of $TiO_2$ are well established and therefore, composite sorbent cost is required to be considered. Cross-linked resin inhibited leaching of valuable sorbent and as an added advantage, composite polymer chains helps in the expansion of the distance between the clay galleries thus facilitates diffusion of metal ions and implies a better interaction and accommodation of metal ions within the opened layer. Table 2 implies that titanium loss will reduce drastically which is at least 10 times costlier compared to acrylamide, where cross-linked polyacrylamide loss is almost negligible, as well as main constituent material (acrylamide) is also cheap and cost effective compared to other [22–25] conversion related resin based valuable recovery process The whole process is also easy, no special equipment is required and less time consuming and can be performed without skilled laborer.

## 5. Conclusion

The main purpose of the study is to reduce/minimize the attrition loss of titanium dioxide by introducing a core shell structure for metal ions sorption. Obviously repeated uses of hybrid beads introduce weakening and eventual degradation in structure. The void space between cross-linked chains increases the porosity of the sorbent and is said to provide additional durability. The improved mechanical properties and attrition resistance of the sorbents described herein are attributed to the toughening of the crosslinked chain of the binder matrix. Due to this fact, costly $TiO_2$ sorbent may be available for reuse and not only this, the loose matrix i.e. without binder titanium was getting concentrated in the elute. The separation of eluted titanium dioxide from the product effluent again increases unit operations. Thus, the easiest remedy for all these processes is to bind the material ($TiO_2$) with hydrophilic cross-linked binder. In addition, simple and rapid preparation method shows practical utility, as well as easy to implement composite sorbent in column operation.

## Symbols

$TiCl_4$ — Titanium-tetrachloride
$TiO_2$ — Titanium dioxide

Inorganic–organic composite — $TiO_2$_PAAm (hybrid sorbent) polyacryl composite sorbent amide (PAAm)
$Q$ — The amount of metal ions sorbed on to the dry sorbent (µg/g)
$C_0$ and $C_e$ — Concentrations of the metal ions in the initial solution and in the aqueous phase at equilibrium, respectively (µg/ml)
$V$ — Volume of the aqueous phase (ml)
$m$ — Mass of the dry sorbent used (g)
NaOH — Sodium hydroxide
I.D. — Internal diameter
ICP-MS analyzer — Inductively coupled plasma mass spectroscopy analyser

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