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Synthesize of poly (acrylamide-co-itaconic/TiO$_2$) nanocomposite for Ce(III) sorption from monazite leachate

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Abstract:

In this study, Acrylamide (AAM), Itaconic acid (IA) and nano TiO$_2$ were copolymerized using gamma irradiation with $^{60}$Co $\gamma$-rays at a dose of 25 KGY to form a novel nanocomposite; Poly(acrylamide-co-Itaconic acid/TiO$_2$) (P(AAM-co-IA/TiO$_2$)) for Ce(III) sorption from monazite leachate. P(AAM-co-IA/TiO$_2$) nanocomposite is characterized by different physicochemical techniques. The optimum pH for the sorption process at 298 K is 6 and the equilibrium attained after 60 min. Different kinetics and isothermal models is applied. The monolayer adsorption capacity is 76.04 mgg$^{-1}$ at 298 K. The sorption reaction follows a pseudo - 2$^{nd}$ - order mechanism. The process is spontaneous and endothermic.

Keywords: Acrylamide; Itaconic acid; TiO$_2$; Sorption; Monazite; Cerium (III)

1. Introduction

In the recent years, rare earth elements (REEs) have had important applications in industry as aerospace, electronic information and atomic energy [1-2]. Cerium and its derivatives are used extensively in metal alloys, glass, adsorbent, catalysts, and biomedical applications [3]. Monazite, lanthanide, xenotime, bastnaesite, allanite, loparite and phosphate rocks are all rich in REEs [4]. Cerium (Ce) is the RE element with the highest concentration
in light RE ores, CeO$_2$ /∑REO in bastnaesite (REFCO$_3$) reaches 50 percent, while CeO$_2$ / ∑REO in monazite (REPO$_4$) reaches 45–50% [5].

Various techniques for separating different lanthanides from aqueous solutions have been developed and used, including chemical precipitation [6], ion exchange extraction [7], coagulation[8], flocculation [9], liquid – liquid extraction [10], solid – phase extraction [11], biosorption [12] and classical sorption on different sorbents.

Various soils [13], montmorillonite nanoclay [14], HKUST-1 framework [15] and chert rocks [16] were used as sorbents for Ce(III) from aqueous solutions. However, there is a still requirement for an efficient sorbent of low cost, selective, high sorption and desorption rates, better thermal stability and mechanical strength, easily regenerated which is the aim of this study.

Organic polymers as poly Acrylic acid, poly Malic acid, poly acrylamide and poly itaconic acid are well known for their uniformity and chemical stability. However, these materials have some drawbacks such as non-adequate mechanical strength and flexibility. Introduction of nano inorganic material as metal oxides to organic monomers to develop polymeric-inorganic nanocomposite greatly enhances its mechanical strength, toughness, glass transition temperature, optical and tensile strength, etc. [17, 18]. The adsorption capacity of single polymers has been improved by copolymerization process.

Our study aims to prepare a novel nanocomposite for Ce(III) sorption from monazite leachate. Poly (acrylamide-co-Itaconic/TiO$_2$) nanocomposite prepared using gamma irradiation with $^{60}$Co $\gamma$-rays at a dose of 25 Kgy. Characterization of P(AAM-co-IA/TiO$_2$) performed by using FT-IR, DTA-TGA, SEM, particle size analysis, TEM and pore size distribution. Optimization of the parameters affecting sorption process like; pH, contact time,
metal ion concentration and sorbent weight carried out. The mechanism of the sorption reaction is proposed by applying different kinetic models and isotherm models. Finally, the prepared nanocomposite used as sorbent with optimum parameters for Ce(III) from monazite leachate.

2. Experimental

2.1 Materials and procedure

2.1.1. Reagents

All of the reagents utilized in this study were analytical grade and were not purified further. Acrylamide (AM) was supplied by Fuchen Chemical Co., Ltd., Tianjin, China. Methylene bis-acrylamide (DAM) and itaconic acid (IA) was used as polymeric monomers (Merck, Germany). Cerium (III) chloride heptahydrate (CeCl$_3$·7H$_2$O) was purchased from Sigma Aldrich.

The nuclear materials authority in Cairo, Egypt, provides monazite concentrate (monazite content of 90%). Bidistilled water used for the composite's preparation, pH – normalization provided (HCl) and (NaOH). ADWIC (Egypt)

2.1.2. Sorbent manufactured

2.1.2.1. Synthesized of nano TiO$_2$

TiO$_2$ nanoparticles is synthesized by the sol-gel hydrolysis technique of titanium alkoxide [19]. The hydrolysed product gel is dried at 60°C/48hours and used for the nanocomposite preparation.

2.1.2.2. Synthesized of P(AAM-co-IA/TiO$_2$) nanocomposites
To synthesize the P(AAM-co-IA/TiO$_2$) nanocomposites, different molar ratios of AAM and IA were copolymerized with nano TiO$_2$ as shown in Table 1 in the presence of methylene bis acrylamide (DAM) as a cross-linker.

Acrylamide (AAM) is mixed with Itaconic acid (IA) and TiO$_2$ nanoparticles in the presence of methylene bis acrylamide (DAM) in 50 ml deoxygenated water. The mixture is stirred for 2 hours and ultrasonically treated for 10 min. The details of the monomer compositions taken are given in Table (1). The mixture was subjected to gamma irradiation dose from a $^{60}$Co unit at a dose 25 KGy. The materials were cut into small pieces and soaked in acetone for 2 hours to eradicate water and contaminants before being dried in a vacuum oven at 333K for 24 hours and sieved to size (< 300µm).

2.1.3. Instruments

The morphology of the particles investigated by scanning electron microscope combined with energy-dispersive X-ray spectroscopy and electron backscatter diffraction (SEM, Philips XL 30 ESEM (25-30 keV accelerating voltage, 1-2 mm beam diameter and 60-120 seconds counting time). The existence functional groups achieved by Fourier transform infrared spectra (FT-IR) (KBr pellet technique on a Perkin Elmer 1600 FTIR Spectrophotometer in wave number range 600-4000 cm$^{-1}$). The thermal stability of the composite determined by DTA-TGA analyses (Shimadzu DT- 60, Japan). The crystalline phase structure assigned by (XRD) (Philips XPERT multipurpose X-ray diffractometer with copper emission lines). The concentration of REEs solutions is determined by Inductive Coupled Plasma Optical Emission Spectrometer type (Prodig Axial high dispersion ICP-OES model, USA and the...
concentration of Ce(III) is measured by an atomic absorption spectrophotometer (Buck Scientific, VGP 210).

2.2. Sorption studies

Sorption of Ce(III) onto the highest sorption efficiency C6P(AAM-co-IA/TiO₂) nanocomposite studied. The optimum conditions for the sorption process maintained by variation of the reaction parameters. i.e. pH (2-7), contact time (15-120 minutes), initial concentration (50-500 mgL⁻¹) and sorbent weight (m). (0.05) g of the sorbent contacted with 20 mL of the sorbate solution and after sorption time; samples were filtered and thus separated from the solution.

The Sorption efficiency of Ce(III) ions at each interval of time is given by equation (1):

\[
\text{Sorption efficiency(\%)} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100
\]  

(1)

sorbed amount q (mgg⁻¹) is calculated using equation (2):

\[
q = \left( C_0 - C_e \right) \frac{V}{m}
\]  

(2)

Where \(C_o\), \(C_f\) and \(C_e\) is the initial, final and equilibrium concentrations of the Ce(III) ions, respectively. m is the mass of the C6P(AAM-co-IA/TiO₂) (g) and V volume of solution (L).

2.3. Kinetic modelling:

Pseudo 1st order, pseudo 2nd order and Elovich model are applied through this work to arrive to a proposal for the mechanism of the sorption reaction.

The pseudo 1st order equation is given by equation (3) [20]:

\[
\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t
\]  

(3)

Where \(q_e\) and \(q_t\) are the sorbed amounts of Ce(III) ions; (mgg⁻¹) at equilibrium time and at any time t, respectively; \(k_1\) (min⁻¹) is the pesudo 1st rate constant.
The pseudo 2\textsuperscript{nd} order is described by the equation (4) [21]:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

(4)

Where \( k_2 \) (gmg\textsuperscript{-1} min\textsuperscript{-1}) is the pseudo 2\textsuperscript{nd} order rate constant.

The surface coverage and activation energy are indicated in Elovich equation (5)[22]

\[
q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t
\]  

(5)

Where the Elovich constants are \( \alpha \) and \( \beta \). \( \alpha \) (mgg\textsuperscript{-1} min\textsuperscript{-1}) is the rate of chemisorptions at zero coverage, whereas \( \beta \) (gmg\textsuperscript{-1}) is the extent of surface coverage and chemisorption activation energy.

2.4. Isotherm Modelling

Langmuir [23], Freundlich [24] and Temkin isotherm [25] are applied through this work

Langmuir isothermes model applied by equation (6)

\[
\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \left( \frac{1}{C_e} \right)
\]  

(6)

Where \( Q \) is the monolayer sorption capacity (mgg\textsuperscript{-1}), \( b \) sorption free energy constant (b \( \alpha \) e\textsuperscript{-}\( \Delta G/RT \)) and \( C_e \) is the metal ion concentration at equilibrium.

The free energy, \( \Delta G^0 \), was used to quantify the spontaneity of the sorption process. Negative \( \Delta G^0 \) values indicate that the sorption process is occurring spontaneously. Using the following Eq. (7), \( \Delta G^0 \), may be computed.

\[
\Delta G^0 = -RT \ln K_c
\]  

(7)
Where, $R$ represents the general gas constant (8.314 JK\(^{-1}\)mol\(^{-1}\)), $T$ represents the absolute temperature (K), and $K_c$ represents the sorption equilibrium constant. The product of the Langmuir isotherm constant $Q$ and $b$ can be used to derive $K_c$ values. The following equation was used to derive the values of other thermodynamic parameters such as $\Delta H^0$ and $\Delta S^0$:

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$ (8)

The linear Eq.(9) represents Freundlich model

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$ (9)

Where, $K_f$ denotes for Freundlich constants, and $n$ denotes for sorption capacity and intensity.

Temkin considers that the sorption heat varies linearly with the degree of overlap. The following is the model: Eq. (10):

$$q_e = \frac{RT}{b_T} \ln (A_T C_e)$$ (10)

where $A_T$ is the maximal binding energy (Lmol\(^{-1}\)), $b_T$ is the sorption heat, $R$ is the universal gas constant (8.314 JK\(^{-1}\)mol\(^{-1}\)), and $T$ is the absolute temperature (K).

2.5. Desorption studies

The cost of the sorbent, its sorption efficiency, and its desorption ability are used to determine the success of the sorption process. The desorption behaviour of C6P(AAM-co-IA/TiO\(_2\)) was investigated using three different concentrations of HCl, HNO\(_3\), and acetic acid; 0.002molL\(^{-1}\), 0.2molL\(^{-1}\), and 2 molL\(^{-1}\) at 298K for 24 hours. The mixture was filtered to separate the solid from the liquid phase, and the concentration of Ce(III) was then measured by atomic absorption spectrophotometer. The desorption percent percentage was calculated using equation (11):
Desorption (%) = \frac{C_{aq}}{C_s} \times 100 \quad (11)

Where \( C_{aq} \) is the concentration of Ce(III) in the aqueous phase and \( C_s \) is the concentration of Ce(III) in the solid-phase.

3. Result and discussion

3.1. Characterization of the prepared nanocomposite:

3.1.1. Zero Point charge:

Zero point charge is defined as the pH\(_{pzc}\) at which the charge on the surface is zero. The surface has a positive charge when the pH of the solution is less than pH\(_{pzc}\), and a negative charge when the pH of the solution is more than pH\(_{pzc}\). A small value of pH\(_{pzc}\) is considered a sign of a good sorbent since it allows for a wide range of pH in its application for cation sorption.

pH\(_{pzc}\) of C6P(AAM-co-IA/TiO\(_2\)) nanocomposite was determined practically by modifying pH for a series of 50 ml flasks, each of which contained 0.1g of sorbent and 10 ml of 0.01 molL\(^{-1}\) (NaCl), and pH was varied from 1.0 to 12. (pH\(_{initial}\)). After shaking the mixture for 24 hours, the pH of the solutions was determined (pH\(_{final}\)). The pH\(_{pzc}\) is then calculated by graphing pH\(_{initial}\) against ΔpH (pH\(_{final}\) - pH\(_{initial}\)).

As shown in Fig. 1, the pH\(_{pzc}\) of C6P(AAM-co-IA/TiO\(_2\)) nanocomposite is 3.2. Cations sorption onto C6P(AAM-co-IA/TiO\(_2\)) nanocomposite requires a pH greater than 3.2. At pH greater than 3.2, the carboxylic groups deprotonate, allowing negatively charged carboxylate ligands (–COO\(^-\)) to bind Ce(III) ions. This suggests an ion exchange mechanism between negatively charged nanocomposite and positively charged nanocomposites.
3.1.2. Measurements of particle size

The particle size of nano TiO$_2$ particles are distributed in the range from 39 to 412 nm in Fig. 2a. More than 90% of TiO$_2$ particles has nanocharacter. The incorporation of nanoparticles into a polymer can lead to a considerable improvement of mechanical properties [26]. However, the particles size of the composite increased in the range between 220-340 nm in Fig. 2b due to agglomeration of TiO$_2$ nanoparticles and particle growth in the nanocomposite [27].

3.1.3. SEM and TEM-analysis

SEM of C6P(AAM-co-IA/TiO$_2$) nanocomposite shown in Fig. 3a clarified the rough surface of the nanocomposite. This is due to the incorporation of the agglomerated TiO$_2$ nanoparticles at the surface of the nanocomposite. The agglomeration of TiO$_2$ nanoparticles is depicted in the TEM in Fig. 3b where the particle size of the nanoparticles is smaller than 50 nm. This result seems to be less than that obtained by particle size measurements due to agglomeration of the particles [28]. The agglomeration of TiO$_2$ increases at the surface of the polymers leading to an increase in the particle size and this result confirmed by particle size measurements of C6P(AAM-co-IA/TiO$_2$) nanocomposite (Fig.3c).

3.1.4. X-ray diffraction

The amorphous nature of the nanocomposite is depicted from Fig. 4. The amorphous peaks intensities at, 2$\theta$ = 25.16°, 25.63°, 36.08° and 49.17° confirm the presence of anatase
phase of TiO$_2$ Nanoparticles [29]. The amorphous character is due to the huge amounts of
water content C6P(AAM-co-IA/TiO$_2$) nanocomposite as a result of -COOH presence from
Itaconic acid.

### 3.1.5. FT-IR analysis

Fig. 5 investigates the different molecular vibrations acquired by C6P(AAM-co-IA/TiO$_2$)
nanocomposite. A broad band from 3000-3600 cm$^{-1}$ referred to O-H stretching vibration band
overlapping with N-H bending. The absorption bands at 2934, 1608 and 1412 cm$^{-1}$ assigned
to –CH$_2$ stretching band, O-H and –COO symmetric vibration band, respectively. The
stretching vibration of carbonyl group -C=O represented by the absorption band at 1666 cm$^{-1}$.
The amide group at C6P(AAM-co-IA/TiO$_2$) nanocomposite is identified by the vibration
stretching band C-N at 1450 cm$^{-1}$ and 1191 cm$^{-1}$ for –NH$_2$ bending vibration band [30]. The
interaction between TiO$_2$ Nanoparticles and AAM, IA is confirmed by the Ti-O-C
deformation structure at 1120 cm$^{-1}$ absorption band [31]. The bands at 775 cm$^{-1}$ and 524 cm$^{-1}$
were as a result of the Ti-O bond stretching mode of the TiO$_2$ [30]

### 3.1.6. Thermal analysis

The thermal stability of the prepared nanocomposite indicated in Fig.6. A total 66% of
the total weight of the nanocomposite lost up to 600 °C. Two endothermic peaks at
96.38°C and 233.4 °C with weight loss percentage 6.9% due to evaporation of physically
adsorbed water and structural water, respectively. Three exothermic peaks at 409.8 °C, 459°C
and 524°C due to degradation of C6P(AAM-co-IA/TiO$_2$) nanocomposite and combustion of organic materials.

3.1.7. Surface measurements

The porous materials reveals its efficiency for sorption process. However, only open pores take a part in sorption process as active sites. The difference between Apparent density and bulk density express the extent of open pores in the sample. C6P(AAM-co-IA/TiO$_2$) nanocomposite has ~ 27% porosity. The average pore diameter is 88 nm indicate macropores structure expecting an increase in sorption and desorption efficiency.

3.2. Sorption study

The sorption efficiency (%) and distribution coefficients of P(AAM-co-IA/TiO$_2$) nanocomposites towards Ce(III) are given in Table 3. It is observed that sorption efficiencies (%) and distribution coefficient of C6P(AAM-co-IA/TiO$_2$) composition show high sorption efficiency compared with the other compositions of the prepared samples. Thus, sample C6P(AAM-Co-IA/TiO$_2$) selected for the aim of the study.

3.2.1. Effect of pH:
Hydrogen ion concentration considers as an important parameter effecting the sorption reaction. In Figure 7a, the influence of pH on Ce(III) sorption onto C6P(AAM-co-IA/TiO2) nanocomposite is investigated in the range 2-7. It is indicated that the amount sorbed of Ce(III) is increased by increasing pH levels. When the pH is more than 6, the sorption efficiency increase from 80.11% to 85% but Ce(III) precipitate, making it impossible to distinguish between the amount of Ce(III) sorbed onto the nanocomposite and the precipitated amount [32]. Therefore, the optimum pH value was maintained at pH = 6. As value of pH is less than 6, the hydronium ion [H3O+] compete Ce(III) for occupying the active sites on C6P(AAM-co-IA/TiO2) nanocomposite surface and so the sorption of Ce(III) is decreased. Increasing pH value, decreasing concentration of [H3O]+, led to a decrease in the competition and so the sorption of Ce(III) onto the C6(PAAM-co-IA)/TiO2 nanocomposite is increased.

Figure 7b shows the Ce(III) speciation diagram in aqueous solution at various pH levels. It demonstrates that Ce(III) ions are provided at the optimal pH of 6, indicating that Ce(III) ions are trivalently sorbed. Hydroxides began to form at pH levels greater than 6 [33].

The distribution coefficient of Ce(III) at 298 K onto C6P(AAM-co-IA/TiO2) (Fig. 7c) increases as the pH increase at V/m ratio 400. This is owing to increase of the electrostatic attraction between the cerium ions and the surface of the composite.

3.2.2. Impact of contact time

The impact of contact time on sorption process studied at range (10–240 min) and represented in Fig. 8. The sorbed amount increases gradually till the equilibrium time of the sorption process which reached attained nearly at 60 minutes. The high sorption efficiency at
the initial stage of the process owing to the great number of vacant active sites on the
C6P(AAM-co-IA/TiO₂) surface as well as the high concentration of Ce(III) ion solution.

3.2.3. Effect of sorbent weight

Fig.9 includes the plot of C6P(AAM-co-IA/TiO₂) nanocomposite weight against the
sorption efficiency and the sorbed amount. The sorbed amount of Ce(III) onto C6P(AAM-co-
IA/TiO₂) nanocomposite increases from 44.47 to 88.80 mgg⁻¹ by increasing the weight of
C6P(AAM-co-IA/TiO₂) nanocomposite from 0.01 to 0.1 g at an initial concentration of
Ce(III) 200 mgL⁻¹. This is due to the fact that the sorption capacity influenced by surface
activity. The increase in the amount of C6P(AAM-co-IA/TiO₂) nanocomposite weight will
increase specific surface area which increases the number of sorption sites available for
Ce(III) surface interactions as well as increase in diffusion path length [34].

3.2.4. Effect of metal ion concentration & temperature

Even if the sorbed amount increases, the sorption efficiency of C6P(AAM-co-
IA/TiO₂) decreases in percentage with raising original Ce(III) ion concentration. This is
owing to the active sites on the sorbent becoming available at low Ce concentrations (III).
The sorption effectiveness diminishes as the quantity of metal ion increases because the
number of available binding sites reduces [35].
From the results shown in Fig.10 for the sorbed amount of Ce(III) onto C6P(AAM-co-IA/TiO$_2$) nanocomposite at different temperatures at 298, 308, and 318 K, it is obvious that the sorbed amount increases by raising the temperature due to acceleration of some originally slow sorption steps or due to the enhanced mobility of Ce(III) ions from the solution to the functionalized C6P(AAM-co-IA/TiO$_2$) surface [36].

3.3. Kinetic modelling

Fig.11 a, b shows the pseudo 1$^{\text{st}}$ order and pseudo 2$^{\text{nd}}$ order fitting plots. Table 4 contains the kinetic parameters. The identity value of $q_e^{\text{exp.}}$ with the value of the experimental data $q_e^{\text{cal.}}$ and the high $R^2$ for pseudo 2$^{\text{nd}}$ order for Ce(III) elucidate that the sorption of Ce(III) onto C6P(AAM-co-IA/TiO$_2$) nanocomposite controlled by pseudo 2$^{\text{nd}}$ order mechanism. The pseudo 2$^{\text{nd}}$ order reaction mechanism of C6P(AAM-co-IA/TiO$_2$) nanocomposite are synchronised. with chemisorption reaction and valence electrons sharing or ion exchange between Ce(III) and H$^+$ [37].

Fig.11c shows the interpretation of Elvoich Eq. (5). The linear relation with correlation coefficient $R^2 = 0.96$ accumulate for the agreement of the reaction mechanism with Elvoich and a good correlation for C6P(AAM-co-IA/TiO$_2$) heterogeneous surface [38]. $\alpha$ and $\beta$ parameters listed in Table 4.
3.4 Isotherm models

Fig. 12a shows the linear plot of $C_e/q_e$ versus $C_e$ illustrating the sorption process fitted with Langmuir model with high correlation coefficient, $R^2 = 0.99$. The values of the monolayer capacity, $Q$, at different temperatures were estimated from the slope and represented in Table 5. The sorption capacity of Ce(III) at 298 K onto C6P(AAM-co-IA/TiO$_2$) nanocomposite is 76.05 mg g$^{-1}$. The sorption capacity increased with the temperature. The process is favourable because $0 < R_L < 1$

By graphing log $q_e$ versus log $C_e$, (Fig. 12b), straight lines were produced at different temperatures. The values of Freundlich constants, $1/n$ and $k$, are determined from the slope and intercept, respectively, and given in Table 5.

The numerical of $n > 1$ suggested that C6P(AAM-co-IA/TiO$_2$) bind with a highest strength multiple binding sites of sorbent and the sorption capacities were only slightly inhibited in relative low equilibrium concentration. The correlation coefficients of the Langmuir isotherm model ($R^2$) were higher than those of the Freundlich isotherm model, indicating that the sorption process fits the Langmuir model better.

The constants of $A_T$ and $b_T$ for Temkin fitting determined from the slope and intercept of the plot of $q_e$ against $\ln C_e$ in Fig. 12c. These constants correlated to the sorption capacity and intensity of sorption. $R^2$, correlation coefficient value is close to unity indicating the sorption mechanism which is governed by chemisorptions process confirming pseudo 2$^{nd}$ order and Elvoich model.

[15]
3.5. Thermodynamic studies

The slope and intercept of the plot of Fig. 13, according to Equations (7-8), can be used to derive the values of \( \Delta H^\circ \) and \( \Delta S^\circ \), respectively, represented in Table 6. The endothermic character of the sorption process is indicated by the positive value of \( \Delta H^\circ \), and the increase in randomness at the nanocomposite/solution interface is indicated by the positive value of \( \Delta S^\circ \). The negative value \( \Delta G^\circ \) indicates the sorption process is spontaneous. The increase in negative Gibbs free energy with increasing temperature indicates that the process is becoming more spontaneous. Furthermore, positive values of \( \Delta S^\circ \) suggest that Ce(III) exchanges with mobile ions exist on C6P(AAM-co-IA/TiO\(_2\)) nanocomposite, resulting in an increase in entropy value via the sorption process.

3.6. Desorption studies

Fig. 14 represents the variation of accessible desorption efficiency with the different concentration of acids. The percentage of desorption increased as the concentration of the
acids increased. The order of desorption efficiency is $\text{HCl} > \text{HNO}_3 > \text{acetic acid}$ and $2 \text{ molL}^{-1} \text{HCl}$ is the most proper eluent for Ce(III) with 70.7% desorption efficiency.

3.7. Comparison with other Ce(III) sorbents:

The sorption capacity of C6P(AAM-co-IA/TiO$_2$) nanocomposite toward Ce(III) is compared with other sorbents [39-44]. The results, illustrated in Table 7, shown that the C6P(AAM-co-IA/TiO$_2$) nanocomposite could be considered as a promising material to retain Ce(III).

3.8. Sorption of Ce(III) from monazite leachate:

Sorption of Ce(III) and some rare earth ions (RE$^{3+}$) onto C6P(AAM-co-IA/TiO$_2$) nanocomposite is measured using inductive coupled plasma optical emission spectrometer. 0.14g of C6P(AAM-co-IA/TiO$_2$) contacting with 20 mL of the monazite leachate solution at 298 K and pH 6. The results for energy dispersive X-ray spectra of loaded C6P(AAM-co-IA/TiO$_2$) is shown in Fig. 15. The spectrum shows La, Ce, Eu,… bands besides C,O,N, and Na consistent with the elemental formula of monazite[44] and nanocomposite. The roughness of the surface of C6P(AAM-co-IA/TiO$_2$) at the end of the sorption processes as depicted in Fig 15. Furthermore, the mapping images of loaded C6P(AAM-co-IA/TiO$_2$) nanocomposite with REEs indicate that REEs ions are adequately adsorbed at the surface of the nanocomposite and they are distributed uniformly. La, Ce and Eu are taken as examples of REEs to confirm sorption process. Table 8 includes the sorption efficiency and desorption percentage of light rare earth ions (LRE$^{3+}$) and heavy rare earth ions (HRE$^{3+}$) onto C6P(AAM-co-IA/TiO$_2$) nanocomposite. The results show a sorption selectivity for C6P(AAM-co-IA/TiO$_2$) nanocomposite towards HRE$^{3+}$ where the sorption efficiency is
70.94% compared to 54.09% for LRE$^{3+}$. Thus, C6P(AAM-co-IA/TiO$_2$) nanocomposite could be used for group partial separation of LRE$^{3+}$ than HRE$^{3+}$. The desorption percentage shows any selectivity for RE$^{3+}$, as both LRE$^{3+}$ and HRE$^{3+}$ have similar desorption percentage. Ce(III) shows 61.62% sorption for the initial concentration at monazite leachate 577.652 mgL$^{-1}$. The sorption efficiency for Ce(III) decreased in single component system than in multicomponent system in case of monazite leachate solution these is due to selectivity of C6P(AAM-co-IA/TiO$_2$) nanocomposite towards HRE$^{3+}$ possessing low ionic radii [45].

4. Conclusion

Poly(acrylamide-co-Itaconic acid/TiO$_2$) (P(AAM-co-IA/TiO$_2$)) nanocomposite is successfully prepared by copolymerization of Acrylamide (AAM), Itaconic acid (IA) and nano TiO$_2$ using gamma irradiation with $^{60}$Co $\gamma$-rays at a dose of 25 K Gy$^{-1}$. Characterization of the prepared samples performed by different analytical techniques. C6P(AAM-co-IA/TiO$_2$) used as a sorbent for Ce(III) from monazite leachate. Optimization of the parameters affecting sorption process is carried out. The equilibrium sorption reaction achieved after about 60 min. The sorption process has endothermic nature; the results indicated that, the sorption reaction is regulated by pseudo-2$^{nd}$ order mechanism. The experimental equilibrium data tested for Langmuir and Freundlich isotherm. The monolayer capacity of Ce(III) onto C6(P(AAM-co-IA/TiO$_2$)) at 298 K, pH =6 is 76.05 mgg$^{-1}$. Using C6(P(AAM-co-IA/TiO$_2$)) nanocomposite as a sorbent for Ce(III) in multicomponent system of monazite leachate shows sorption efficiency 61.62% for 577.652 mgL$^{-1}$ initial concentration. Therefore, the prepared C6(P(AAM-co-IA/TiO$_2$)) nanocomposite can be considered as a promising material for the sorption of Ce(III).
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Figure 1

Determination of \( \text{pH}_{\text{pzc}} \) for C6P(AAM-co-IA/TiO2) nanocomposite [using 0.1 g of the C6P(AAM-co-IA/TiO2) nanocomposite with 10 ml of 0.01 mol\( \cdot \)L\(^{-1}\) NaCl at 298 K]

Figure 2

Particle size of a- TiO2 nanoparticles b- C6P(AAM-co-IA/TiO2) nanocomposite using distilled water as dispersing media
Figure 3

a- SEM of C6P(AAM-co-IA/TiO2) nanocomposite b- TEM of TiO2 nanoparticles c- TEM of C6P(AAM-co-IA/TiO2) nanocomposite.

Figure 4

X-ray diffraction of C6P(AAM-co-IA/TiO2) nanocomposite
Figure 5

FT-IR spectrum of C6P(AAM-co-IA/TiO2) nanocomposite

Figure 6
DTA-TGA analysis of C6P(AAM-co-IA/TiO2) nanocomposite

Figure 7

a- Sorbed amount and Sorption efficiency of Ce(III) onto C6P (AAM-co-IA/TiO2) composite at different pH
b- Speciation diagrams for the Ce(III) ion

c- Distribution coefficient of Ce(III), Kd, mLg⁻¹ [Co of Ce(III) 200mgL⁻¹, 298 K, V/m = 0.4 Lg⁻¹, shaking time = 24h]

Figure 8
Effect of contact time on the sorption efficiency and sorbed amount of Ce(III) onto C6P(AAM-co-IA/TiO2) nanocomposite [Co of Ce(III) 200 mgL-1, 298K, V/m =0.4 Lg-1, pH=6]

Figure 9

Effect of sorbent weight on the sorbed amount and sorption efficiency of Ce(III) onto C6P(AAM-co-IA/TiO2) nanocomposite at [Co of Ce(III) 200mgL-1, 298 K, pH=6, equili. time = 60 min]

Figure 10
Effect of initial concentration of Ce(III) on the sorbed amount and sorption efficiency, b- Effect of temperature on the sorbed amount of Ce(III) onto C6P(AAM-co-IA/TiO2) nanocomposite [ V/m =0.4 Lg-1 , pH=6, equili. time = 60 min]

Figure 11

Kinetic models fitting for sorption of Ce(III) onto C6P(AAM-co-IA/TiO2) nanocomposite. a- pesudo 1st order fitting b- pseudo 2nd order fitting c- Elvoich fitting [Co of Ce(III) 200mgL-1 , 298K, V/m =0.4 Lg-1 , pH=6]
Figure 12

Isotherm models fitting for sorption of Ce(III) onto C6P(AAM-co-IA/TiO2) nanocomposite a- Langmuir fitting b- Freundlich fitting c- Temkin fitting [ V/m =0.4 Lg⁻¹, pH=6, Eq. time = 60 min]

Figure 13

Thermodynamic plot for the sorption of Ce(III) onto C6P(AAM-co-IA/TiO2) composite [pH=6, v/m =0.4 Lg⁻¹ and Co of Ce(III) 200 mgL⁻¹]
Figure 14

Desorption efficiency of loaded C6P(AAM-co-IA/TiO2) with different concentrations of HCl, HNO3 and Acetic acid. [V/m = 0.4 Lg-1, contact time 24 hours, 298 K]

Figure 15

SEM of loaded P(AAM-co-IA/TiO2) nanocomposite with REEs after shaking with monazite solution for 2 hours at 298 K

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