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Simultaneous Adsorption of Multicomponent Lanthanide Ions on Pectin Encapsulated Zeolite A

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Abstract: In this study, pectin encapsulated Na-zeolite A particles (P-ZA) was synthesized using the impregnation method and it was used as an adsorbent for adsorption of multicomponent lanthanides ions. The Na-zeolite A (zeolite A) was prepared from natural kaolin by the hydrothermal method, while pectin was isolated from white pith of citrus maxima fruits. Scanning electron microscope (SEM) images suggested that P-ZA composite adopts a nest-like shaped surface morphology occupied by zeolite A particles or pectin encapsulated skeleton system of zeolite A particles. The size of P-ZA particles was approximately 125 μm. The highest adsorption capacity of La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, and Dy^{3+} on P-ZA composite is 4.81×10^{-5} M, 4.65×10^{-5} M, 6.19×10^{-5} M, 6.04×10^{-5} M, and 6.03×10^{-5} M, respectively, at the contact time of 60 mins. The lanthanides ions are adsorbed on the P-ZA surfaces through either ion exchange with Na-zeolite A or coordination with the functional groups of pectin, and are further stabilized by their hydrolysis on the P-ZA surfaces. The results suggest that P-ZA composite has the potential to be utilized as an adsorbent for the initial step of separation and purification of lanthanides after leaching from the metallurgical ores.

Keywords: Adsorption efficiency; Lanthanides; Na-A zeolite; Pectin-ZA composite

1. Introduction

Rare earth element (REE) is well-known as lanthanide. REE comprise 17 elements including all of the lanthanides (La – Lu, Sc, and Y). It is noted that REEs are considered as critical minerals. These elements are essential for modern technologies, defense military, energy, medical, and economic sectors. All critical minerals such as lithium (Li), cobalt (Co), nickel (Ni), REEs, tellurium (Te), indium (In), graphite, manganese (Mn), copper (Cu), silicon (Si), chromium (Cr), and zinc (Zn) need large percentage growth up to 2050 to meet the demand of growing low-carbon energy technology and net zero emission.

In 1900 to 1960, REE sources mostly came from monazite ores. Due to their essential applications in the advanced technologies, the extraction of REEs from other sources has become a major task in many countries, such as China, United stated of America, Brazil, Malaysia, Indonesia, and India. From the exploration of different potential REE sources, for instance, mining wastes of tin extraction, such as low grade bauxite from Bintan island was found to contain trace lanthanides[1-3)], including lanthanum oxide (La_2O_3, 0.0052%) and yttrium oxide (Y_2O_3, 0.041%)[4-5)]. Lanthanides along with yttrium (Y) are economically valuable as essential materials in a wide range of applications in catalysis, optic, energy, metallurgy, luminescence, laser, superconductor, batteries, electronic, chemical, automotive, and nuclear power[6,7)]. As a catalysis, for example, lanthanides are used to produce 5-hydroxymethyl-furfural, which is an alternative material for development of petroleum-based energy resources and chemicals[8)].

The demand for REEs increases year by year. Due to the increasing demand, extraction of lanthanides from low grade bauxite and tin slag has received much attention[9)]. The separation and purification of lanthanides contained in leachate extracted from low grade bauxite are known to be difficult due to their similar chemical and physical properties[10)]. In particular, the trivalent lanthanide ions are most thermodynamically stable in an aqueous solution. In the literature, it has been reported that lanthanides can be separated by several techniques, including adsorption, ion exchange, solvent extraction, gravitation, magnetism, and fractional precipitation[1-5,11)]. Among them, adsorption is considered as the simplest method often used as an initial step of separation and purification[1)]. High selectivity of cost-effective adsorbents makes this technique more competitive and applicable in a wide range of industrial scales[12,13)].

Kaolin is a white hydrated aluminosilicate crystalline mineral with a plate-like appearance, Si/Al ratio of 1 with the chemical composition of $Si_2Al_2O_5(OH)_4$, and a 1:1 layered structure consisting of SiO_4 tetrahedrons combined with $Al(O,OH)_6$ pseudo-hexagonal symmetry. The basic ingredient is kaolinite {Al_2O_3, $2SiO_2$, $2H_2O$ or $Al_2Si_2O_5(OH)_4$} which is dehydroxylated into metakaolin through a calcination reaction. The formation of metakaolin occurs at temperatures in the range of 500-925°C. In metakaolin, the bond between AlO_2 and SiO_2 is broken to produce amorphous Al and Si compounds which are then reacted with alkali metal hydroxide at a high pH. The synthesis of zeolite from metakaolin is carried out through a hydrothermal process. If kaolin is not calcined first, but it is directly used and reacted with alkali metal hydroxide (NaOH), the resulting product will be feldspathoid or hydroxysodalite. Kaolin which is a naturally available cheap raw material[14)] as a source of zeolite-A has the ratio of Si/Al nearly unitary.

The natural kaolin with the production reaching 32 million tons as of 2009 is one of the mineral resources in Indonesia. Thus, kaolin has a very good economic value, which can be seen from its feasibility in technical, operational, and marketing[15)]. However, adsorption capacity of synthetic dyes on the raw kaolin surface was reported to be relatively low[16)].

As compared to kaolin, zeolite A is known to have higher porous structures of aluminosilicates with higher surface area[17)]. Zeolite A also has the ratio of Si/Al nearly unitary, and consists of a three-dimensional framework. Importantly, the basal surfaces of zeolite A are negatively charged. The electronegative surface offers exchangeable counter ions. The Al and Si atoms on its basal surfaces facilitate high ion-exchange capacity of zeolite A. With its relatively cost effectivity and high specific surface area[18)], zeolite A is more attractive to be applied as adsorbents. The low silica zeolite, for example zeolite A, exhibits the greatest ion exchange capacity. It can be used for gas separation and water softening[19)].

The adsorption selectivity of zeolite A towards lanthanum (La^{3+}) and neodymium (Nd^{3+}) ions was implemented and controlled by pH, as it has been reported to be optimum in acidic condition[20)]. Kusrini and coworkers had also reported the adsorption of La^{3+} ion using pectin from durian rind as an adsorbent, where the optimum adsorption capacity of La^{3+} (41.2 mg/g) occurred at contact time of 90 min, pH 4, and 25°C[1)].

It is interesting to note that pectin is among superior adsorbents for the removal of synthetic dye[21)]. The advantage of pectin as an adsorbent is due to its gel formation in aqueous solution, rich functional groups, simple regeneration, easy recovery of the spent adsorbent and recovery adsorbed metals, and low toxicity[21-23)]. Driven by the advantages of pectin, in this study, zeolite A was encapsulated with pectin to increase the performance of pectin-zeolite A (P-ZA) as an adsorbent, and this adsorption is considered as the preliminary step of separation and purification of Lanthanides from aqueous solution of leachate extracted from low grade bauxite. Interactions between zeolite A and pectin in P-ZA is schematically illustrated in Fig. 1. The effect of pH on adsorption of lanthanides on the synthesized P-ZA was also investigated.

2. Materials and method

2.1 Materials and characterization

Natural kaolin was originated from Bangka, Belitung Island, Indonesia. Hydrochloric acid (HCl), sodium hydroxide (NaOH) pellets, lanthanum nitrate hydrate ($La(NO_3)_2 \cdot 6H_2O$), samarium hydrate ($Sm(NO_3)_2 \cdot 6H_2O$), neodymium nitrate hydrate ($Nd(NO_3)_3 \cdot 6H_2O$), cerium nitrate hydrate ($Ce(NO_3)_3 \cdot 6H_2O$), and dysprosium nitrate hydrate ($Dy(NO_3)_2 \cdot 6H_2O$) were purchased from Merck (Germany) and Sigma Aldrich Co. (USA). All these chemicals were of analytical grade and were used as received. Pectin was isolated from citrus maxima (CM) fruits.

Functional groups of P-ZA before and after adsorption process were identified based on their vibrational bands recorded using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer, USA). The surface morphology of P-ZA was determined using a scanning electron microscopic-energy dispersive X-ray (SEM-EDX) analysis (FEI-QUANTA FEG 250). The amount of lanthanides adsorbed on P-ZA was quantified using an X-Ray fluorescence (XRF) spectrophotometer (PerkinElmer, USA).

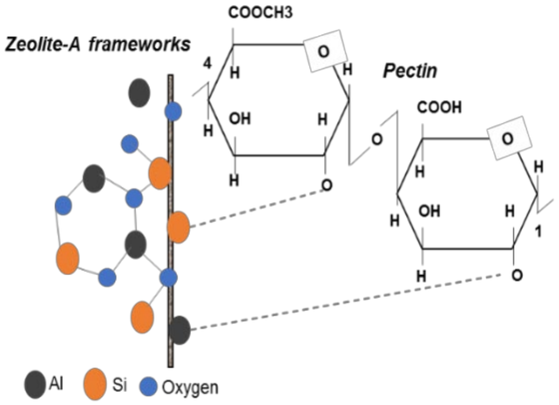

Fig. 1: A schematic illustration of interaction between zeolite A and pectin.

2.2 Isolation of pectin from citrus maxima

Pectin was isolated according to procedures reported by Daud and coworkers[24]. This citrus maxima (CM) was obtained from a local plantation in Labi, Belait District, Brunei Darussalam. The fruit was peeled off and the spongy albedo (white pith) was separated from the flavedo (peel) and flesh (endocarp). The white pith was cut and dried at 65°C. When dried, the pith was crushed into powder and screened through a 355-micron stainless steel sieve. 5 g of the pith powder was dispersed in distilled water (150 mL) under stirring. Into the suspension, L-(+)-tartaric acid was then slowly added until pH of the mixture was in the range of 1.0 and 2.0. The mixture was soaked in water bath at 60–80°C for 60–120 min. After keeping at room temperature overnight, the mixture was decanted and the filtrate was precipitated using 96% ethanol in ratio of 1:1 v/v under ice-bath (0–4ºC) for 3 h. The extract was passed through a filter paper under vacuum via a Büchner funnel, and was then centrifuged at 4000 rpm for 20 min. The extracted pectin was subsequently washed with 55% and 75% ethanol. Finally, the extracted pectin was dried in an oven at 65°C, and the dried pectin was collected and kept in desiccator until it was used in other experiments.

2.3 Preparation of pectin-zeolite A

The preparation of P-ZA is schematically illustrated in Fig. 2. Zeolite A was prepared from natural kaolin by calcining this natural kaolin at 750°C for 3 h to form metakaolin. Subsequently, the resulting metakaolin was converted to zeolite A by the hydrothermal method using 3 M NaOH at 60 °C and 750 rpm for 3 h. The gel of zeolite A was then filtered, followed by washing with distilled water to reach pH 10.

The gel of zeolite A was added into an aqueous solution of pectin (1 w%). The suspension was sonicated for 30 min, and was stirred continuously for 24 h at 25°C. The suspension was then centrifuged, and the resulting solid of P-ZA was retrieved and washed thoroughly with deionized water, followed by drying at 100°C for 2 h. The P-ZA was then crushed by using an agate mortar.

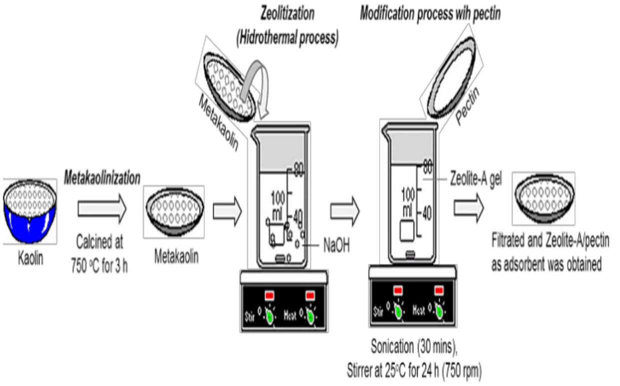

Fig. 2: Schematic illustration of preparation of P-ZA.

2.4 Adsorption study

A mixture of lanthanides was prepared by mixing individual solutions of $La(NO_3)_2$, $Ce(NO_3)_3$, $Nd(NO_3)_3$, $Sm(NO_3)_2$, and $Dy(NO_3)_2$ in distilled water, so that the concentration of each lanthanide in the multicomponent solution was 7×10^{-4} M. This multicomponent solution was used as a representative leachate from which the lanthanide ions were simultaneously adsorbed on the P-ZA surfaces. The adsorption experiment is illustrated in Fig. 3. Here, 100 mg of P-ZA was mixed with 50 mL of the multicomponent lanthanide solution under stirring at 200 rpm for 2.5 h. The contact time was set to be within 30 to 60 mins. The pH of the multicomponent lanthanides solution was adjusted to be in the range of 4−10 by adding a few drops of 0.1 M HCl or 0.1 M NaOH.

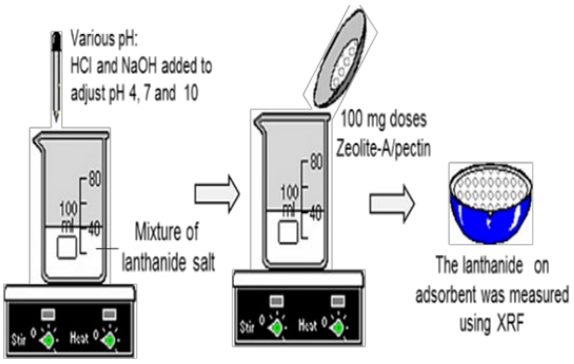

Fig. 3: Schematic illustration of the adsorption process of multicomponent lanthanide ions using P-ZA.

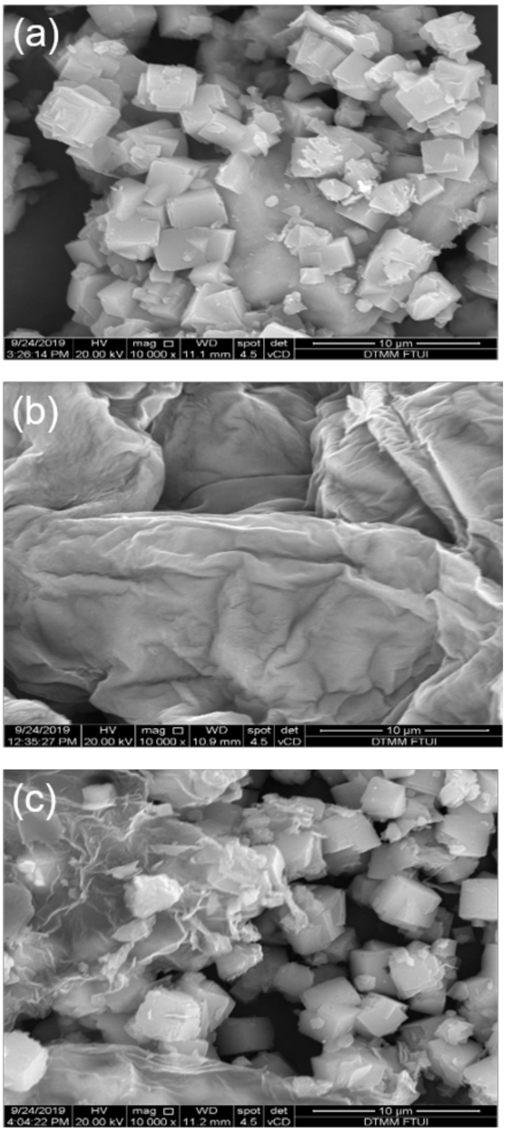

Fig. 4: The surface morphology of (a) zeolite A, (b) pectin, and (c) P-ZA with magnification of 10,000×.

3. Results and discussion

3.1 Characterization of pectin-zeolite A

The surface morphology of zeolite A, pectin, and P-ZA was analyzed by SEM. The SEM image showed that zeolite A particles are cubic in shape with sharp edges, as shown in Fig. 4(a). Zeolite A or Linde Type-A (LTA) is the result of the synthesis of alumina silicate minerals which have a cube morphology with blunter cube ends. Meanwhile, Na-Zeolite A (NaA) has the morphology of a perfect cube with sharp cube edges[25]. This difference in morphology can be caused by concentration, time or charge balancing ions in the manufacturing process[25].

On the other hand, the SEM image suggested that the pectin surface consisted of a lumpy sheet, while P-ZA adopts a nest-like shaped surface morphology occupied by zeolite A particles (Fig. 4(b)). The SEM images suggested that pectin encapsulated skeleton system of zeolite A particles (Fig. 4(c)). Based on the SEM images, the average size of zeolite A, pectin, and P-ZA particles was roughly estimated to be 4, 550, and 125 µm, respectively.

The EDX elemental analysis indicated that zeolite A consists of mainly Al and Si with the ratio of Si/Al being 2.469, as displayed in Table 1. This Si/Al ratio is higher than that of zeolite A (Si/Al ratio 1.097) synthesized by hydrothermal and calcination[26], or by other different sequences of hydrothermal and calcination.

FTIR spectra of zeolite A, pectin, and P-ZA are shown in Fig. 5. The vibrational bands of zeolite A appear at 2175 cm^{-1}, 1989 cm^{-1}, and 879 cm^{-1} (see Fig. 5(a)), where the main band at 879 cm^{-1} is assigned to the internal vibrations of Si-O and Al-O bonds and asymmetric stretching within the tetrahedral zeolite structure[27]. The vibrational spectrum of P-ZA (Fig. 5(c)) indicated the successful formation of pectin-encapsulated zeolite A, as revealed by the emergence of a very important vibrational bands of pectin at 1650 cm^{-1} and 1750 cm^{-1} (Fig. 5(b)) which were marked as free acid (–COOH) and esterified carboxylic (–COO–) groups[28].

Table 1. Chemical composition of zeolite A, pectin, P-ZA determined by EDX.

Atom	Mass (%)			Ratio Si/Al	
	Pectin	Zeolite A	P-ZA	Zeolite A	P-ZA
C	36.49	3.147	8.113		
O	65.05	40.217	38.083		
Na	0.705	11.303	14.137		
K	0.59	-	-		
Ca	0.878	-	-		
Ti	1.045	-	-		
V	0.085	-	-		
Si	0.175	32.003	21.18	2.469	1.145
Al	0.193	12.96	18.49		
La	-	0.37	-		

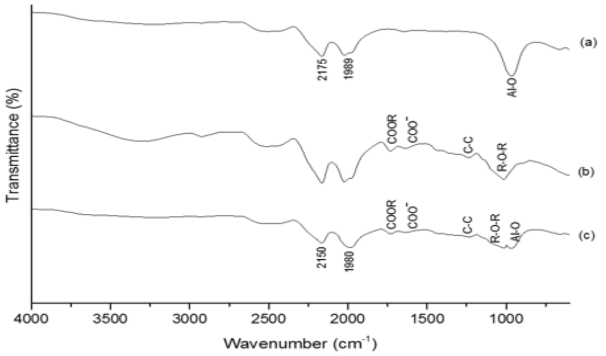

Fig. 5: FTIR spectra of (a) zeolite A, (b) pectin, and (c) P-ZA.

3.2 Adsorption of lanthanides

P-ZA was tested as an adsorbent to adsorb the multicomponent lanthanide ions (La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, and Dy^{3+}) simultaneously from an aqueous solution. Assuming that the ionic radius of lanthanides differs from each other, P-ZA is considered to be able to separate and adsorb selectively different sizes and types of lanthanides. To exemplify this idea, the effects of contact time and pH of the medium on the adsorption of lanthanides were investigated. As summarized in Table 2, it is clearly evidenced that the adsorption efficiency enhanced with the contact time from 30 to 60 mins. The highest adsorption efficiency of La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, and Dy^{3+} is 4.81×10^{-5} M, 4.65×10^{-5} M, 6.19×10^{-5} M, 6.04×10^{-5} M, and 6.03×10^{-5} M, respectively, at the contact time of 60 mins. This finding is similar to that reported by Marek and coworkers, where the adsorption of lanthanides on zeolite A showed the highest efficiency for Nd^{3+} at alkaline pH[20)].

Table 2. The concentration of Lanthanides adsorbed on P-ZA.

pH	t (min)	Concentration (10^{-3} M)				
		La	Ce	Nd	Sm	Dy
4	30	0.0145	0.0225	0.0335	0.0452	0.0477
7	30	0.0417	0.0407	0.0507	0.0496	0.0477
10	30	0.0449	0.0431	0.0525	0.0502	0.0479
4	60	0.0154	0.0261	0.0423	0.0567	0.0613
7	60	0.0481	0.0465	0.0619	0.0604	0.0603
10	60	0.0445	0.0426	0.0524	0.0507	0.0487

It was also found that the adsorption efficiency of the lanthanides enhanced abruptly when pH of the medium was increased from 4 to 7. However, increasing the pH from 7 to 10 did not show any effect on the adsorption efficiency of the lanthanides onto P-ZA composite. It can be understood that the P-ZA surface is negatively charged at pH>4 due to deprotonation of pectin, but as the pH of the medium across the pH of point zero of charge of pectin[21)] and zeolite A[22)], the negative net charge on the P-ZA surface remains unchanged. Thus, the adsorption efficiency of lanthanides is not much altered at different pHs from 7 to 10.

It has been pointed out that hydrolytic properties of REE ions affect their adsorption process. In this sense, the charge distribution on the P-ZA surface is attributed to the distribution of rate constant of the proton exchange[20)]. The pH of the solution greatly affects the distribution of rate constant of the proton exchange of an REE ion in the solution. The high affinities of Nd and Sm to P-ZA however hampered an estimation of the distribution constant at pH > 6[20)].

Therefore, the ability of REE ions to be absorbed on the P-ZA surface is most probably through the following two mechanisms, namely (i) lanthanides undergo ion exchange with other metal ions on the P-ZA surface, as presented by Equation (1), and (ii) lanthanides undergo hydrolysis on the P-ZA surface, as described by Equation (2).

$$\mathrm{Ln}^{3+} + 3\mathrm{HP-ZA} \leftrightarrow \mathrm{LnP-ZA} + 3\mathrm{H}^{+} \qquad (1)$$

$$p\mathrm{LnP-ZA}^{3+} + q\mathrm{H_2O} \leftrightarrow Ln_p\mathrm{P-ZA}_{3p}(OH)_q^{-q} + q\mathrm{H}^{+} \quad (2)$$

Table 3 shows adsorption of lanthanides on different reported adsorbents, as a comprehensive comparison. It is interesting to note that, similar to other adsorbents derived from agricultural wastes[2,29-31)], magnetic nano-particles[32)], and activated carbon[33)], and biopolymers[34)], P-ZA composite is also capable to adsorb multicomponent REE ions. This suggests that P-ZA composite has the potential to be utilized as an adsorbent for the initial step of separation and purification of lanthanides after leaching them from the metallurgical ores.

Furthermore, it also has the potential to be an adsorbent for separation of hydrocarbon-water by replacing the synthetic zeolite A with polyurethane (PU) and also introducing the graphene oxide (GO) into the PU[35)].

Table 3. Comparison of simultaneous adsorption of multicomponent Lanthanides using different adsorbents.

Type of Adsorbent	Lanthanides	References
Grapefruit peel	La^{3+}, Ce^{3+}	29)
Magnetic iron oxide nanoparticles	La^{3+}, Gd^{3+}	32)
Activated carbon form banana peels	La^{3+}, Y^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+},	2)
Durian rind	La^{3+}, Y^{3+}	30)
Pectin-activated carbon from banana peels	La^{3+}, Y^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+},	33)
Pectin-Chitosan composite	La^{3+}, Y^{3+}	34)
Orange peel powder	La^{3+}, Y^{3+}	31)
P-ZA	La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3}	This study

4. Conclusion

Pectin encapsulated Na-zeolite A particles was synthesized using the impregnation method and it was used as adsorbent in simultaneous adsorption of multicomponent REE ions from aqueous solution. Pectin was introduced onto Na-zeolite A to produce P-ZA composite to increase adsorption performance of the composite. The contact time was varied from 30 to 60 mins and pH to be in the range of 4 and 10. The average particle size of zeolite A, pectin, and P-ZA composite was roughly estimated to be 4, 550, and 125 µm, respectively. The highest adsorption efficiency of La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, and Dy^{3+} is 4.81×10^{-5} M, 4.65×10^{-5} M, 6.19×10^{-5} M, 6.04×10^{-5} M, and 6.03×10^{-5} M, respectively, at the contact time of 60 mins. The adsorption mechanism of lanthanide ions is proposed to be ion exchange with other metal ions and hydrolysis on the P-ZA surface. The results suggest that P-ZA composite was potential to be utilized as an adsorbent for the initial step of separation and purification of lanthanides after leaching from the metallurgical ores. In future, this adsorbent is also potential as a desicant for drying of corn, tea leaves and other agriculture products.

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