Research Article



Opeyemi Atiba-Oyewo¹ [∞], Maurice S. Onyango¹, Christian Wolkersdorfer^{2,3}

¹Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria 0001, South Africa ²SARChI Chair for Mine Water Management, Department of Environmental, Water, and Earth Sciences, Tshwane University of Technology, Pretoria 0001, South Africa

³Lappeenranta University of Technology, Laboratory of Green Chemistry, Sammonkatu 12, 50130 Mikkeli, Finland © E-mail: Atiba.opeyemi@gmail.com

E-mail. Aliba.opeyemi@gmail.com

Abstract: This study describes the preparation, characterisation and application of pelletised immobilised alginate/ montmorillonite/banana peels nanocomposite (BPNC) in a fixed-bed column for continuous adsorption of rare earth elements and radioactive minerals from water. The materials was characterised by Fourier transform infrared, X-ray diffraction and scanning electron microscopy analyses. Analyses indicated that the pellets are porous and spherical in shape. FT-IR analysis showed that the functional groups responsible for the coordination of metal ions were the carboxylic (–COO–) and siloxane (Si– O–Si and Si–O–AI) groups. XRD analysis showed two additional peaks which were attributed to alginate and montmorillonite. The influence of the initial concentration, bed depth and flow rate were investigated using synthetic and real mine water in order to determine the breakthrough behaviour of both minerals. The processed bed volume, adsorbent exhaustion rate and service time, were also explored as performance indices for the adsorbent material. Furthermore, the breakthrough data were fitted to both the Thomas and Bohart–Adams models. The BPNC exhibited high affinity for U, Th, Gd and La in the real mine water sample. However, studies may still be required using waters from different environments in order to determine the robustness of BPNC.

1 Introduction

Rare earth elements (REEs) and radioactive minerals are inner transition metals with high industrial demand worldwide. The mining of REE and radioactive minerals are continuously processed by creating new operations in order to meet their increasing demand. As the mining process of ores increases, there is also an increase in the likely presence of these metals in the effluent from the mine water, which finds their way into wastewater stream [1]. REEs and radioactive minerals could cause neural development in foetus, which could result in mental retardation when the child is finally born [2]. These minerals were also reported to be carcinogenic, increases the risk of heart attack, and their primary toxic effects occurs when consumed in water [3].

A variety of treatment technologies have been studied for the removal of REEs and radioactive minerals from water sources. This includes chemical precipitation, membrane separation, ion exchange and adsorption [4, 5]. Nevertheless, most of these technologies are associated with disadvantages such as high-energy requirement, high operational and maintenance cost, incomplete metal removal, and generation of voluminous toxic sludge that pose a serious risk during disposal [6, 7]. However, the adsorption process offers benefits such as simplicity, high efficiency and cost-effectiveness, making it a technology of choice for decontaminating polluted water sources even when the polluting ions are at trace levels.

Adsorption process for water treatment could be operated in a batch or continuous mode. Batch adsorption mode provides useful fundamental information about the effectiveness of the material. However, the fixed-bed operation is preferred for the treatment of large volume of water especially with a low concentration of metals. The performance of the fixed-bed operation can be described through the concept of the breakthrough curve (BTC). The basic and fundamental information required to design fixed bed adsorption system for real industrial application could also be

obtained from the BTC [8]. The performance of any adsorption process is highly dependent on the choice of the adsorbent media. Thus, different types of media have been used to remove radioactive elements and REEs from aqueous environments. They include activated carbon, molecular sieves, polyurethane foam, cellulosic adsorbents and resins [9, 10]. Activated carbon has been reported to be highly efficient in the removal of REEs and radioactive minerals from water. However, its cost-ineffectiveness is generally considered to be dependent on the type of the pollutant removed [9-12]. Other highly efficient adsorbents are those derived from cellulose [13], but their application in real industrial situation is a major challenge as not much data is available. The cost-effectiveness of cellulosic adsorbents is envisaged to depend on source raw materials. Consequently, attention has been focused on the development of cellulosic adsorbent from natural/waste materials, which are readily available especially in South Africa.

Banana peels contain ~ 75% of cellulose and was used in our previous study for the development of low-cost cellulose nanofibrils [14]. The material, in nanofibrils form, was efficient in the removal of REEs and radioactive minerals from mine water in a batch adsorption mode [15]. Nanofibrils application in a fixed-bed operation is a great challenge. Owing to their small size, the flow of water through the column would be characterised with channelling and high-pressure drop. For these reasons, manipulation of these nanocellulose fibrils into pellet form in order to display more unique properties for continuous adsorption process is required.

In continuation of our previous study, BPNC was synthesised, pelletised, characterised and utilised for the removal of REEs and radioactive minerals from water. The performance efficiency was evaluated in fixed-bed column using synthetic and real mine water. Service time, bed volumes processed and adsorbent exhaustion rate were used as performance indicators. A number of process conditions such as initial concentration, bed size and flow rate were

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Fig. 1 Synthesis of alginate immobilised banana peels nanocomposite



Fig. 2 Experimental setup for column studies

varied. Breakthrough data obtained were analysed using Thomas and Adams-Bohart models.

2 Experimental

2.1 Materials

The deionised water used for the prepared solution in this study was produced with the Purite water system, Model Select Analyst HP40, UK. Montmorillonite was purchased from ECCA Holdings Limited, South Africa. All other chemicals used were obtained from Sigma-Aldrich, South Africa, and they were of analytical grade. Binary components lanthanide synthetic solution was prepared, wherein lanthanum and gadolinium were used as examples of REEs. This was done by dissolving lanthanum nitrate hexahydrate (La (NO₃)₃·6H₂O), and gadolinium nitrate hexahydrate (Gd (NO₃)₃·6H₂O) in deionised water. The pH of the solution was adjusted with 0.1 M NaOH or 0.1 M HCl. Moreover, the performance of BPNC in radioactive minerals removal was evaluated using real mine water obtained from gold mine in South Africa. The mine water sample was analysed and found to contain radioactive minerals, which includes U, Th, La, Gd, Sm, Eu, As, Al, K, Ca, V, Cr, Fe, Cd, Li and Mo.

2.2 Preparation of BPNC pellets

The preparation of banana peels nanoadsorbent has been reported elsewhere [16]. For this study, the banana peels nanosorbent was pelletised using sodium alginate as a binder and montmorillonite as a filler to densify the material. Alginate salts easily form beads through the crosslinking of the glucuronic rich segments by divalent cations such as Ca^{2+} , Sr^{2+} and Ba^{2+} . Using this information, 60 mL of 1.2% (m/v) sodium alginate solution was prepared and used to bind 9 g of banana peels nanosorbent and 4.5 g of montmorillonite. The mixture was stirred vigorously with a magnetic stirrer in a beaker at room temperature for 1 h in order to achieve homogeneity. Then, the BPNC mixture was cast into a reactor containing 3.5% (m/v) of calcium chloride solution (crosslinking medium) by extruding dropwise under the force of gravity using a syringe. The pellets formed were incubated in CaCl₂ solution overnight (24 h) at room temperature to maintain stability. Thereafter, the wet pellets were rinsed extensively with deionised water until the pH was neutral in order to eradicate the residual reagents. Subsequently, the BPNC pellets were vacuum- and ovendried at 90°C until the mass remained constant. A schematic representation of the preparation of BPNC composite pellets and the cross-linking process is shown in Fig. 1.

2.3 Characterisation

The detailed composition and mineralogical properties of BPNC before and after adsorption were investigated using suitable analytical methods such as Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The FTIR spectroscopic analysis was carried out using a Perkin Elmer Spectrum 100 spectrometer recorded in the 500–4000 cm⁻¹ range, at a resolution of 4 cm^{-1} . The morphology and composition of the BPNC were characterised by SEM/Energy dispersive spectroscopy using a JEOL JSM-7600F field emission scanning emission microscope (FESEM), running at 2 kV accelerating voltage. The crystallinity was analysed using Xray diffractometer (XRD) (PANalytical Empyrean) under the following conditions; 45 mA, 40 kV and monochromatic Cu Ka radiation ($\lambda = 0.15406$ nm) over a scan range of 5.0149–89.9809°. The phase identification analyses were conducted using high-score plus program. The peaks obtained from the experiment were compared with the XRD peaks in the program database.

2.4 Adsorption studies

The fixed-bed adsorption column studies were done using perspex glass column of 300 mm height and internal diameter of 20 mm. BPNC pellets were packed in the middle of the column supported by glass wool and inert beads at the bottom and top ends. Synthetic solution of lanthanides/real mine water was introduced into the column using peristaltic pump (Colepalmer Master Flex L/S-USA) in an up-flow mode. This was to ensure complete and uniform streaming, and to minimise the chances of channelling due to gravity. The schematic setup is shown in Fig. 2.

The effects of bed loading, initial concentration and volumetric flow rate on breakthrough behaviour were investigated. The pH of initial synthetic solutions was kept constant at 5.20, which was the optimum pH as reported in our previous study [16]. The samples were taken at regular time interval of 30 min until equilibrium was reached. The residual REEs and radioactive minerals concentrations in the aqueous phase were then analysed using inductive coupled plasma atomic emission spectrometer (ICP-AES, 9000, Shimadzu), at different wavelengths for U, Th, La and Gd determination. Thereafter, the performance of the fixed-bed adsorption was presented by BTCs, which in our case are plots of C_t/C_0 versus time t, whereby C_t (mg/L) is the effluent concentration of REEs and radioactive minerals at any given time and C_0 (mg/L) is the initial concentration. The effect of bed loading (3, 5, 10 and 15 g) was first studied using REEs synthetic solution of 20 mg/L and influent flow rate of 2.5 mL/min. Similarly, the effect of initial concentration was explored by varying REEs concentration from 10 to 100 mg/L, while maintaining constant bed loading (5 g) and constant volumetric flow rate of 2.5 mL/min. The effects of the volumetric flow rate were investigated by varying flow rate from 0.68 to 5.0 mL/min at constant influent concentration (20 mg/L) and constant bed loading (5 g).

The industrial applicability of BPNC pellets in the real mine water treatment was also explored. The main contaminants of interest (U, Th, Gd and La) were found in substantial concentrations in mine water. Particularly, the concentration of U, Th, Gd and La were found to be 48.8, 18.8, 12.24 and 4.8 mg/L, respectively. The concentrations of these minerals are quite higher than the South African and WHO allowable discharge limits. Therefore, further treatment is required. Thus, BPNC performance was then evaluated using bed mass and influent flow rate of 5.0 g and 2.5 mL/min, respectively.

The total column capacity q_o (mg) was determined as

$$q_o = \frac{Q}{1000} \int_{t=0}^{t=\text{total}} (C_{\text{ad}}) \mathrm{d}t \tag{1}$$

where $C_{ad} = C - C_t$ is the total adsorbed concentration (mg/L) of REEs and radioactive minerals. For a given bed mass (g), equilibrium bed capacity q_s (mg/g) can be calculated as

$$q_{\rm s} = \frac{q_{\rm o}}{m} \tag{2}$$

The number of bed volumes (BV) processed was given by the following equation:

$$BV = \frac{V_{b(L)}}{V_{\text{packedbed}(L)}}$$
(3)

The overall adsorbent exhaustion rate (AER) during continuous flow operation can be determined as

$$AER = \frac{m(g)}{V_{\rm b}(L)} \tag{4}$$

The different kinetic models, Thomas model, Bohart–Adams model and bed depth service time model were applied to the experimental BTC data in order to predict the fixed bed adsorption breakthrough behaviour, and the effect of each process variable on continuous adsorption. The characteristic expressions are presented in (5)–(7), respectively.

$$\frac{C_{\rm t}}{C_{\rm o}} = \frac{1}{1 + \exp\left[K_{\rm Th}\left(\frac{q_{\rm Th}^m}{Q}C_{\rm o}t\right)\right]} \tag{5}$$

$$t = \frac{q_{\rm m}}{C_{\rm F}U}H - \frac{1}{k_{\rm b}C_{\rm F}}\ln{\binom{C_{\rm F}}{C}} - 1$$
(6)

$$t = \frac{N_{\rm o}}{C_{\rm o}u} L \frac{1}{K_{\rm a}C_{\rm o}} \ln \left(\frac{C_{\rm o}}{C_{\rm t}} - 1\right) \tag{7}$$

The details of the parameter have been reported in the literature [16–20].

3 Results and discussion

3.1 Characterisation of BPNC

3.1.1 Fourier transforms infra-red (FT-IR) spectroscopy: The FT-IR spectra of BPNC before and after adsorption of REEs are presented in Fig. 3. The bands at 1435 and 2920 cm⁻¹ were attributed to the stretching vibration of C–H and CH₂, respectively. The broad bands from 3286 to 3486 cm⁻¹ correspond to the stretching vibrations of O–H groups. This band became less broad and relatively more intense after adsorption process, indicating a decrease in hydrogen bonding. The bands between 1000 and 980 cm⁻¹ were due to Si–O–Si and Si–O–Al linkage in the montmorillonite [16]. The band at 1730 cm⁻¹ corresponded to the carbonyl C=O group [17], while the band at 889 cm⁻¹ was ascribed to the amide vibration. The peak, which appeared at 1248 cm⁻¹, was the (C–O–C) stretching vibration of sodium alginate, and was due to its saccharide structure [18].

3.1.2 Scanning electron microscopy analysis: The morphological properties of BPNC composite pellets before and after adsorption of REEs were investigated by SEM analysis Fig. 4. The micrograph before adsorption Fig. 4a showed that the BPNC pellets were porous and spherical in shape. The pellets had homogenous rough surface, which was characteristic of a good adsorbent and would facilitate easier penetration of water. The average particle size of the pellets was found to be 2.54 mm [19]. The inset scan of Fig. 4b after adsorption form clearly exposed the BPNC rough surface and porous nature.



Fig. 3 FT-IR spectra of BPNC (BPNC) before and after adsorption (afteruse form)



Fig. 4 SEM images of BPNC (a) BPNC before adsorption, (b) BPNC after-use form

 Table 1
 EDS data of alginate immobilised banana peels nanocomposite

Element wt%	BPNC	BPNCA
С	36.51	22.79
0	45.89	50.20
Ν	_	—
Н	_	—
Na	0.78	—
Al	2.01	4.47
Si	7.42	13.33
К	1.05	0.49
Р	0.42	—
CI	2.27	—
Са	3.15	2.12
Fe	_	1.61
Mg	0.50	1.12
La	_	2.87
Gd	_	1.00
sum	100	100

3.1.3 Energy dispersive spectroscopy: The elemental composition of BPNC analysed using EDS revealed that C, O, Si, Al, Fe, Ca, Cl, Mg and K are the main elements. Additional minerals such as La and Gd could be noticed in the BPNC after adsorption form, obviously due to sorbed lanthanides, this indicates the chemical interaction between BPNC, and lanthanides (La and Gd) (see Table 1). The high percentage of carbon on the surface of both media revealed that the materials are rich in carbon and could be regarded as organic materials.

3.1.4 X-ray diffraction (XRD) analysis: Fig. 5 displays the XRD patterns of BPNC before- and after-adsorption (BPNCA) forms. Table 1 showed that the most prominent peaks corresponded to amine and carboxylic groups, which are the main groups



Fig. 5 X-ray diffraction patterns of BPNC and BPNCA

Table 2	Mine water characterisation result
Element	Concentration, µg/L
La	12,244
Ce	12.44
U	48,816
Th	18,801
Sm	12.62
Eu	4.04
As	3360
Gd	4811.71
K	375
Са	398,398
Fe	7,151,533
Li	1275



Fig. 6 *Effect of BPNC bed mass on gadolinium removal (initial conc. 20 mg/L, flow rate 2.5 mL/min, column diameter 20 mm)*

responsible for the sorbent ability to remove metal ions. The appearance of additional peaks around 20° and 22° was noticed upon immobilisation (BPNC) which are attributed to the alginate and montmorillonite used as supporting materials [16, 20].

However, the reduction in BPNCA intensity around 29° and 60°, was noticed which suggests a decrease in crystallinity of BPNC pellets after adsorption process.

The peaks at 20°, 22° and 62° corresponded to montmorillonite in the form of pure sillimanite (Al₂SiO₅). The reduction of these additional peaks was observed in the after-use form (BPNCA) suggesting that these materials also participated in the removal of actinides/lanthanides from mine water. The diffraction peaks of phenolic compound ($C_{12}H_{28}N_4O_{12}$) are slightly shifted to lower angles, with a slight reduction in intensity, which could be attributed to the adsorption of lanthanides. Notably, the changes in shape and size of individual peaks were not significant. Thus, an indication that the structure of the adsorbent did not change after adsorption.

3.1.5 *Mine water characterisation:* The mine water used was obtained from one of the gold mines in South Africa. The mine water sample was used without pH adjustment due to the higher concentration of iron in the sample to avoid precipitation. However, the pH of the mine water sample was measured and found to be 3.86. Table 2 displayed the concentration of minerals present in the mine water sample.

3.2 Adsorption results

Although Gd and La were used as an example of lanthanides in this study, the adsorption results only focused on the performance of BPNC on Gd adsorption from aqueous solution; while its behaviours on other REEs and radioactive minerals were investigated using real mine water sample [21]. In this regard, the REEs BTCs were analysed from different breakthrough points (C_t/C_o) ranging from 0.002 to 0.2.

3.2.1 Effect of bed loading: The influence of adsorbent loading on BTCs is presented in Fig. 6 and a summary of the calculated column performance indices in Table 3. The bed mass was varied from 3 to 15 g with a corresponding increase in bed height from 1.3 to 6 cm. Consequently, the breakthrough time increased with an increase in bed height. This was due to the fact that the increased bed mass provided more surface area and adsorptive sites that enabled improved adsorption efficiency. In terms of volume of water treated, Table 3 shows that 375 mL was obtained when 3 g of adsorbent was used and the value increased to 2335 mL when 15 g bed mass was used. The breakthrough time t_b and saturation time t_s also increased from 150 to 930 min and from 1290 to 3810 min, respectively (Table 3).

3.2.2 Effect of volumetric flow rate: One of the important process variables used to evaluate the fixed-bed column adsorption efficiency is volumetric flow rate. The effect of flow rate on breakthrough behaviour was investigated by using 0.68, 1.67, 2.5 and 5 mL/min at constant adsorbent bed mass of 5 g and Gd initial concentration of 20 mg/L. The results are illustrated in Fig. 7. The influent flow rate was observed to be indirectly related to both $t_{\rm b}$ and t_s . For example, the bed saturation time t_s for 0.68, 1.67, 2.5 and 5 mL/min were found to be 4770, 3090, 2250 and 1110 min, respectively. This is due to the fact that flow rate relates to residence time in the bed. At a higher flow rate, the residence time was highly reduced which resulted in less interaction between the adsorbing species and the sorbent. The performance was consequently compromised. Conversely, low flow rate is characterised with higher residence time and, hence, better performance. Furthermore, the observation could be explained by the fundamental mass transfer principle whereby convective flow maybe the mass transfer rate controlling mechanism at higher flowrate [22]. The higher the influent flow rate, the more Gd species was supplied and this increased the competition for the limited adsorption sites and, as a result, the bed becomes saturated faster. On a positive note, higher flow rate reduced the external mass transfer resistance on BPNC's surface. Based on the combination of factors such as increased convective mass transfer and reduced Gd residence time inside the bed, poor adsorption capacity was observed. The AER values obtained increased from 7.0 to 7.7 g/L as the flow rate increased from 0.68 to 5 mL/min, indicating that exhaustion rate increased with an increase in flow rate [23].

3.2.3 Effect of initial concentration: The concentration of REEs and radioactive minerals in mine water are different based on mining site. Therefore, the performance of BPNC at different solute concentrations was investigated and breakthrough behaviour was examined and presented in Fig. 8. The increase in influent

Table 3 Summary of fixed bed column parameters at breakthrough point for Gd ads	orption
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Varied parameters	EBRT, min	<i>t</i> _b , min	T _s , min	<i>q</i> _b , mg/g	q₅, mg/g	BV	AER, g/L	V _b , mL
adsorbent mass (g)								
3	1.63	150	1290	2.5	12.0	91.81	8.0	375
5	2.51	270	2250	2.7	13.2	107.4	8.4	675
10	4.65	560	2979	2.8	14.5	107.6	8.8	1400
15	18.9	930	3810	3.1	17.5	108.9	8.9	2325
initial conc. (mg/L)								
10	2.51	530	3090	2.65	9.05	210.9	3.8	1325
20	2.51	270	2250	2.7	13.2	107.4	7.4	675
50	2.51	180	1290	4.5	18.4	71.61	11.1	450
100	2.51	120	690	6.0	21.8	47.74	16.7	300
flow rate (mL/min)								
0.68	9.24	1050	4770	2.85	7.9	113.6	7.0	714
1.67	3.76	410	3090	2.74	11.7	108.9	7.3	685
2.5	2.51	270	2250	2.7	13.2	107.4	7.4	675
5	1.26	150	1110	3.0	15.6	119.5	7.7	650



Fig. 7 Effect of flow rate of BPNC onto gadolinium (initial conc. 20 mg/L, bed loading, and column diameter 20 mm)



Fig. 8 Effect of concentration of gadolinium onto BPNC (flow rate 2.5 mL/min, bed loading 5 g, column diameter 20 mm)

concentration correspondingly reduced the bed service time. This was because at higher solute concentration, the binding sites are rapidly filled up with lanthanides ions (Gd) due to the high driving force for adsorption process. Therefore, influent concentration was inversely related to t_s and t_b , whereby the values of t_b and t_s decreases from 530 to 120 min and from 3090 to 690 min, respectively, as the initial concentration increased from 10 to 100 mg/L. Similarly, the bed capacity q_e also decreased with an increase in influent concentration, which implies that not all active sites of BPNC were saturated [24]. The result suggests that REEs

removal by BPNC-fixed bed is more favourable at low influent concentrations (Table 4).

Moreover, the volume of water processed at breakthrough point decreased from 1325 to 300 mL as the initial concentration increased from 10 to 100 mg/L. As a result, AER values increased with increase in concentration (see Table 3).

3.2.4 Alginate immobilised banana peels nanocomposite behaviour in real mine water treatment: The performance of BPNC in real mine water sample was investigated with tailing seepage obtained from gold mine site in Randfontein,

Table 4 Summary of fixed-bed column parameters for REEs and radioactive minerals in real mine water onto BPNC

Element	Co, mg/L	t _b , min	t _s , min	<i>q</i> ₀, mg/g	q₅, mg/g	BV	AER, g/L	V _b , mL
U	48.8	120	690	2.93	10.6	47.74	16.7	300
Th	18.8	180	930	1.69	5.9	71.61	11.1	450
La	12.4	210	1170	1.29	5.3	83.6	9.52	525
Gd	4.81	360	1890	0.87	2.71	143.2	5.56	900



Fig. 9 Adsorptive performance of BPNC in the removal of minerals (U 48.8, Th 18.8, La 12.24 and Gd 4.8) in real mine water (flow rate 2.5 mL/min, bed loading 5 g, column diameter 20)



Fig. 10 Thomas and Bohart-Adams modelling of gadolinium BTC (flow rate 2.5 mL/min, bed loading 5 g, concentration 20 mg/L and column diameter 20)

3.3 Modelling of BTCs

Johannesburg (South Africa). Several minerals were found in the mine water (Table 2), but this experiment focused on U, Th, Gd and La in the mine water sample based on the objective of this study. The breakthrough profile obtained with a bed mass of 5 g and an influent flow rate of 2.5 mL/min is shown in Fig. 9. The breakthrough time (t_b) and saturation time (t_s) were related to the mineral concentration. For instance, the values of $t_{\rm b}$ for U (48.8), Th (18.8), La (12.24) and Gd (4.8) mg/L are 120, 180, 210 and 360 min, respectively. Conversely, adsorption capacity increased with an increase in inlet initial concentration. As already, indicated, higher concentration provides higher driving force for adsorption leading to the observed trend [25]. The observations reported in this work were similar to the outcomes of many investigations related to mine effluent treatment using agricultural-based adsorbent [19, 26]. Generally, the performance of BPNC was reduced with mine water, which could be ascribed to the complex nature of the mine water. In such case competition amongst coexisting ions also play a role in determining their performance.

ity increased model [28]

of the effluent BTCs. The Thomas model [27], Bohart–Adams model [28] and the BDST model [29] were used to analyse the breakthrough behaviour of BPNC–REEs system in this study. A critical analysis of fixed-bed breakthrough models was done by Han *et al.* [30]. Thomas (5) and Bohart-Adams (6) parameters were evaluated through the concept of correlation coefficient R^2 using GRG non-linear engine solver in excel solver-add in [27]. The breakthrough experimental data fitted with non-linear Thomas and Bohart–Adams models are presented in Figs. 10 and 11. Using correlation coefficient R^2 as a measure of degree of fitness, the fixed-bed experimental data fitted satisfactory well in Thomas model than with Bohart–Adams model for both synthetic and real mine water. This indicated that the sorption of REEs and radioactive minerals are not limited to only chemical interaction

The successful design of a fixed-bed adsorber requires accurate

prediction of the effluent BTCs. To achieve this, different kinetic

models were applied to the experimental data obtained from REEs

and radioactive minerals fixed-bed adsorption. This was in order to

evaluate the effect of each process variable and accurate prediction



Fig. 11 Thomas and Bohart–Adams modelling of U, Th, and Gd and La BTCs (flow rate 2.5 mL/min, bed loading 5 g, concentration U (48.8), Th (18.8), La (12.24), Gd (4.8) mg/L and column diameter 20 mm)

 Table 5
 Thomas and Bohart–Adams models parameters obtained under different experimental conditions for Gd adsorption onto BPNC

Parameters	k _{Th} × 10 ^{−5} , mL/min mg	q ₀ , mg/g	R^2	k _{BA} × 10 ^{−5} , L/mg min	N ₀ ,mg/L	R^2
adsorbent mass (g)						
3	3.21	9.65	0.9999	8.41	13,803.4	0.8421
5	2.11	8.69	0.9998	4.18	16,372.1	0.7582
10	1.60	6.43	0.9998	2.56	13,584.1	0.7511
15	1.50	6.82	0.9996	2.27	10,906.9	0.8020
initial conc. (mg/L)						
10	2.59	7.44	0.9998	7.90	11,129.6	0.8460
20	2.09	8.69	0.9998	4.18	16,372.1	0.7581
50	1.23	12.46	0.9997	2.87	21,949.9	0.7980
100	1.22	12.7	0.9988	1.98	24,711.1	0.7171
flowrate (mL/min)						
0.68	1.05	7.12	0.9988	2.89	9280.3	0.8750
1.67	1.23	9.84	0.9987	3.84	14,839.7	0.8502
2.5	2.09	8.69	0.9988	4.18	16,372.1	0.7581
5	3.15	10.56	0.9888	6.39	18,548.5	0.7832

Table 6 Thomas and Bohart–Adams models parameters obtained for U, Th, La, Gd adsorption onto BPNC

Element of interest	Thomas model $k_{\rm Th} \times 10^{-5}$, mL/min	<i>q</i> ₀ , mg/g	R^2	Bohart–Adams model $k_{BA} \times 10^{-5}$, L	_/mg N ₀ , mg/l	- R ²
	mg			min		
uranium	2.70	7.9	0.9955	4.75	124.6	0.7458
thorium	4.69	3.10	0.9914	9.34	685.2	0.7778
lanthanum	5.96	3.0	0.9890	9.96	617.6	0.7245
gadolinium	8.66	2.16	0.9767	25.04	337.7	0.8021

with BPNC, but also by the mass transfer at the interface. This observation is similar to the reported results in the study conducted by Negrea *et al.* [31] whereby all BTCs fitted satisfactory well into Thomas model.

It could also be observed from Table 5 that a decrease in $k_{\rm Th}$ values occurred with increase in bed loading, which is characteristic of an increased mass transport resistance. The $k_{\rm Th}$ values increased from 1.05×10^{-5} to 3.15×10^{-5} (mL/min mg) as the flow rate increased from 0.68 to 5 mL/min; a similar observation was also noticed in real mine water breakthrough prediction (Table 6). Meanwhile the q_0 values predicted by the Thomas model are lower than q_e obtained experimentally for all process variables. This deviation could be attributed to the assumption made during modelling that the adsorption process followed Langmuir adsorption–desorption isotherm with no axial dispersion. Consequently, the adsorption capacities q_0 at 5 g bed loading and 2.5 mL/min flow rate were computed and found as

8.69 mg/g for Gd in synthetic water, and 7.9, 3.10, 2.16 and 3.0 mg/g for U, Th, Gd and La, respectively, in real mine water.

The evaluation of the column capacities and the variation of service time with bed height were also evaluated using BDST model and shown in Fig. 12. This model disregards all the effects of both external and intraparticle mass transfer resistances. In addition, this model provides all the necessary information for the design of fixed-bed system. The breakthrough point was taken at random ($C_t/C_0 = 0.002$, 0.1 and 0.2) due to unknown REEs allowable limit. The values of K_a were calculated from the intercept and N_0 from the slope of BDST plot at a breakthrough point. Tables 7 and 8 showed that the values of N_0 and K_a were 2.62 g/L and 0.25 L/mg h, respectively. The service time-bed depth plot at $C_t/C_0 = 0.002$. The high correlation factor (R^2) obtained from BDST model in Gd adsorption was 0.998, and conform to the fixed-bed experimental data. However, the linear regression fits of



Fig. 12 Linear plot of BDST for gadolinium onto BPNC

Table 7 Computed BDST equation parameters at breakthrough points ($C_t/C_0 = 0.002, 0.1, \text{ and } 0.2$)

Breakthrough point (C_t/C_o)	Gadolinium						
	а	b	<i>N</i> o × 10 ³ , mg/L	Ka, mg/L, h	R^2		
0.002	164.6	-65.74	2.62	2.5 × 10 ^{−1}	0.999		
0.1	153.7	-97.88	2.44	11.2 × 10 ^{−3}	0.988		
0.2	165.8	-192.8	2.63	3.59 × 10 ⁻⁴	0.996		

 Table 8
 Predicted breakthrough times based on the BDST constants for a new flow rate or new influent concentration (Z = 2cm) for gadolinium adsorption

C_t/C_o	a ¹ , min,cm ⁻¹	b ¹ , min	t _c , min	<i>t</i> _e , min	E %
$Q^1 = 5 \text{ mL/min, } C_0 =$	= 20 mg/L				
0.002	82.31	-65.74	230.32	240	4.00
0.1	76.84	-97.88	251.6	440	42.8
0.2	82.91	-192.8	358.6	530	32.3
$Q^1 = 1.67 \text{ mL/min}, 0$	$C_0 = 20 \text{ mg/L}$				
0.002	246.4	-65.74	558.5	410	36.2
0.1	230.0	-97.88	557.9	690	19.1
0.2	248.2	-192.8	689.2	870	20.8
$Q^1 = 2.5 \text{ mL/min, } C_0$	_o = 50 mg/L				
0.002	65.85	-26.29	158	150	5.33
0.1	61.47	-39.15	162.1	240	32.5
0.2	66.3	-77.12	209.8	270	22.3
$Q^1 = 2.5 \text{ mL/min, } C_0$	_o = 10 mg/L				
0.002	329.24	-131.5	789	750	5.2
0.1	307.34	-195.76	810.36	810	0.04
0.2	331.64	-385.6	1048.9	990	5.86

the experimental data were performed and the correlation coefficients (R^2) were obtained.

The data used for this graph were taken from breakthrough point ($C_t/C_0 = 0.002$, 0.1 and 0.2). The values of K_{BDST} were calculated from the intercept and N_0 from the slop of BDST plot at breakthrough point

Note:
$$t = az - b$$
 (8)

where

$$a = \frac{N_{\rm o}}{C_{\rm o}u} \tag{9}$$

$$b = \frac{1}{K_{\rm a}C_{\rm o}} \ln \left(\frac{C_{\rm o}}{C_{\rm t}} - 1\right) \tag{10}$$

Note: Error function (E) can be expressed as

$$E = \frac{t_{\rm c} - t_{\rm e}}{t_{\rm e}} \times 100 \tag{11}$$

where t_e experimental breakthrough time and t_c is the predicted breakthrough time

The predicted time (t_c) and experimental time (t_e) together with percent values of error (*E*) are shown in Table 8. The lower the values of *E*, the more accurate are the predictions. For instance, from Table 8, the prediction for a flow rate of 5 mL/min at $C_t/C_o = 0.002$ was considered good prediction due to small percentage error of 4% in Gd adsorption. Considering the assumptions obtained from scale-up study, it could be concluded that the BDST model provided useful design information with regard to the changes in system parameters.



Fig. 13 The desorption of REEs from BPNC

(a) Effect of different eluents on the desorption of lanthanide from BPNC, (b) Adsorption-desorption of lanthanide from BPNC (duration 24 h, initial concentration 100 mg/L, pH 5.20)

3.4 Desorption and reusability studies

The desorption of REEs from BPNC was investigated in a batch reactor using deionised water, 0.5 M NaOH and 0.5 M HCl eluents as presented in Fig. 13a. The percentage quantities desorbed using deionised water and NaOH were below 2% for both La and Gd. However, HCl was able to desorb 82 and 61% of La and Gd, respectively. Subsequently, 0.5 M HCl was used in adsorptiondesorption cycles. Fig. 13b shows the adsorption-desorption results after four repeated cycles using 100 mg/L adsorbate and 0.5 M HCl eluent. The percentage removal for Gd decreased from 98.5 to 59.0% and La from 95.6 to 35.0% with an increase in reusability of BPNC. The loss in adsorption capacity is an indication that Gd and La were chemically bonded to BPNC. Loss of adsorption capacity with repeated use of adsorbent has been observed and reported in different studies [32-34]; hence, the observation in our study is not peculiar.

4 Conclusions

The preparation, characterisation and the performance of nanocomposite pellets obtained from banana peels (BPNC) for the removal of REEs and radioactive minerals from wastewater was investigated using fixed-bed column. The BPNCs were porous, spherical in shape, and with rough surfaces Fourier transform infrared analysis revealed the presence of siloxane (Si-O-Si and Si-O-Al) groups which confirmed the presence of supported materials (montmorillonite) in immobilisation studies. XRD analysis revealed additional phases after immobilisation, which were ascribed to the alginate and montmorillonite. The breakthrough behaviour mainly depended on process variables such as bed loading, volumetric flow rate and influent concentration. The volume of water treated increased with an increase in bed loading for Gd adsorption. Also, the bed capacities of BPNC were observed to increase with an increase in bed height for La and Gd adsorption. Thomas and BDST model fitted the U, Th, La, Gd experimental BTCs with high correlation coefficients of 0.999 in almost all experiments. The BDST model was used to predict the relationship between service time and breakthrough point at different conditions. However, the predicted theoretical breakthrough times at 0.002 and high flow rate (5 mL/min) are in good agreement with experimental values with small E%. Adsorption-desorption study confirmed loss of adsorption capacity with the repeated use of the adsorbent.

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