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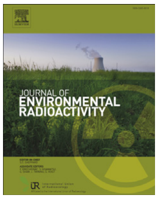

Application of banana peels nanosorbent for the removal of radioactive minerals from real mine water

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ABSTRACT

Transformation of agricultural waste such as banana peels into a valuable sorbent material has been proven effective and efficient in wastewater treatment. Further, transformation into nanosorbent to enhance the removal capacity of actinides (uranium and thorium) from synthetic and real mine water is extensively investigated in this study. The nanosorbent samples before and after adsorption were characterised by X-ray diffraction (XRD), Fourier transform infra-red (FTIR), zetasizer nanoseries and scanning electron microscopy (SEM) while the amount of radioactive substances adsorbed was determined by inductively coupled plasma optical emission spectroscopy. Results revealed that there was a crystallite size and particle size reduction from 108 to 12 nm and <65,000 nm to <25 nm respectively as a function of milling time. Furthermore, appearance and disappearance of nanofibers via milling was noticed during structural analysis. The functional groups responsible for the banana peels capability to coordinate and remove metal ions were identified at absorption bands of 1730 cm^{-1} (carboxylic groups) and 889 cm^{-1} (amine groups) via FTIR analysis. Equilibrium isotherm results demonstrated that the adsorption process was endothermic for both uranium and thorium. The Langmuir maximum adsorption capacity was 27.1 mg g^{-1}, 34.13 mg g^{-1} for uranium and 45.5 mg g^{-1}, 10.10 mg g^{-1} for thorium in synthetic and real mine water, respectively. The results obtained indicate that nanostructured banana peels is a potential adsorbent for the removal of radioactive substances from aqueous solution and also from real mine water. However, the choice of this sorbent material for any application depends on the composition of the effluent to be treated.

1. Introduction

Radioactive contaminants were first discovered prior to World War II during a test carried out on mineral waters from the mines. The results indicated the presence of abnormally high concentrations of natural radioelements. This was because the newly discovered materials seemed to possess curative powers (Eisenbud and Gasell, 1997). Aside from the mines, radionuclides such as uranium (U) and thorium (Th) find their way into the environment and ground water through the nuclear, metallurgy and ceramic industries in which their usage is paramount. Thorium can also be used as a nuclear fuel through breeding to uranium-233 (U-233). In fact, major possibilities for U contamination to the ground water might be from industrial operation of extracting plutonium from irradiated U. It has been reported by Dutch research organisations that the rising demand for uranium to produce nuclear energy has led to an increase of uranium mining in several African countries (Sheree, 2011). Chantelle (2015) also reported that heavy rainfalls have resulted in the rapid rise of radioactive substances in underground water levels in Johannesburg, South Africa. The fact that radioactive substances such as U and Th are very toxic and highly harmful in small amounts, gives an additional reason for extensive investigation in the area of radioactive removal.

Even though U and Th are weakly radioactive and unstable, they are mostly in a constant state of decay, searching for more stable arrangement, they were still discovered to be present in municipal and drinking water (Organization, 2004). This has led some countries to require that the labels on bottled mineral waters should

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contain information on the measurement of radioactivity of the spring from which the water was obtained (Lewis, 1955). Lorenz (1944) reported the incidence of one multigenerational uranium miner in United Kingdom diagnosed with fatal lung diseases which later resulted to lung cancer. This was contacted through erosion by flowing U water in the mine environment. Therefore more research has to be done to develop technologies that can remove completely radioactive materials from mine water before it is discharged to the environment.

The techniques used to address this problem by several researchers have been largely inefficient and ineffective. For instance, techniques like coagulation, co-precipitation, filtration, ion exchange, membrane separation and adsorption (Rein, 2013) have been investigated for the treatment of radioactive laden water. Riodan et al. (1997) combined precipitation and biosorption methods using residual brewery yeast as biosorbent media and reported 360 mg/g biosorption capacity. This confirms the efficiency of these methods; however, they are not environmentally friendly due to the requirement of large settling tanks for the precipitation of voluminous alkaline sludge which requires subsequent treatment. Adsorption process is highly economical and capable of removing contaminants even at trace level. The use of this technique in water and wastewater treatment due its simplicity, low cost of operation and wide end use has been reported before (Naeem et al., 2007). However, the performance of any adsorption process is highly dependent on the choice of an appropriate media. Activated carbon is one of the common adsorbents that are highly efficient in uranium and thorium removal from aqueous solution and acidic medium, but it is highly expensive to develop (Ahmed et al., 2014; Loukiahadjittofi, 2012). Anirudhan et al. (2013) reported 2.4 mg/g adsorption capacity for thorium removal onto carboxylate-functionalized graft co-polymer derived from titanium dioxide-densified cellulose. This is considered an inefficient and non-effective adsorbent due to its lower capacity compared to natural materials with high content of cellulose. For instance, pineapple peels, sugarcane bagasse, coconut coir, citrus limetta peels (Hossain et al., 2012; Sachin and Sanjeev, 2014) and banana peels nanosorbent (used in this study) are cellulose constituent materials. The major structural components of banana peels are cellulose (75%) and nanofibers (5.1%). Cellulose is a glucose polymer bounded in the β-1,4 linkage configuration (Riantong et al., 2013; Franceiele et al., 2014).

Even though banana peels have been used earlier as a base material for the development of many adsorbents to remove metal ions, low adsorptive performance was reported (Bakiya and Sudha, 2012; Ashok et al., 2010). It is speculated that the effect of some properties such as surface area and particle size in material preparation could be responsible for this low performances. For instance, Castro et al. (2011) reported the use of banana peels (particle size 35–45 μm) with adsorption capacity of 20 mg/g for copper removal from aqueous solution. This implies that the performance would have been more efficient with increment of active sites. It was reported that advances in nanoscience and nanotechnology have expanded the ability to develop nanomaterials with enhanced properties to solve the current problems in water treatment. As a result of their small size, nanomaterials can exhibit an array of unique novel properties which can be utilized in the development of new metal treatment technologies and improvement of existing ones (Arup and Jayanta, 2015).

In this study, banana peels were transformed into nano size in order to take advantage of their improved chemical and physical properties for mine water treatment. Nanostructure formation was confirmed through characterization and radioactive substances removal performance explored in a batch adsorption mode. Adsorption isotherm results were interpreted using Langmuir and Freundlich isotherms.

2. Experimental

Banana peels (*Musa paradisiacal*) were simply separated from bananas and cut into smaller pieces while still wet. The peels were washed with deionized water to remove the adhering dirt and then sun dried for 10 days. The dried peels were crushed and screened to obtain a particle size of <65 μm. Acidic and alkali treatment was then done to enhance their sorption capacity using NaOH and HNO_3. These chemicals were obtained from Sigma Aldrich, South Africa and were of analytical grade.

Mechanical milling of crushed banana peels (<65 μm) was carried out in a planetary continuous ball mill machine (PM 100 CM) at a constant speed of 200 rpm using 10:1 powder to ball ratio. The energy consumption of the milling process was determined to be 1.5 kJ/h. The wet milling was done for 30 h and the samples were taken at 10 h intervals to observe the structural changes. Ethanol was used as a process control agent as well as a bleaching agent to remove the yellowish colour of ripe banana peels. The microstructural characterization of milled banana peels was carried out with a wide angle diffractometer using analytical empyrean advance diffractometer with a quartz sample holder, with Cu K α radiation (λ = 0.15,406 nm, 40 kV, 40 mA and increment 0.01°). The high score plus program was used to determine the crystalline sizes at different milling times (0 h–30 h), using the PROFILE-FIT package (Mhadhbi et al., 2010). Moreover, the physical profiles such as width broadening of the peaks were calculated from the integral width of the physical broadening profile by the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta\ COS\ \theta} \tag{1}$$

where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; K is a dimensionless shape factor with a value close to unity; λ is the X-ray wavelength; and β is the line broadening at half the maximum intensity (FWHM) after subtracting the instrumental line broadening in radians and θ is the bragg angle.

The Fourier transform infrared spectroscopy (FTIR) analysis was done to identify the functional groups using a Perkin Elmer Spectrum 100 spectrometer. The spectra were recorded in the 500–4000 cm^{-1} range at a resolution of 4 $cm^{-1.}$ The morphology and composition of the milled samples were characterized by SEM/EDX using a JEOL JSM-7600F Field Emission Scanning Emission Microscope (FESEM), running at an accelerating voltage of 2 kV. The adsorbent zeta potential analysis was done using zetasizer nanoseries (Malvern instruments). Synthetic water was prepared in binary solution using uranium and thorium nitrate salts. Real mine tailing seepage was obtained from one of the gold mining operations in South Africa situated at about 40 km South-West of Gauteng province. Batch equilibrium experiments were performed to determine the adsorptive performance of banana peels nanosorbent (BPN) on the removal of radioactive substances from aqueous solution. Firstly, the effect of solution pH was studied in order to determine the optimum pH for the process. Using either NaOH (0.1 M) or HCl (0.1 M), the initial pH was adjusted from 2 to 10 (the equilibrium pH is presented in Table 3). In addition, 0.1 g of BPN was added to 100 mL plastic bottles containing 50 mL solution of actinides (radioactive) in synthetic and real mine water. U and Th of similar initial concentrations (100 mg/L) were employed in synthetic water in binary solution. The real mine water contained 55.8 mg/L and 18.8 mg/L of U and Th, respectively. Thereafter, the bottles were placed in a thermostatic shaker operated at 200 rpm for 24 h. At the end of the contact period, the samples were filtered