

The performance of nano-sized Banana Peels in the removal of vanadium from mine water

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Abstract

South African mine water might contain several harmful contaminants such as, but not limited to vanadium. Therefore, this study described the development and application of a newly developed banana peel nano-adsorbent (BPN) for the removal of vanadium from synthetic water. The adsorbent was characterized using scanning electron microscopy (SEM), Fourier transform infra-red (FT-IR), particle size distribution while the amount of rare earth elements (REEs) adsorbed were determined by ICP-OES. It could be shown that the milling process reduced the particle sizes from smaller than 65 μm to below 25 nm and the crystallite sizes from 108 to 12 nm. FT-IR analysis revealed that the coordination and the lanthanide removal results from amine and carboxylic groups with adsorption bands at 889 cm^{-1} and 1730 cm^{-1} , respectively. Langmuir isotherms gave a good description of vanadium adsorption onto BPN with maximum adsorption capacity of 27.94 mg g⁻¹. However, the matrix of the mine water to be treated substantially determines which sorbent needs to be used

Keywords: mine water, mechanical milling, batch adsorption, agricultural waste, rare earth elements

Introduction

South Africa economy might not survive without mining operation as it has become their source of income over the years. Toxic metals mined such Pb, Cr, and V are used industrially worldwide but also contaminates the surface and underground water due to their bioavailability. In addition, South Africa has been recognised as the second largest steel maker in which vanadium is an important additive in steel making. The contamination is significant therefore also finds its ways into the environment from the industries in which its usage is paramount.

Even though vanadium-laden water has been treated by many researchers via various techniques and mechanisms such as chemical precipitation, solvent extraction, micellar ultrafiltration, ion exchange and adsorption (Lynn and Kerry 2005 ; Srivastava 2006). It has been reported that the use of adsorption process remain the most cost effective meth-

od (Alimohammadi et al. 2016; Bakiya et al. 2012)

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 is reported (Naeem et al. 2007). However, the success of the above mentioned process is highly dependent on the choice of appropriate media. As such, a number of sorbent materials have been investigated for the removal of vanadium from wastewater which include polymer composite, zeolite, clay and agricultural waste (Abollino et al. 2008; Kaczala et al. 2009; Kurniawan et al. 2006; Mariangela et al. 2012).

Agricultural resources considered as waste, such as sugarcane bagasse, pineapple peels, coconut coir, apple waste and banana peels have been employed to remove metals from waste water. This is possible due to



the presence of useful constituents and acid groups such as cellulose, carboxylic and phenolic groups that are necessary for the effective treatment of industrial effluent. These materials can also be used in metal speciation, as in the case of Cr (VI) sorption by coconut coir (Gonzalez et al. 2008). Advances in nanoscience and nanotechnology have expanded the ability to develop nanomaterials with enhanced properties to solve the current problems involving water treatment. The main property that makes nanomaterials attractive is that they are extremely small in size (1-100 nm), which provides higher surface area per unit mass compared to their micron size counterparts (Arup and Jayanta 2015). In this study, nanostructured banana peels were developed in order to take advantage of their improved chemical and physical properties in vanadium removal from aqueous solution.

Experimental

Banana peels (*Musa paradisiacal*) were obtained, cut into chips and 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 <65µm. The details of mechanical milling of crushed banana peels (<65µm) and all necessary characterization analyses was reported elsewhere (Oyewo et al. 2016).

Batch equilibrium experiments were performed to determine the performance of BPN on vanadium removal from aqueous prepared by decomposition of ammonium metavanadate in deionised water at around 200 °C (Crans 2005).

Firstly, the effect of solution pH was explored by varying pH from 2 to 10 using either NaOH (0.1 M) or HCl (0.1 M) for initial pH adjustment. The effect of sorbent loading was explored by varying the mass of the sorbent

from 0.01 g to 0.2 g while the effect of concentration was explored by varying the concentration of the V synthetic solution from 20 to 200 mg/L. Finally, the effect of temperature was determined by varying the temperature from 25 to 45 °C, with a 50 mg/L V solution at a pH of 2.10. The sorbent mass was fixed at 0.2 g for the latter experiments. For each experiment, 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 using 0.2 µm pore size polypropylene syringe filters and the filtrate was analysed by inductive coupled plasma optical emission spectroscopy (ICP-OES) to determine the equilibrium concentration of V.

The percentage removal efficiency R_t was calculated (equation 1):

$$R_t = \frac{C_o - C_e}{C_o} \cdot 100 \quad (1)$$

where C_o (mg·L⁻¹) is the initial lanthanides concentration, C_e (mg·L⁻¹) the concentration of lanthanides at equilibrium. All batch tests were performed in polypropylene tubes and sorbents separation as well as filtrate analysis was done accordingly.

Results and discussion

Characterization result

It was observed that as the milling progressed, the fracturing of the particles increased and more nanoparticles were formed as shown in Table 1. Clearly, mechanical milling gives a narrow size distribution of BPN which is a necessary precondition for a good adsorption media.

Adsorption results: Effect of pH

The nano-sized banana peels (BPN) removed very high concentration of V at pH 2 (Fig. 1.). A steep decrease in V uptake was observed

Table 1. Summary of TEM and particle size distribution analyses of milled banana peels

| Milling time (h) | Average particle size (nm) | Mean crystalline size (nm) | Lattice strain (%) |
|------------------|----------------------------|----------------------------|--------------------|
| 0 | < 65000 | 108 | 0.24 |
| 10 | < 300 | 71 | 0.63 |
| 20 | < 65 | 20 | 0.64 |
| 30 | < 25 | 12 | 0.69 |



with an increase in pH up to 8, indicative of the interaction of cationic V species with the surface hydrophilic of BPN. At low pH, positively charged V species predominant, therefore higher percentage removal observed might be due to hydrophobic interactions and hydrogen bonding since BPN is highly electronegative throughout the pH range (Oyewo et al., 2016). At pH 4–8, anionic V species predominate (Crans 2005) and this could explain the lower removal rates within this range. Crans (2005) reported that a higher pH causes a higher degree of protonation and polymerisation of V ions, which could limit removal of anionic V species, even at optimum pH. Therefore, adsorption of V onto BPN was pH dependent, and mainly occurred due to interaction between hydrophilic surface of BPN and the cationic V group.

Adsorption result: Sorption isotherms

The temperature dependence of V sorption from synthetic water was explored by varying the temperature from 25 to 45 °C (Fig.2). It was observed that an increase in equilibrium concentration increased V equilibrium uptake for all the temperatures studied. Moreover, the adsorption capacity increased as the temperature rose, indicating that V sorption on BPN is temperature dependent. The enhanced sorption at higher temperatures may

have been due to a decrease in the thickness of the boundary layer surrounding the BPN. There is also a possibility that the increased movement of the molecules as the temperature rose increased the uptake. The data provided from sorption equilibrium are used to describe the interaction between adsorbate and adsorbent for effective design of an adsorption process. Furthermore, sorption equilibrium data are used in comparing the performance of different media for a given sorption process. Consequently, the experimental data were analysed using Langmuir and Freundlich models (Table 1).

The linear form of the Langmuir and Freundlich adsorption isotherm equations are given in equation (2) and equation (3), respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where C_e (mg/L) is the concentration of V at equilibrium, q_e (mg/g) the V equilibrium uptake, b is the Langmuir constant and q_0 is the adsorption capacity of the monolayer; K_F and n are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively.

The Langmuir isotherm parameter q_0 , which measures the monolayer capacity of the adsorbent, increased with an increase in temperature, as did the predicted K_F values

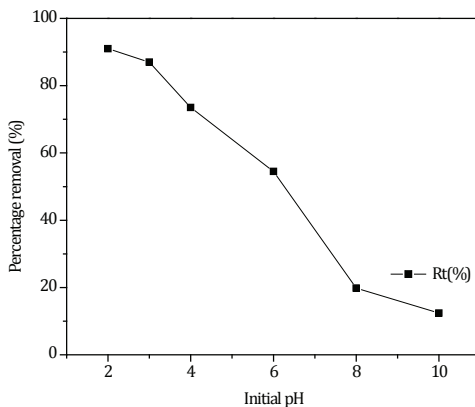


Figure 1 Effect of solution pH in the adsorption of vanadium in synthetic water onto banana peels nanosorbent (BPN)

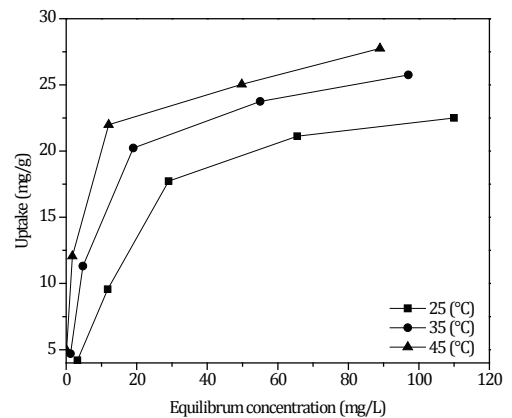


Figure 2: Isotherm for vanadium synthetic water onto BPN



Table 1. Isotherms parameters for vanadium adsorption onto BPN

| Temperature (°C) | Langmuir isotherm parameters | | | Freundlich isotherm parameters | | |
|------------------|------------------------------|------------|-------|--------------------------------|----------------------|-------|
| | q_m (mg/g) | b (L/mg) | R^2 | K^f (L/g) | $1/n$ | R^2 |
| 25 | 26.2 | 17.10 | 0.997 | 2.69 | 4.9×10^{-1} | 0.946 |
| 35 | 27.2 | 6.62 | 0.999 | 5.27 | 3.8×10^{-1} | 0.931 |
| 45 | 27.9 | 2.48 | 0.997 | 9.56 | 2.6×10^{-1} | 0.968 |

from the Freundlich isotherm; an inconsistent pattern was noted for the Langmuir constant b . K_f is related to the sorption capacity, and its increase matched the enhanced sorption (Table 1). Comparing the Langmuir and Freundlich adsorption isotherm correlation values (R^2), the Langmuir isotherm gave a good description of V adsorption onto BPN. This was similar to the results reported by Manohar et al. (2005).

Conclusions

In this study, nanostructure formation of banana peels and its performance in Vanadium removal from aqueous solution has been demonstrated. The surface area increment of crushed banana peels powder (1.0694-4.5547 m²/g) was observed as milling time increased (0 to 30 h) (Oyewo et al. 2016). The extent of adsorption was controlled primarily by pH and temperature. A solution pH of 2.10 was adopted for the sorption of Vanadium from synthetic water, which is consistent with the chemical interaction between the hydrophilic surface of BPN and the cationic Vanadium species. It was observed that a dosage of 0.2 g of BPN was required for 91 % removal of Vanadium from 100 mg/L initial concentration (aqueous solution). The Langmuir isotherm model gave a good description of Vanadium adsorption onto BPN compare to Freundlich isotherm model. Considering the availability of banana peels as a waste material, and the competitive sorption capacity achieved through milling, this material can be a potential candidate for treatment of vanadium-laden mine water.

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References

- Abollino O, Giacomino A, Malandrino M, Mentasti E (2008) Interaction of metal ions with montmorillonite and vermiculite. *Appl Clay Sci* 38(3):227-236. doi:10.1016/j.clay.2007.04.002
- Arup R, Jayanta B (2015) *Nanotechnology in industrial wastewater treatment*. IWA Publishing, 12 Caxton street, London
- Alimohammadi Z, Younesi H, Bahramifar N (2016) Batch and Column Adsorption of Reactive Red 198 from Textile Industry Effluent by Microporous Activated Carbon Developed from Walnut Shells. *Waste and Biomass Valorization* 7(5):1255-1270. doi:10.1007/s12649-016-9506-4
- Bakiya LK, Sudha PN (2012) Adsorption of Copper (II) ion onto chitosan/sisal/banana fiber hybrid composite. *J Environ Sci* 3(1):453. doi:10.6088/ijes.2012030131044
- Crans DC, (2005) Fifteen years of dancing with vanadium. *Pure Appl. Chem.*, 9(77):1497-1527. doi: 10.1351/pac200577091497.
- Oyewo OA, Onyango MS, Wolkersdorfer C (2016) Nanostructure formation, characterization and application of banana peel in trivalent lanthanides removal from aqueous solution. *Tshwane university of technology*, p 1-17
- Gonzalez MH, Araujo GCL, Pelizaro CB, Menezes EA, Lemos SG, de Sousa GB, Nogueira ARA (2008) Coconut coir as biosorbent for Cr(VI) removal from laboratory wastewater. *J Hazard Mat* 159(2-3):252-256. doi:10.1016/j.jhazmat.2008.02.014
- Kaczala F, Marques M, Hogland W (2009) Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto *Pinus sylvestris* sawdust. *Bio-*



- resource Technology 100(1):235-243. doi:http://dx.doi.org/10.1016/j.biortech.2008.05.055
- Kurniawan TA, Chan GYS, Lo W-h, Babel S (2006) Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of The Total Environment* 366(2-3):409-426. doi:http://dx.doi.org/10.1016/j.scitotenv.2005.10.001
- Lynn EK, Kerry AK (2005) Treatment of produced water using a surfactant modified zeolite / vapour phase bioreactor system. Dept. of Civil, Architectural and Environmental Engineering University of Texas Austin, Texas 78712
- Manohar DM, Noeline BF, Anirudhan TS (2005) Removal of vanadium (IV) from aqueous solutions by adsorption process with aluminum-pillared bentonite. *Ind Eng Chem Res* 44(17):6676-6684
- Mariangela G, Gul K, Vincenzo B, Guisy L (2012) Removal of emerging contaminants from water and wastewater by adsorption process. In: Grassi M (ed) *Emerging Compounds Removal from wastewater*. vol 2, Via Ponte don Melillo, 84084 Fisciano (SA), Italy, p 15-24
- Naeem A, Westerhoff P, Mustafa S (2007) Vanadium removal by metal (hydr)oxide adsorbents. *Water Res* 10:37-146
- Srivastava VC (2006) Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. *Chemical Engineering Journal* 0315

