Thermodynamic Study Of The Adsorption Performance Of Spent Coffee Beans For The Removal Of Cadmium From Coal Tailing Leachates

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Abstract

In this study spent coffee beans were transformed into biochar using a hydrothermal method where after it was pre-treated through surfactant impregnation to enhance its adsorption capacity. The non-treated and pre-treated biochars were characterized using FTIR spectroscopy analysis, which revealed a successful preparation of biochar with the potential for adsorption. The adsorption potential and mechanism was predicted using thermodynamic study.

The adsorption of cadmium on the pre-treated (PT) biochar was found to occur spontaneously while it was the case for the non-treated (NT) biochar the adsorption reaction was not thermodynamically favourable. For both adsorbents, the adsorption of the cadmium was endothermic in nature due to the large positive enthalpy values, confirming that the adsorption of cadmium on NT biochar and PT biochar occurred through a chemisorption mechanism. Although the high concentrations of metals in the coal leachate resulted in competition for binding sites at the surface of adsorbent, relatively high adsorption capacity was achieved for the removal of cadmium from the coal leachate.

It could be therefore concluded that the temperature change substantially influences the adsorption behaviour and capacity of the prepared adsorbents.

Keywords: Spent coffee beans, biochar, surfactant impregnation, cadmium, coal tailings leachate, thermodynamic, adsorption

Introduction

The substantial decrease of coal grade over time has contributed to the increased production of large amount of fine coal with lower value from the separation processes which is over discharged in the environment in the form of tailing dumps (Oruc et al. 2010). These tailings dumps contain considerable amount of inorganic impurities such as metals which are often mobilised and released from the tailings following the formation of acid mine drainage itself due to the weathering or oxidation of sulphide minerals such as pyrite (Fosso-Kankeu et al. 2017a). The dispersion of metal such cadmium in surface and ground waters constitutes an environmental risk, due to the potential of cadmium adversely affect the equilibrium of the aquatic system and cause harm to human or animal relying on contaminated water. Concerns related to such risks have been growing over the years as the as recurrence of AMD formation has been reported in several geographical areas in the past decades. Furthermore, the conventional methods so far considered to remediate pollution are very expensive and not affordable in developing countries. The quest for affordable and sustainable technologies has resulted into the development of adsorption technologies that make use biodegradable, widely available adsorbents that can be obtained at negligible or no cost. Biochar can be produced by using organic materials as a feedstock. One of these materials is spent coffee grounds. Over 120 million bags of coffee are produced worldwide each year , which correspond to 7 million tons of coffee waste (Zuorro & Lavecchia 2012). These spent coffee grounds have no commercial value and are usually sent to compost facilities for disposal (Zuorro & Lavecchia 2012). This makes spent coffee beans an abundant feedstock available for the production of biochar. The adsorption capacity of biochar can be improved through physical or chemical methods. Temperature plays an important role during adsorption, in principle higher temperatures provide enough energy to reactants for them to react or come into contact; it is therefore expected that higher temperature will enhance the adsorption of metal onto the adsorbents. However, the multitude of studies have shown different trends, an increase of the adsorption of palladium onto immobilized bayberry tannin with increase of temperature (from 30 to 50°C) was reported by Wang et al. (2005), while Fujiwara et al. (2007) recorded a decrease of adsorption of different metals onto L-lysine modified crosslinked chitosan resin at higher temperature. According to these findings, it should be important to determine the optimum temperature for a specific adsorption process. Hence the focus of this study, which consists to investigate the effect of temperature on the performance of spent coffee-based biochar during the adsorption of cadmium.

Methods

Biochar production

A slurry of spent coffee beans was prepared for a 3 vol% biomass loading. The hydrothermal liquefaction (HTL) reactor tanks were filled with 60 L slurry, sealed and pressurized with Nitrogen gas (Baseline 5.0 bar) to 90 bar, where after the reactor temperature was increased to 305 °C. The HTL plant produced a product which is a mixture of an aqueous oil phase and biochar solid phase. The biocrude was separated from the aqueous phase via pressure filtration. The filtered biocrude was then dissolved in acetone to separate it from the biochar. The produced biochar was finally separated from the acetone solution in a Büchner filter. Before drying it for 12 hours at 105 °C. The dried biochar was crushed to a particle size less than 250 µm using a ceramic mill.

Biochar pre-treatment

The biochar was impregnated with sodium dodecyl sulphate (SDS) by adding 10 g of biochar to 1 L SDS solution (10 g/L); the mixture was incubated and stirred at 120 rpm for 24 hours at 60 °C.

The solution was then filtered by Büchner filtration. The biochar was then dried at 65°C for 12 hours, then the dried biochar was crushed to finer particles using a ceramic bowl.

Characterization of the biochar

The pre-treated (PT) and non-treated (NT) biochars were characterized by Fourier Transform Infrared Spectroscopy (FTIR) having an IRAffinity-1S from Shimadzu. The spectrometer had a spectral range from 4000 to 400 cm^{-1}. This process was used to identify the functional groups of the biochars.

Adsorption experiments

All the adsorption experiments were carried out in a batch system using NT and PT biochars separately. The biochar dosage was fixed at 0.2 g per 50 mL solution. The adsorption capabilities of treated and untreated biochar were tested, thus 2 sets of adsorbents were tested for each experiment. The effect of temperature on the adsorption behaviour was done by performing kinetics experiment for initial cadmium concentration of 50 mg/L and the temperature of the solution was increased from 35°C, 45°C and 55°C respectively.

Results and discussion

Characterization of adsorbents

The spectra of the treated and not treated biochars (Figure 1) show almost the same pattern of peaks. Substantial peaks were observed in the range 2100-2200 cm^{-1} which can be ascribed to the presence of adsorbent group C≡C deriving from the alkynes functional group. The peak at 2650 cm^{-1} suggests the formation of formic acid dominated by the carboxylic group which plays an important role in the binding of metals. Important binding groups such as C-H stretch and C=O can relate and play substantial roles during the adsorption process (Kantcheva 2003).

Thermodynamic study

To evaluate the thermodynamic properties of the biochar, batch adsorption experiments were conducted at three different temperatures (35°C, 45°C and 55°C).

To calculate the enthalpy change (ΔH°, KJ/mol), entropy change (ΔS°, J/mol/K) and gibbs free energy (ΔG°, KJ/mol) the van't Hoff equation below was used:

$$lnK_a = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (1)$$

where ka is the distribution coefficient, which is equal to q_e/c_e; T is the absolute temperature in Kelvin (K); and R is the universal gas constant (0.008314 KJ/mol/K). The values of ΔH and ΔS can be calculated from the respective slope and intercept of the trendline equation of Van't hoff plot (Figure 2) (lnka vs 1/T) (Lalvani et al. 1997; Leudjo et al. 1997; Fosso-Kankeu et al. 2017b). The values obtained were tabulated as shown in Table 1.

To determine the thermodynamic properties of the biochar Figure 2 was constructed by plotting lnK vs 1/T.

The positive values of the Gibbs free energy of the NT biochar (Table 1) indicate that the adsorption of cadmium on the char was not spontaneous in nature, while the adsorption onto the PT biochar exhibited a negative Gibbs free energy implying that the adsorption on the latter was spontaneous and therefore thermodynamically favourable. It is therefore clear that the chemical treatment has contributed to enhance the adsorption capacity of the biochar, given that PT biochar is more likely to interact and adsorb cadmium. On the other hand, the enthalpy for the adsorption of cadmium on both adsorbents was positive implying that the adsorption reaction was endothermic, which can be due to the well solvated metal ions, confirming that the adsorption of cadmium on NT biochar and PT biochar occurred through a chemisorption mechanism (Fosso-Kankeu et al. 2017b). The positive entropy values obtained for the PT biochar suggest randomness in the solid/liquid interface

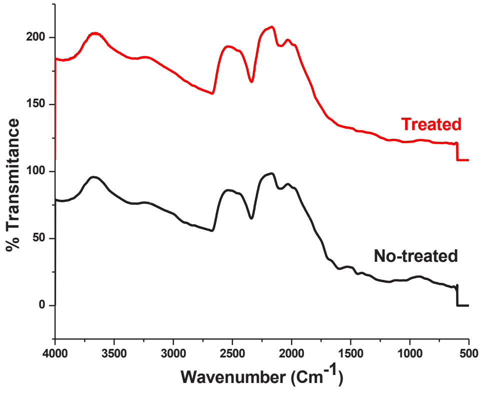

Figure 1 FTIR spectra of Non-treated and Pre-treated biochars

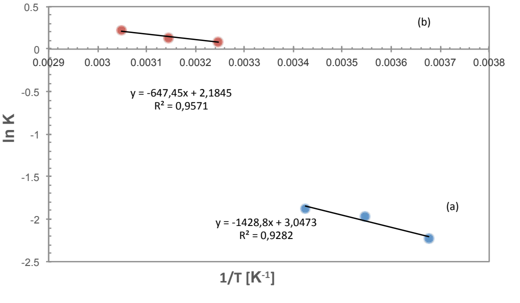

Figure 2 Thermodynamic analysis on the adsorption of Cd with (a) NT biochar, and (b) PT biochar with SDS

Table 1 Thermodynamic properties

Adsorbent	Ka	Temperature	ΔG (kJ/mol)	ΔS (J/mol/K)	ΔH (kJ/mol)
	0,1071	308	4075,79		
NT biochar	0,1406	318	3822,43	25,3	11879
	0,1532	328	3569,08		
	1,0941	308	-210,98		
PT biochar	1,142	318	-392,6	18,2	5382
	1,2442	328	-574,21		

where there are few structural changes in the adsorbent and adsorbate for the adsorption of Cd.

The Arrhenius activation energy Ea allows a better understanding of the mechanism of adsorption, it was therefore determined by plotting $\ln K_2$ vs 1/T) which is a relationship between the temperature and kinetic studies as illustrated in Figure 3.

The Arrhenius equation (Equation 2) allows to determine the activation energy as well as the adsorption rate.

$$K_2 = Ae^{-Ea/(RT)} \qquad (2)$$

Where K_2 is the equilibrium constant of the pseudo-order model, A is the pre-exponential factor and E_a is the activation energy.

The Ea can therefore be calculated from the slope of Equation (2). Ea > 40 KJ/mol is an indication of a chemical adsorption process, Ea < 40 KJ/mol indicates a physical adsorption or attraction process (Leudjo et al. 2018). The activation energy values calculated 6.6 KJ/mol and 7.8 KJ/mol for the NT biochar and PT biochar respectively were < 40 KJ/mol, implying that of the attraction of cadmium onto the adsorbents was predominantly of a physical nature. It could therefore be concluded physisorption and chemisorption concurrently take place during the uptake of cadmium by the adsorbents, which is due to the porosity of biochar as well as the presence of active groups at the surface which chemically react with cadmium.

Application of biochar for the treatment of coal tailings leachate

Samples of 100, 200 and 250 mg/L dissolved metals in coal leachate were spiked with 30 mg/L cadmium then exposed to the different biochars for adsorption. The results are shown in Figure 4.

As seen from Figure 4 at a 100 mg/L metal concentration, the adsorbent showed the highest affinity for cadmium adsorption from the solution. With the increase of the total metallic concentration the adsorbents ability to adsorb the cadmium decreases substantially due to competition for binding sites on the adsorbents by other metals present in solution. This trend was shown by both the NT and PT biochar. It is however clear that the PT biochar outperformed the NT biochar for each metallic feed concentration, validating the use of SDS impregnation in the removal of cadmium from aqueous mine tailings solutions.

Conclusions

The aim of this was to valorise organic waste for the treatment of water polluted with cadmium. It was found that biochar generated from spent coffee beans has the potential to adsorb cadmium from aqueous solution; the performance of biochar was enhanced through chemical treatment using the surfactant sodium dodecyl sulphate. The adsorption capacity of the both adsorbents increased with an increase of temperature; however, only the reaction between cadmium and the pretreated biochar was thermodynamically favourable. The adsorption was found to occur through a combination of physical and chemical mechanisms. The pretreated biochar achieved high adsorption capacity for the removal of cadmium from the coal leachate and could therefore be considered industrially for the treatment of such solution. The use of spent coffee beans as adsorbent could an

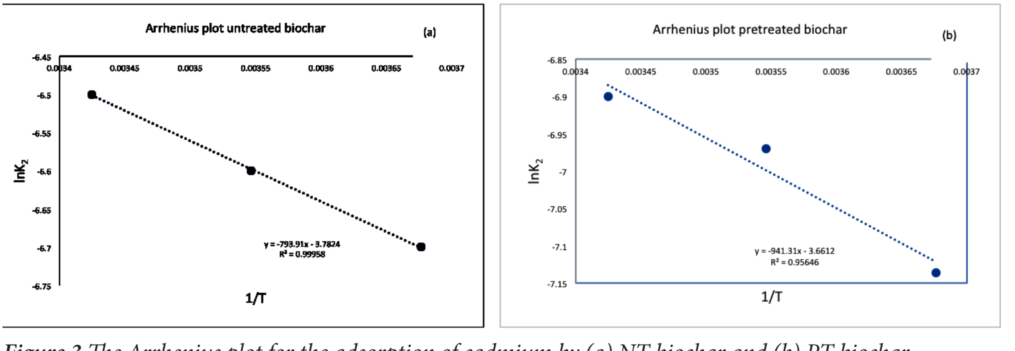

***Figure 3** The Arrhenius plot for the adsorption of cadmium by (a) NT biochar and (b) PT biochar*

economically viable alternative as it could be obtained at no cost.

Acknowledgements

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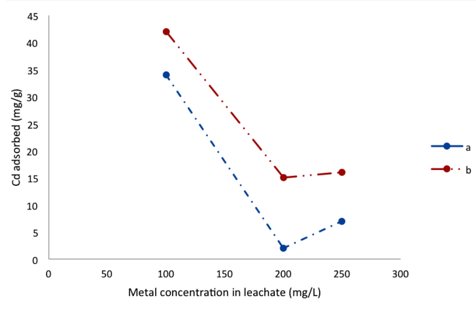

Figure 4 *Effect of whole solution concentration on the adsorption of Cd with (a) NT biochar and (b) PT biochar*

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