Adsorption of Metal Ions from Fine Coal Tailings Dump Waste Water using Bio-char

Elvis Fosso-Kankeu, Reinhardt Weideman, Dumisane Moyakhe, Frans Waanders and Quentin Campbell

***Abstract*— Coal mining operations produce large amounts of tailings which contains heavy metals. Heavy metals such as cadmium (Cd) can cause environmental problems. The adsorption capacities of biochars produced from spent coffee beans and brewery waste were explored for the removal of Cd from single and multi-component solutions. The biochars were prepared by hydrothermal liquefaction (HTL) and characterized by scanning electron microscope analysis (SEM) and Fourier transform infrared microscopy (FTIR). The developed adsorbents were utilized in batches of pre-treated and untreated biochar for the removal of Cd metal ions. The pre-treatment was done through surface impregnation with sodium dodecyl sulfate (SDS). The pseudo second order kinetic model was suitable in this study to predict the adsorption capacity of the pre-treated and untreated biochar; it was found that the pretreatment of biochar with SDS contributed to increase its adsorption capacity from 4.824 to 10.672. The pre-treated and untreated biochar can be used for the treatment wastewater contaminated with Cd.**

***Keywords*—** Adsorption, biochar, coal tailing, cadmium, surface impregnation

I. Introduction

Coal mining operations produce a large amount of coal spoil and tailing wastes that may cause environmental problems [1]. Because of the expansion of coal industries globally and locally (South Africa) more tailings are subsequently produced. These tailings need to be disposed of. If proper care is not taken, the wastewater from coal mining can pollute the environment. The release of heavy metals into the environment represents one of the most important environmental concerns related with the extraction of coal [2].

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However, intake of water containing high levels of these essential elements, or toxic elements such as Al, As, Ba, Cd, Cr, Pb, Hg, Se, and Ag, may cause acute or chronic toxicity [3]. Heavy metals such as Cd, Co, Cr, Mn, Pb, Ti, and V can be found in the rivers flowing through for example coalfields in Mpumalanga, South Africa at concentrations above the allowed levels. The Takht coalmine in Iran started in 2002 and has already had adverse effects on the quality of water resources in the area since the concentration of heavy metals in downstream groundwater is higher than in upstream water. The mining activities increased the Ba, Cr, Ni and Pb concentration in the area's surface water and groundwater [2]. In China, data from 72 mining areas showed from the pollution and health risk assessments that the soils surrounding the mining areas are seriously polluted by heavy metals emitted from mining activities [4]. From this, it can be deducted that heavy metal pollution from coal mining tailings is a local as well as a global issue.

Precipitation and coagulation is a widely used method to remove heavy metals from aqueous solutions. The negative aspects of this process is that it generates large amounts of low-density aerated sludge, which in turns generates dewatering and disposal problems[5]. Membrane filtration is a very effective method for the removing of heavy metals from wastewater. A huge disadvantage is the cost associated with this method. This method is however considered because it is simple, flexible in plant design and operation [5]. Other methods include ion exchange, electrodeposition, Reverse osmosis, electroplating, etc [6]. The main drawback with these methods are the high capital and/or operational costs involved. Adsorption processes are used for the removal of heavy metals from wastewater streams, they are cost effective and ecofriendly [7-18]. Activated carbon is widely used for water and wastewater treatment. The main issue with activated carbon is that it remains an expensive material. It is a widely used adsorbent in the treatment of wastewaters due to its exceptionally high surface areas, which range from 500 to 1500 $m^2 g^{-1}$, well-developed internal micro porosity structure as well as the presence of a wide spectrum of surface functional groups [19].

An alternative adsorption method makes use of bio-char for the removal of heavy metals from wastewater. Biochar is considered as an alternative method because of the recent development of bio-chars for the absorbance of materials including heavy metals. This is due to the dominance of oxygen-containing functional groups in the highly porous

structure of bio-char. This makes the bio-char suitable for the adsorption of a range of contaminants including heavy metals [20]. Adsorption of heavy metals with bio-char in an aqueous solution has attracted increased attention. Experiments have shown that bio-chars are effective for removing heavy metals from aqueous solution [21].

Benefits of bio-char include the facts that it is made at a very low cost, it is eco-friendly, the wide range of feedstocks available, diversity of the bio-char with each type of feedstock, and the mechanical and thermal stability of the material [22]. Despite the good sorption ability of biochar, powdered bio-chars are difficult to separate from the aqueous solution when applied in the wastewater treatment process due to the small particle sizes and lower density. To overcome this disadvantage, several adsorbents have been modified with magnetic materials or other chemicals to achieve better separation after adsorption [23, 24]

II. Experimental

A. Biochar production

A slurry of spent coffee beans was prepared for a 3 vol% biomass loading. The coffee bean slurry was mixed with reverse osmosis (RO) water to produce a 60 L solution. RO water is used instead of tap water to prevent damage to the stainless steel inside the reactor due to the high chlorine content of normal tap water. The slurry was then soaked overnight.

The hydrothermal liquefaction (HTL) reactor tanks were sealed and pressurized with Nitrogen gas (Baseline 5.0 bar) to 90 bar after 60 L slurry was placed into the reactor. The reactor temperature was increased to 305 °C. As soon as the reactor reached its target temperature the flow to the reactor was set to 120 L/h. This gives the slurry a residence time of 10 minutes inside the reactor which had a 20 L volume.

When all the slurry had flowed through the reactor the hot oil plant was switched off and left to cool overnight. After the reactor had cooled down the tanks were depressurized, and the product was sampled.

The HTL plant produces a product which is a mixture of an oil aqueous phase and biochar solid phase. The biochar was separated from the aqueous phase with pressure filtration. The filtered biocrude was then dissolved in acetone to separate it from the biochar. This was done by placing the biocrude in a 1 L Erlenmeyer flask with 1 L acetone for 48 hours on a magnetic stirrer. This process was repeated to ensure all the oil was separated from the char to ensure a low oil content which increases the porosity of the biochar. The biochar was separated from the aqueous phase with Büchner filtration. The biochar was then dried for 12 hours at 105 °C. The biochar was then crushed

B. Biochar pre-treatment.

The biochar was treated with sodium dodecyl sulfate (SDS). This process was done by soaking 10 g of biochar in a solution of 10 g/L SDS. The solution was placed in a shaking incubator (Figure 1) for 24 hours at 120 rpm 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.

C. Characterization of the biochar

The biochars was characterized by FTIR with the IRAffinity-1S from Shimadzu. It has a spectral range from 4000 to 400 cm-1. This process was used to identify the functional groups of the biochar.

D. Adsorption experiments

ICP-OES (ICP Expert II, Agilent Technologies 720 ICP-OES) was used to measure the Cd content in solution after the adsorption experiments

All the adsorption experiments were done in batch experiments. 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.

2.4.1 Contact time

The first set of experiments was to determine the effect of contact time on the adsorption of cadmium. This was done at 15, 30, 45, 60, 120, 180 and 240 min.

2.4.2 Initial concentration

The second set of experiments was to determine the adsorption capability of the biochar at different initial cadmium concentrations: 10, 20, 30, 40, 50, 60, 70 ppm

III. Results and Discussion

A. Characterization

3.1.1 FTIR

By interpreting the peaks achieved from the FTIR analysis results the composition of the biochar can be determined. With the peaks shown in Figure 3 the results. Significant peaks were observed in the range 2100-2200 cm-1 which can be ascribed to the presence of the alkyne group with high potential of adsorption. The peak at 2650cm^{-1} suggests the formation of formic acid dominated by the carboxylic group which plays an important role in the binding of metals [25].

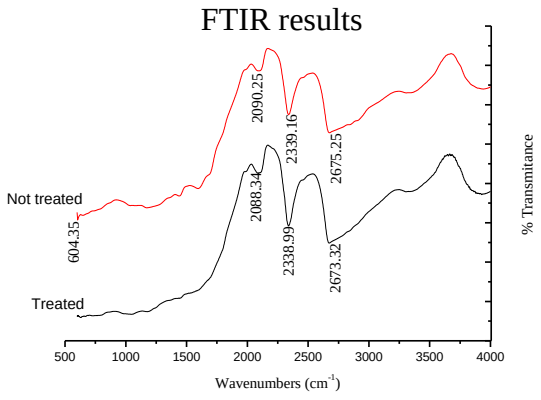

Fig 1: FTIR spectra of the treated and untreated biochars

B. Adsorption behaviour

3.2.1 Contact time experiments

In Figure 2, the effect of contact time on the adsorption of Cd is shown. The adsorbent dosage was kept constant at 0.2g and the initial metal (Cd) concentration was kept at 50 ppm in 50 mL solution. When the contact time increased the adsorption remained relatively constant. This indicates that the adsorption of the Cd occurs relatively quickly, where the metal interacts with the biochars' binding sites rapidly and sutures the adsorbent within 15 minutes. According to the trend observed in Figure 2 the SDS treated biochar adsorbed much more Cd indicating more than double the adsorption capacity than the untreated spent coffee bean biochar.

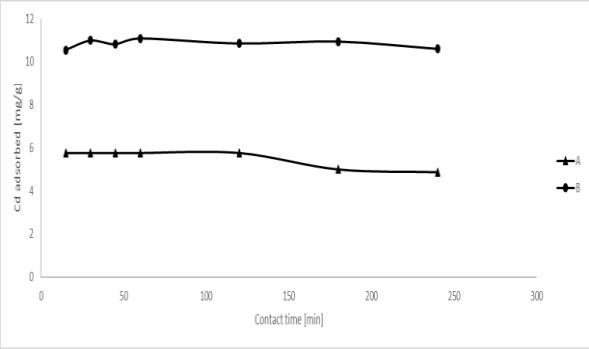

Fig 2: Effect of contact time on the adsorption of Cd with A) NT biochar, and B) PT biochar with SDS

3.2.2 Varying initial concentration experiments

In Figure 3, the effect of initial metal (Cd) concentration is shown. The adsorbent dosage was kept constant at 0.2 g, with 50 mL of solution used at different metal concentrations with the contact time kept constant at 60 min. From Figure 3 it can be observed that at 60 ppm the adsorbent reaches its maximum capacity. According to the trend observed in Figure 3 the SDS treated biochar adsorbed much more Cd indicating more than double the adsorption capacity than the untreated spent coffee bean biochar.

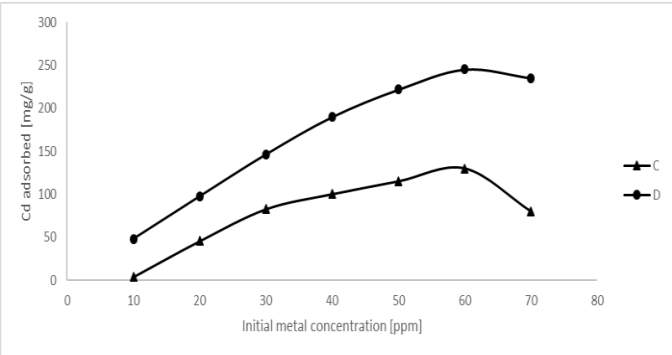

Fig 3: Effect of initial metal concentration on the adsorption of Cd with C) NT biochar, and D) PT biochar with SDS

C. Isotherm and kinetic models

The Langmuir and Freundlich isotherms were considered to better understand the adsorption mechanisms of the two biochars.

To validate the Langmuir and Frendlich isotherm models, the adsorption data at various initial Cd concentrations were considered and the isotherm parameters determined by plotting C_e/q_e vs C_e and $log\ q_e$ vs $log\ C_e$, respectively.
The constants achieved from this process are shown in Table 1:

TABLE I: LANGMUIR AND FREUNDLICH CONSTANTS

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	b	R^2	n	kf	R^2
NT	45.249	-0,061	0.999	-1,343	14.611	0.999
PT	9.320	-1,089	0.997	-0,156	3.199	0.997

From Table 1 it can be observed that the coefficient of determination (R^2) in all cases is close to unity, therefore, the Langmuir and the Freundlich isotherm models fit the adsorption equilibrium data for the adsorption of cadmium by both the the treated and untreated biochars, implying that cadmium binds to groups at the surface and in the pores of adsorbents (homogeneous and heterogeneous surface) [26-35].

Kinetic rate experiments were conducted to validate the pseudo first and second order isotherms. The adsorption data overtime were considered and the kinetic parameters for pseudo first order kinetic model and pseudo second order kinetic model were determined by plotting $ln(q_e - q_t)$ vs t and t/q vs t, respectively. The kinetic parameters are reported in Table 2.

TABLE II: PSEUDO FIRST AND SECOND ORDER CONSTANTS

	Pseudo first order			Pseudo second order		
Adsorbent	qe (mg/g)	k1	R2	qe (mg/g)	K2	R2
NT	0.872	-0,0035	0.828	4.824	-0,0277	0.995
PT	9.449	5*10-5	0,039	10.672	-0,0803	0.999

The ability of the model to predict the adsorption behaviour of the biochar can be determined by considering the cofficient of determination (R^2). From Table 2 it is clear that the Pseudo second order model fits the kinetics of both biochar samples considered, while the pseudo first order kinetics is not sutable for the prediction of the reaction kinetics.

The pseudo second order adsorption capacities clearly shows that the pre-treated biochar had an increse in the adsorption capability, more than double the non-treated biochar. This shows that the impregnation with SDS was succesfull with q_e = 10.67 mg/g compared to the non-treated biochar with q_e = 4.82 mg/g. These results corroborate to the findings of our previous work [36].

IV. Conclusion

In this study the removal of cadmium, from solution with the use of untreated and treated spent coffee bean biochar with SDS. It was shown throughout this study that the modification with SDS significantly improved the adsorption capabilities of the biochar.

With the increase of the initial concentration of the Cd, the biochar adsorbed an increased amount of Cd up to 60 ppm where the adsorption of the Cd remained relatively the same.
The Langmuir and Freundlich isotherm models were found to be both suitable for the prediction of Cd adsorption by both untreated and treated biochars, implying that the Cd was adsorbed through several layers of the adsorbents.

The suitability of the prediction of Cd adsorption rate by the pseudo second order model clearly indicates that the adsorption of Cd onto both biochars occurred through a chemisorption mechanism. It was predicted that the pretreatment of biochar with SDS contribute to increase its adsorption capacity from 4.824 to 10.672 mg/g.

From the results obtained, the spent coffee bean biochar can be used to remove Cd from solution. Pre-treatment with SDS improves the sorption capability by more than double and can thus be considered to develop effective adsorbent for the treatment of wastewater.

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