Application of biosorbents for the adsorption of cadmium in water

Samuel M. Mugo and Casey J. Rusin

***Abstract*—**Development of affordable, eco-friendly and sustainable water remediation technologies remain areas of desired research breakthrough. The use of sorbents derived from agricultural residues meet the criteria for low cost, value addition and sustainable technology. It is demonstrated in this article that biosorbents, including biochar (from pin chips (PC) and paper sludge (PS)), coconut lignin (CL), nanocellulose (CNC) and lignin-nanocellulose composite (LNC) derived from coconut husks are effective sorbents for removal of cadmium from contaminated water. The performances of the biosorbents were heterogeneous, with biochar from paper sludge (PS) having the highest adsorption capacity. The surface morphology and chemistry were found to critically determine biosorbents performance, with their characteristics evaluated by scanning electron microscope(SEM) and Fourier Transform Infrared Spectroscopy (FTIR). An inductively coupled plasma-optical emission spectrometer (ICP-OES) was used to determine the cadmium content in solution after sorbents adsorption.

***Keywords*—**Adsorption, Cadmium, Lignin, Nanocellulose.

I. Introduction

Water contamination by heavy metals remain a global health concern. Heavy metals that are of health concern include copper, lead, arsenic, cadmium, chromium and mercury. Sources of these metals include metal plating, batteries, fertilizers, refineries, fossil fuels, pesticides and paints [1,2]. While it could be argued that heavy metals contamination is a more concerning problem in developing countries with less stringent regulations, globalization and the mobility of manufactured products (e.g. toys, cosmetics etc.) across countries suggests, this is a universal problem. The recent example of heavy metal contamination of imported toy products in Canada is a case in point [2]. The sink for the heavy metals leached from these products after their useful life is surface and ground water, negatively impacting the environment due to their toxicity to organisms. Notably, some of the heavy metals like Hg and Cd biomagnify and bioaccumulate in organisms exacerbating their toxicity [1-4]. Cd is a toxic metal with carcinogenic effects and binds metallothionein in the liver, resulting in renal failure. [3,4].

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Different methods have been employed for removal of metals in water including ion exchange, reverse osmosis, chemical precipitation, and filtration methods [1,5,6]. While these methods are in general effective, the practical challenge is cost and scalability of these techniques if a large body of contaminated water needs remediation. Biosorbents such as biochar, have attracted attention as a cost effective and easily scalable sorbents. Other biosorbents of research interest are lignins and nanocellulose. Nanocellulose is a new class of forest product derived from hydrolysis of cellulose into nanoscale materials with unique properties. Depending on the hydrolysis and purification methods, nanocellulose can be divided into cellulose nanofibers and cellulose nanocrystals, the former being of lower preparation cost than the later. Some of the properties of nanocellulose include high tensile strength, good porosity, rich surface chemistry that is amenable to derivatization to increase functionality (e.g. hydrophobicity). Methods employed for nanocellulose preparation include, acid hydrolysis or TEMPO oxidation in tandem with mechanical processing using an ultra-fine friction grinder [7-10].

The objective of this research is to examine the adsorption of Cd from pin chips (PC) and paper sludge (PS) biochars, lignin and cellulose nanofibers from coconut husks. The surface character of the biosorbents were evaluated by SEM and FTIR, which will give justification on sorbents performance for Cd adsorption. The Cd remaining after adsorption was determined by ICP-OES. A comparative study of percent adsorption among different biosorbents at variable cadmium concentrations as a function of incubation time was evaluated. Temperature and pH were unaltered to replicate a natural-like environment. The intent was to determine a premium biosorbent in the adsorption of cadmium, towards a universal water filter for household use.

II. Methods and Materials

A. Biochar Preparation

The PC biochar was donated by Alberta biochar initiative (ABRI), while the Alberta Newsprint Company (ANC) PS was a gift from Alberta Innovates Technology Futures (AITF).

B. Coconut Lignin and Nanocellulose Preparation

The coconut husks were removed from coconut fruit bought from a local grocery store. All other reagents used were obtained from Sigma Aldrich, Canada.

Twenty five grams of ground coconut husk was extracted three times with 200 mL of 3M NaOH at 80ºC , resulting in lignin concentrated Kraft liquor. The coconut lignin (CL) was obtained by acid precipitation of the Kraft liquor at pH of 2.5. The precipitate was recovered by centrifugation.

The remaining cellulosic material was bleached by adding 200 mL of 10% H_2O_2 and the mixture stirred at 90ºC for 16 hours. The cellulose was then washed with 0.1 M HCl to remove dissolved metals, followed by hydrolysis with 300 mL of 3M HCl at 80ºC for 5 hours. The coconut nanocellulose (CNC) was centrifuged and washed until pH of the washing solution was ~ 4.0.

The lignin-nanocellulose composite (LNC) on the other hand was prepared by stirring 10-grams of nanocellulose with 100 mL of lignin liquor adjusted to a pH of 2.5. The mixture was stirred for 16 hours and then filtered and air dried. It was envisioned that lignin would coat around the surface of the nanocellulose particles due to the high affinity between the two materials.

C. Adsorption Procedure

Cd working solutions of 1, 5, 10 and 20 ppm were prepared from Cd standard 1000 mg/L supplied by Fluka Inc., Canada.

The optimum adsorption time was determined by incubating 5 ppm Cd solution with biosorbents, for 30, 60, 120, 180, 240 and 300 mins. On determining the optimal incubation time, the % adsorption for each biosorbent was studied for Cd concentrations: 1, 5, 10 and 20 ppm. A 50 mL aliquot of Cd solution was added to one gram biosorbent and stirred in a 125 mL flask at 200 rpm. The incubation temperature was at room temperature (RT) and pH ~ 6.0-7.5.

D. Instrumentation

The surface morphology and functional groups of the biosorbents were evaluated using a Hitachi Tabletop Microscope TM 3000 SEM and a Bruker Platinum ATR-FTIR respectively. The Cd remaining in the filtrate after adsorption was determined by a ThermoFisher iCAP 6000 ICP-OES.

E. Data Analysis

The % adsorption of Cd was calculated using equation 1, below, while the amount of Cd adsorbed per gram of biosorbent was determined by the relationship in equation 2:

$$\%\ adsorbance = \frac{(C_o - C_{eq})}{C_o} \times 100\% \quad (1)$$

$$q_{(t,\,c)} = \frac{(C_o - C_{eq})}{m} \times V \quad (2)$$

where C_o and C_{eq} are the Cd concentration before and after incubation in mg/L, m is the mass (g) of biosorbent, V is the volume of sample solution (L) and $q_{(t,\,c)}$ is the amount of Cd adsorbed per gram of biosorbent (mg/g) (t is time dependent, c is concentration dependent) [9].

III. Results and Discussion

A. Biosorbent Surface Characterization

a. Pin Chips Biochar

As attested in the micrograph in Fig. 1a, the PC biochar have a relatively flat and rigid structural surface with limited surface porosity and surface area. As evident with the IR spectra (Fig. 2a), the PC biochar have limited discrete functional groups. It is therefore expected the adsorption of heavy metals (mainly present in cationic form) would be via weak surface adhesion forces such as Van der Waals forces rather than chelation.

b. Paper Sludge Biochar

Fig. 1b shows the surface of the PS biochar is significantly different from that of the PC biochar, with characteristic high surface porosity and area. The IR spectra for the PS biochar (Fig. 2b) shows an evidence of surface functional groups particularly O-H (3272 cm^{-1}), C=O (1620 cm^{-1}) and C-O (1094 cm^{-1}), a clear indication of presence of carboxylic acid groups. It is therefore probable Cd adsorption on the PS biochar would be by surface adhesion as well as by chelation. From the high porosity a superior adsorption capacity for this biochar compared to PC biochar would be likely.

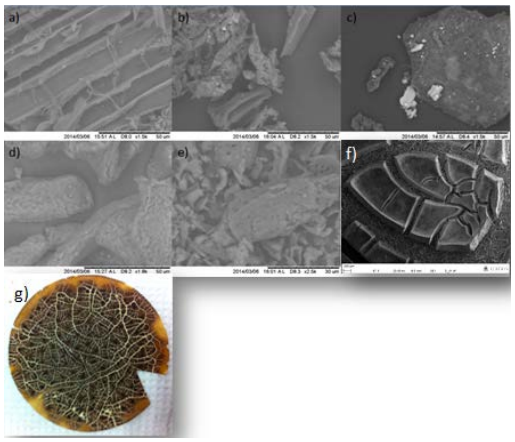

Fig. 1 – SEM images of biosorbents a) PC at 1500x, b) PS at 1500x, c) CL at 1500x, d) CNC at 1800x, e) LNC at 2500x, f) CL interaction with cellulose filter paper, and g) photo of CL interaction with cellulose filter paper

c. Coconut Lignin

The micrograph on Fig. 1c shows the CL surface to be rigid, crystalline and with limited surface porosity. The CL IR spectra (Fig. 2c) confirms major characteristic functional groups including O-H (3329 cm^{-1}), C=C (1593 cm^{-1} and 895 cm^{-1}) and C-O (1037 cm^{-1}) attesting to the rigid aromatic polymeric structure with hydroxyl and carboxyl substituents [6]. It will be curious to compare the adsorptive performance of CL to PS biochar. It can be expected that with limited surface area, porosity and predominant presence of hydroxyl groups, its effectiveness towards heavy metals adsorption may be limited. Nonetheless, it can be hypothesized that lignin may be a good sorbent for organic compounds.

d. Coconut Nanocellulose

As shown in the micrograph (Fig. 1d) the CNC surface is high in character, porosity and surface area. The surface is also functionalized with hydroxyl and carboxyl functional groups as attested by bands at 3325 cm^{-1} (O-H), 2878 cm^{-1} (C-

H), 1592 cm^{-1} (C=O), 1504 cm^{-1} (C=C) and 1026 cm^{-1} (C-O) (Fig. 2d) [9,10]. From these surface features, the CNC is expected to be a good sorbent.

e. Coconut Lignin-Nanocellulose Composite

In this study it was attempted to integrate lignin and nanocellulose into a composite sorbent that may possess superior adsorptive behavior. This study was guided by the observation that lignin has a surface rich in hydrophobic backbone with hydroxyl substituted moieties. However, lignin has limited porosity that could impede its suitability for an effective water filter. Combining lignin with the highly porous nanocellulose could afford a sorbent with their unique. Fig. 1e shows the micrograph of the LNC. The surface morphology and functional groups are not apparently different from CNC, hence similar adsorption efficiencies likely. However, FTIR is not that sensitive and similarity between the two materials expected. Lignin has a strong affinity to cellulose as attested by micrographs in Fig. 1f, g. Work is ongoing to study the lignin nanocellulose interactions and evaluate best methods for preparation of lignin-nanocellulose multi-layered sorbents.

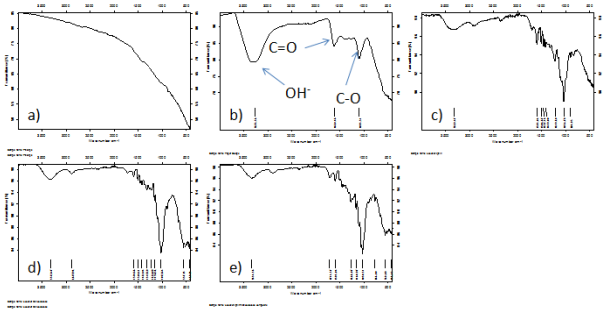

Fig. 2 – FTIR spectra of biosorbents a) PC, b) PS, c) CL, d) CNC, and e) LNC.

B. Cd adsorption time dependent study

Using 1 g of sorbent per 50 mL of 5 ppm Cd standard solution, the adsorption was studied at 30, 60, 120, 180, 240, and 300 min. The results are independent of the pH, temperature and agitation rate as they remained constant throughout the experiment (7.49 pH, RT, 200 rpm).

As demonstrated in Fig. 3, pin chips biochar adsorbed Cd quickly with up to 80% adsorption in 30 minutes. However a cycling of adsorption and release process is over the 300 mins incubation time, with adsorption between 80-90%. The maximum adsorption was at 90% after 180 mins, but with some Cd leaching beyond this time. As mentioned earlier, this is to be expected due to lack of chelating functional groups that could strongly coordinate with Cd ions. Weak surface adhesion would be the prevailing adsorption mechanism.

The % adsorption of PS biochar (Fig. 3) shows a slow increasing adsorption trend, which levels off at 99% after 120 min. This is can be attributed to the slower equilibrium process associated with coordinate dative bond formation between the functional groups (ligand) and the Cd cations. Considering the observed characteristics from SEM and FTIR (high porosity and rich surface functional groups), the high Cd adsorption is not surprising. Conversely, CL was a fast acting sorbent with a rapid adsorption of 57% in the first 30 mins, followed by a low gradient linear increase of only 10% over the 300 mins incubation time. The poor porosity and low surface area of CL may have contributed to the low metal adsorption. Notable is the strong interaction between the Cd and the CL due to the chelation effect. Experimental work in our lab has revealed that CL has the tendency to aggregate and self-polymerize, which could further reduce the surface area. The aggregation is dependent on the CL preparation method. It has been determined in our lab that freeze dried CL is less prone to aggregation, approach that will be taken in our future work.

Lastly, for the CNC and LNC, very similar Cd adsorption efficiencies were observed. The adsorption was rather poor at only 20% with no change over the 300 min incubation time. From the SEM and FTIR data, it is reasonable that their adsorption efficiencies are similar. It was anticipated that the LNC would have superior performance. However, these results indicate the need for improvement in the composite preparation process, currently under study.

It is instructive to quantify the sorbents capacity in amount of Cd adsorbed per gram of sorbent as a function of contact time (q_t). As expected the profile (Fig. 4) was very similar to the % adsorption Fig. 3. The biochars, had the highest q_t, of 0.225 mg/g and 0.241 mg/g for PC and PS respectively, after 180 mins incubation time. The CL adsorption capacity remained constant throughout the incubation period with a maximum q_t value of 0.164 mg/g. The CNC and LNC has a q_t values of about 0.060 mg/g.

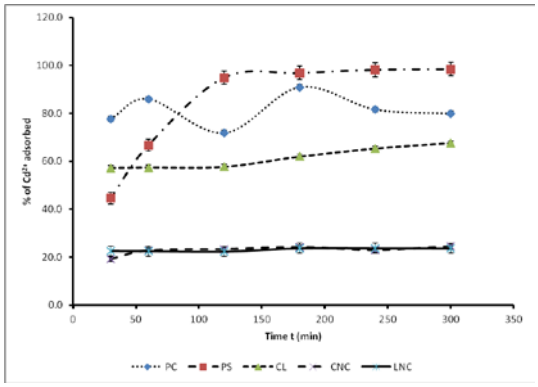

Fig. 3 – Percent adsorption as a function of contact time with 5 ppm initial Cd.

C. Cd adsorption concentration study

Cd adsorption as a function of contact time experiment established the optimal incubation time to be 180 min. Using these established conditions, examination of the sorbents adsorption efficiency as a function of concentration (1, 5, 10 and 20 ppm) was studied.

As shown in Fig. 5, the biochars maintain an overall good Cd adsorption. It is interesting to note that at 1 ppm PC out performs PS biochar with 100% to 93% adsorption respectively. For 5 ppm, the PS % adsorption is 97% compared to 90% for PC biochar. A clear decrease of Cd

adsorption is observed for both biochars as the concentration is increased from 5 to 20 ppm, with the decrease more dramatic for the PC. For 20 ppm, the PC biochar adsorb only 26% while the PS maintains an impressive adsorption of over 70%. This further attests to the importance of chelating groups and high surface area, as indicators of a good sorbent.

Fig. 5 shows CL has fairly low adsorption at 1, 10, and 20 ppm, but a dramatic increase at 5 ppm, a behavior that will need more exploration. The CNC Cd adsorption is 78% for 1 ppm and 60% for the LNC. For 5 ppm, the adsorptions for both CNC and LNC reduce to around 20%. As stated before, the CNC and LNC will require further study. Notably though, CNC seems effective for removal of trace contaminants.

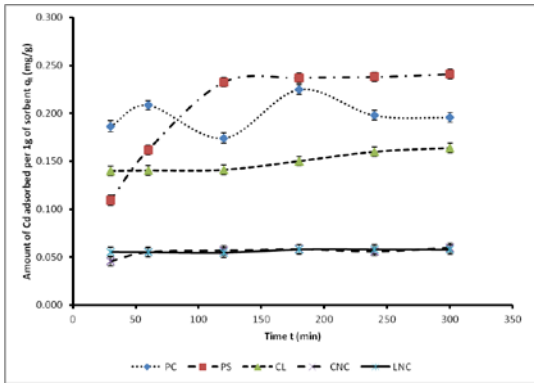

Fig. 4 –Cd adsorbed per gram of sorbent as a function of contact time (q_t) with 5 ppm initial Cd.

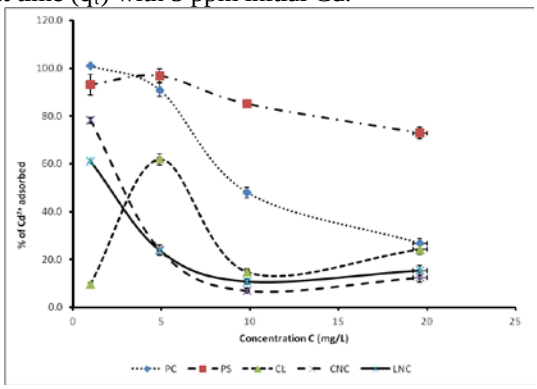

Fig. 5 – Percent adsorption as a function of concentration with incubation period of 180 min.

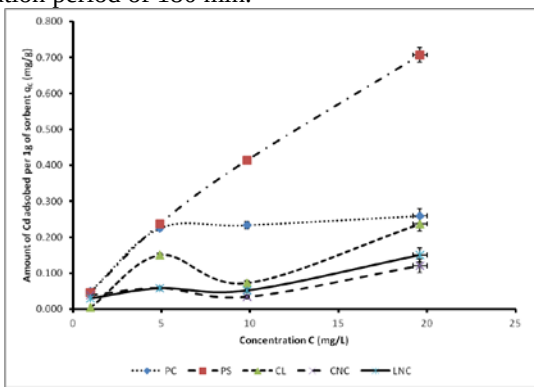

Fig. 6 Cd adsorbed per gram of sorbent as a function of concentration (q_c) with incubation time of 180 min.

The profile on the amount of cadmium adsorbed per gram of sorbent as a function of concentration is demonstrated in Fig. 6. Clearly, one gram of PC biochar for cadmium adsorption is around 5 ppm, while that of PS biochar capacity linearly increases with concentration, a clear indicator that the latter has a larger concentration dynamic range and thus more useful for cadmium water remediation. It is to be noted that, there is a decrease in the gradient in the linear regression for PS biochar after 10 ppm, signifying a decrease in adsorptivity. The CL behavior remains peculiar with a non-uniform adsorption pattern. The CNC and LNC have low Cd adsorption capacity of about 0.06 mg/g at 5 ppm. A more rigorous study on the CL, CNC and LNC as sorbents is however necessary.

IV. CONCLUSION

The PS biochar is by far the best adsorbent for Cd, seen by its ability to adsorb in a wide range of concentration. As for the derived coconut biomasses, lignin should be further examined in order to verify its surface's role in the adsorption. The CNC and LNC composite were very similar in structure and further optimization is needed in their fabrication protocol.

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