

REMOVAL OF HEAVY METALS FROM WATER BY WOOD-BASED LIGNOCELLULOSIC MATERIALS

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ABSTRACT

Drinking water, particularly mine and industrial waters, may contain concentrations of heavy metals above the limits defined by the intended use. Therefore, hazardous heavy metals must be removed by water treatment, which in turn must satisfy the key criteria: to be efficient and inexpensive. The simplest method for treatment of mine and industrial waters is by chemical precipitation in the form of metal hydroxides. For treatment of drinking water, characterized by very low concentration of heavy metals, the adsorption on a solid support, such as activated carbon, is a common practice. The major deficiency of using activated carbon is the slow kinetics, low loading capacity, and high costs. For that reason, substantial research efforts are directed toward the use of natural sorbents, such as cellulose from wood. In this paper, the results will discuss the use of cellulose from wood for removal of cadmium from water of similar characteristics as drinking water. The other results will point to the treatment of water characterized with much higher concentrations of heavy metals, as found in mine waters. The adsorption studies were performed as a function of typical parameters: pH, concentration, temperature, etc. To enhance the sorption capacity and kinetics, the cellulose molecules were modified by esterification, which was found highly beneficial. Regarding the source of cellulose, several wood species were examined. Among these, cottonwood consistently showed superior performance.

Keywords: absorption, cadmium, lead, mercury, copper, zinc, cellulose, kinetics.

1 INTRODUCTION

The common approach to treating the industrial waste waters is by chemical precipitation with calcium hydroxide. The resulting sludge is disposed onto a tailing pond, or stabilized for final disposal on the surface, or returned to the mine, if this was the original source. More expensive methods of treatment are activated carbon adsorption, ion exchange, membrane separation, electrolysis, coagulation/flocculation and chemical precipitation (other than hydroxide).

In this work, the treatment of waters contaminated with heavy metals has taken another approach, the adsorption by lignocellulosic materials in the form of wood sawdust. Cellulose is the most abundant natural, and renewable, biopolymer. It is present in the seed hairs of the cotton plant, but more abundantly, in combination with lignin and hemicellulose, in the cell walls of the woody plants. It is a straight chain polymer consisting of a large number of units. In wood, the other major components are hemicellulose (mixture of polysaccharides) and lignin. It contains plenty of hydroxyl and carboxylic groups as the providers of hydrogen bonding sites that enable long chain polymers to hold together. Lignin, an aromatic compound, provides structural strength, seals the water conduits, and prevents plant degradation. It also contains a variety of functional groups, such as hydroxyl, methoxyl, and carbonyl groups.

The sorption metal ions by lignocellulosic materials is generally described as adsorption, more precisely as biosorption. There are several major advantages of using biosorption for removal of heavy metals: effectiveness, low cost, minimization of chemical sludge, regeneration, no additional nutrients, and possibility for commercial metal recovery. The



least expensive source of lignocellulosic materials is the plant wastes, such as sawdust from wood industry [1]–[3], bark [4], [5], rice husk [6], [7], straw [8], corn stalk [9].

The lignocellulosic materials can be used in their native, or modified form. The modification is performed to improve the sorption capacity for heavy metals. Two main approaches are (1) direct modification, and (2) grafting of cellulose. Direct modification of the cellulose is achieved by esterification, halogenation, oxidation, and etherification. Grafting modification involves a process in which side chain grafts are covalently attached to a main chain of a polymer backbone to form a branched copolymer.

In this work some results will be presented on adsorption of heavy metals on sawdust primarily from cottonwood. Most of cadmium adsorption studies by unmodified sawdust were performed from synthetic solutions. Because the effectiveness of adsorption of cadmium and other heavy metals (Cu, Zn, Pb, etc.) on unmodified sawdust was too low, when mine waters were used, the sawdust modification by esterification had to be employed. The mine water samples came from actual Superfund mining sites, adding to the uniqueness of this work.

2 MATERIALS AND METHODS

2.1 Materials

Lignocellulosic materials were prepared by saw cutting of wood. In addition to cottonwood, sawdust from cedar, pine, fir and maple was prepared as well.

2.2 Solutions

Adsorption studies were performed with synthetic and real mine water solutions. Synthetic solutions were prepared by dissolving an aliquot amount of inorganic metal salt to produce desired concentration. Real mine waters were the samples from three Superfund sites in the USA, (1) Bunker Hill Mine, Berkeley Pit and Blackbird Mine. The composition of the main constituents is given in Table 1, which only lists the major heavy metals. Detailed composition of mine waters can be found in the EPA publications for Bunker Hill [10], Berkeley Pit [11], Blackbird Mine [12].

2.3 Esterification

Esterification of wood sawdust was accomplished according to the methods described by Head et al. [13], and the references cited within.

2.4 Adsorption

Adsorption was studied in a stirred reactor immersed in a temperature controlled water bath. Exact experimental conditions are annotated within the figures. In periodic time intervals, a solution sample was withdrawn for analysis by atomic absorption (Varian Spectra 10/20).

Table 1: Composition of mine waters with regard to the metals of interest.

Metal (mg/L)	Blackbird Mine	Berkeley Pit	Bunker Hill
Cu	123	185	-
Co	26.7	-	-
Zn	-	283	383
Mn	-	29.6	225



2.5 Theoretical

2.5.1 Thermodynamics – adsorption isotherm

In this work two most popular adsorption models were used, Langmuir [14] and Freundlich [15].

Langmuir derived the eqn (1) based on the following assumptions: (1) the adsorbent surface has fixed number of available sites, (2) all sites have the same energy (homogenous surface), (3) adsorption is in dynamic equilibrium (reversible), (4) no lateral interaction between adsorbed species:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \quad (1)$$

where q_e (mg/g) is the amount of adsorbate (cadmium) per unit of adsorbent (sawdust) at equilibrium, q_m (mg/g) is the amount of metal ions required to form a monolayer onto the adsorbent surface (maximum adsorption capacity), K_L (L/mg) is the Langmuir equilibrium constant, C_e is the equilibrium concentration of adsorbate (mg/L). There are several ways to linearize eqn (1), an excellent analysis of each method is done by Tran et al. [16]. In this work, the linearized form of Langmuir eqn used is given in eqn (2):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (2)$$

Freundlich isotherm, an empirical equation, is relevant to the non-homogenous, i.e. heterogeneous, surfaces, eqn (3):

$$q_e = K_F C_e^{\frac{1}{n}}, \quad (3)$$

where K_F (mg/g) L/mg)^{1/n} is the Freundlich constant and $1/n$ (dimensionless; $0 < n < 10$) is a Freundlich intensity parameter signifying the magnitude of the adsorption driving force, or surface heterogeneity. Higher n -value the more heterogeneous the surface is. For $n > 10$, the adsorption is irreversible [16].

The linear form of Freundlich equation is given below,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The adsorption can be governed by either physical or chemical adsorption mechanisms. Physical sorption (physisorption) reflects the weak interactions (van der Waals) between adsorbate and adsorbent surface, while the chemical adsorption (chemisorption) involves the chemical bonding. The free energy change, ΔG^0 , of adsorption is given by:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = -RT \ln K, \quad (5)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), and K is the adsorption equilibrium constant. Eqn (5) can be rewritten in the form of Van't Hoff equation, eqn. (6):

$$\ln K = \frac{-\Delta H^0}{R} \times \frac{1}{T} + \frac{\Delta S^0}{R} \quad (6)$$

Variation of equilibrium constant of adsorption as a function of temperature can be utilized for determination of enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption.



2.5.2 Kinetics of adsorption kinetics

The adsorption reaction mechanisms were explored by employing several reaction rate models, as presented below.

Pseudo-first order model is given in eqn (7),

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

Solution of eqn (7) is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

Pseudo-second order model is represented by eqn (9),

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (9)$$

the solution of which can be represented in the following form, eqn (10),

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (10)$$

where q_e has the same meaning as given above (amount of adsorbate at equilibrium; mg/g), and q_t is the amount of adsorbate per mass of adsorbent (mg/g) at time, t .

Intraparticle diffusion model [17] was proposed for adsorption processes controlled by diffusion within the porous adsorbent, like activated carbon, according to which the uptake varies proportionally with $t^{1/2}$, eqn (11):

$$q_t = k_{id} t^{1/2} + \text{const}, \quad (11)$$

where, k_{id} (mg/g min^{1/2}) is the intraparticle diffusion rate constant.

3 RESULTS AND DISCUSSION

3.1 Adsorption of heavy metals by unmodified sawdust

3.1.1 Adsorption of cadmium

Cadmium adsorption was studied from synthetic solutions. The main adsorption parameters examined were pH, cadmium concentration and temperature.

Effect of pH: Cadmium adsorption results as a function of initial pH are given in Fig. 1. It can be clearly seen that the initial pH has a significant effect on the rate and equilibrium of Cd adsorption. According to Fig. 1, the percent of Cd adsorption increases significantly with the increase of pH. This is consistent with the findings by numerous other researchers [18]–[21], to list a few. Invariably, the increase of Cd uptake by increase of pH is commonly assigned to the competitive adsorption of H⁺ cation, which is more abundant at lower pH. Complexation of cadmium by carbonyl (C=O), or hydroxyl (OH) groups, is another possible mechanism for cadmium uptake, Taty-Costodes et al. [21].

It is important to note that the cadmium adsorption resulted in simultaneous pH increase. Bozic et al. [22] were the first to raise the absence of literature discussions on the mechanisms leading to pH change during adsorption. They have pointed out the importance of ion exchange mechanisms in adsorption by lignocellulosic materials, led by the results from another research group [23], [24]. The primary candidates for exchange with H⁺ and Cd²⁺ in solution are Ca²⁺ and K⁺ within the matrix of the solid sawdust.

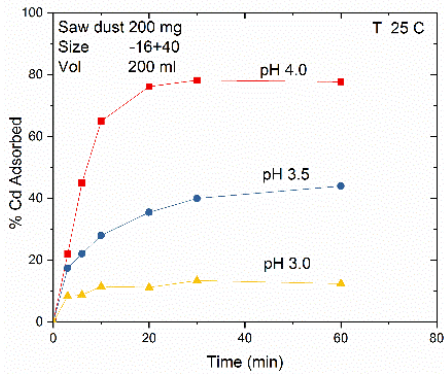


Figure 1: Effect of pH on Cd adsorption by cottonwood sawdust.

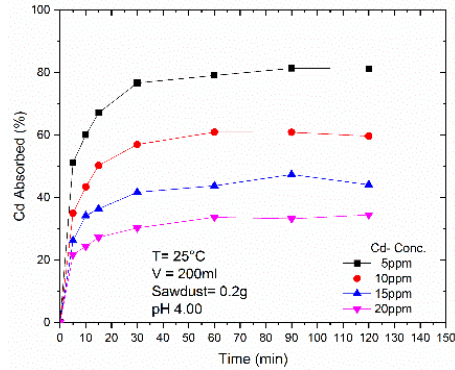


Figure 2: Effect of Cd concentration on adsorption by cottonwood sawdust.

Effect of cadmium concentration: The results from studies of this parameter provide the thermodynamic and the kinetic information. Initial cadmium concentration effect at T 25C is given in Fig. 2. Four different initial cadmium concentrations were used, 5mg/l, 10mg/l, 15mg/l and 20mg/l. It is evident that the cadmium adsorption rate was relatively fast for all studied concentrations, as it took less than an hour to reach the equilibrium.

From the kinetic point of view, cadmium adsorption followed the pseudo-second order model, as t/q_t vs t , eqn (10) was linear, for the results from both, pH and concentration effect. The linear fits produced correlation coefficients, R^2 , better than 0.995. Regular first order kinetics, pseudo-first order (eqn (8)) and intraparticle diffusion (eqn (11)) did not produce satisfactory results.

Effect of temperature: Effect of temperature was studied at 25C, 35C and 45C. The results presented in Fig. 3 show that temperature has little effect on the adsorption within the equilibrium stage. This parameter will be re-examined in the later study with the emphasis on the rate of adsorption during the initial kinetic stages, which will require sampling within first ten minutes of adsorption.

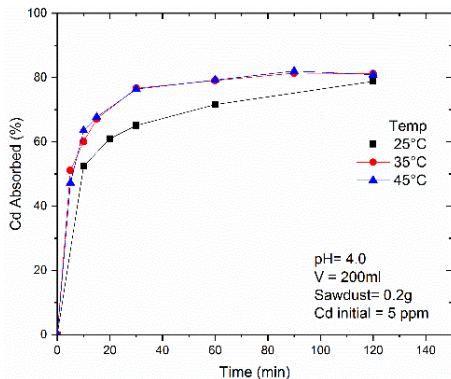


Figure 3: Temperature effect on Cd adsorption by cottonwood sawdust.

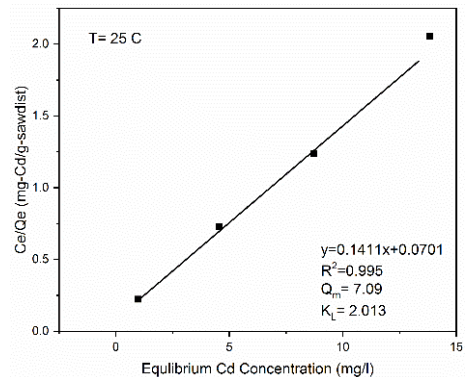


Figure 4: Linearization of Langmuir adsorption isotherm for T=25C.



Adsorption isotherm for cadmium adsorption: The adsorption isotherm is of fundamental and practical importance as it reveals the mechanistic features of adsorption (monolayer versus multilayer), the surface heterogeneity, the interaction between the adsorbate and adsorbent. For practical purpose, the adsorption isotherm provides the information on the loading capacity of adsorbent.

Langmuir type of adsorption produced the best correlation (R^2 values higher than 0.995) between the experimental and theoretical data, Fig. 4. The Langmuir equilibrium constants, K_L , was 2.013 and maximum uptake of cadmium, q_m , of sawdust was 7.09 mg-Cd/g-sawdust.

Adsorption of heavy metals on different species of wood. Cellulose source from different species of wood were examined by using sawdust from cedar, fir, cottonwood and maple trees. The results are given in Fig. 5 and Fig. 6 with respect to adsorption of mercury and lead, respectively.

Adsorption of Hg^{2+} , as $HgCl_2$, on sawdust from various species of wood is presented in Fig. 5. It can be observed that the kinetics of Hg^{2+} adsorption was fast, requiring only about 10–15 minutes to achieve the equilibrium. About 70% of Hg^{2+} was absorbed by fir. The extent of adsorption on cottonwood and pine was only about 50%. It is interesting to note that cedar was desorbing initially adsorbed mercury as the time progressed. The reasons for desorption presently are not known.

Results from adsorption of Pb^{2+} , as $PbCl_2$, are given in Fig. 6. Adsorption of lead was also fast. Cottonwood performed the best, close to 70%, while pine had the lowest extent of adsorption, less than 40% of lead adsorption.

Cadmium adsorption was the least effective, Fig. 7, as the maximum extent of adsorption was on cottonwood, only about 40%.

The adsorption of heavy metals on the species of wood presented here followed pseudo-second order of adsorption. An example of the linearization of eqn. (10) for pine and cottonwood are given in Fig. 8. An excellent linear fit with correlation coefficient R^2 better than 0.999 was produced.

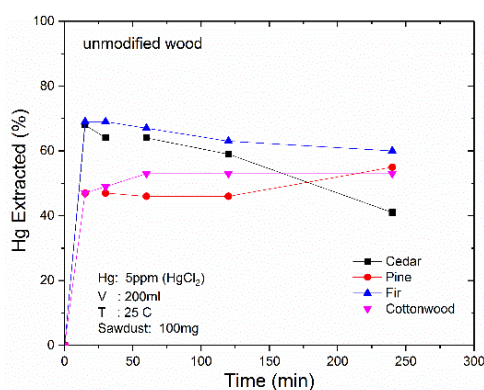


Figure 5: Hg^{2+} adsorption by sawdust from cedar, pine, fir and cottonwood.

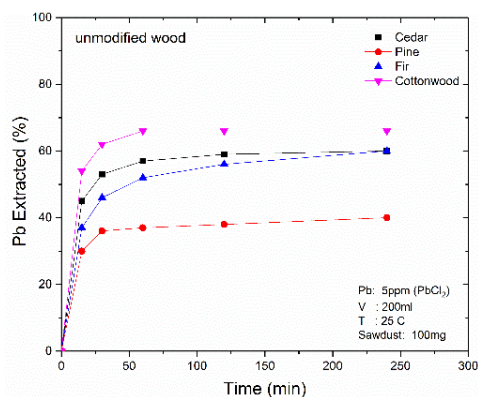


Figure 6: Pb^{2+} adsorption by sawdust from cedar, pine, fir and cottonwood.

3.2 Adsorption on modified sawdust

3.2.1 Preliminary tests – search for effective esterification routes

To achieve chemical modification, sawdust was treated with various reagents, such as acids (HCl, H_3PO_4 , lignosulfonic acid) and basis (NaOH), strong oxidizer (H_2O_2 , Br_2), reducers (NaBH_4), and sulfidizers (Na_2S). The reasons for selection of these reagents varied. For example, NaOH was selected because of its well-known swelling capabilities, to improve the accessibility of wood matrix. Release of OH groups within the matrix would have a positive effect of retaining the heavy metals, most likely as hydroxides. Na_2S was selected for similar reasons. The effect of various reagents was studied mostly on cedar, cotton and cottonwood with respect to adsorption of Hg^{2+} , Pb^{2+} and Cu^{2+} . Only some selected data will be presented here. It was found that Hg^{2+} was always more difficult to remove from water than Pb^{2+} . The best results for adsorption of Hg^{2+} were obtained when cottonwood was pre-treated for 1-hour with NaOH (68% removal) and NaOH+ Br_2 (83% removal). Removal of Pb^{2+} under the same conditions was 100%.

Method of employed modification has a very important role of establishing the efficiency for heavy metal removal by adsorption as can be readily seen in Fig. 9. In this figure, the Cu^{2+} adsorption results from several types of cottonwood modification are presented. It can be seen that unmodified wood responded with the lowest adsorption.

From this point on, it was decided to focus the attention on wood modification by esterification. Urea and phosphoric acid were selected as the reagents of choice to achieve the desired esterified wood product. In numerous experiments, it was found that the esterification with urea + phosphoric acid was quite sensitive on the conditions of esterification with respect to time, temperature and general handling of the wood. With respect to temperature, it appears that 130–135°C is the optimal range. Washing method and wash solution type were also important parameters.

The effectiveness of esterification was verified by the effectiveness of copper adsorption. The results in Fig. 10, clearly show that esterification under boiling conditions was much more extensive than the esterification under baking conditions, because the removal of copper was nearly 100% with the former.

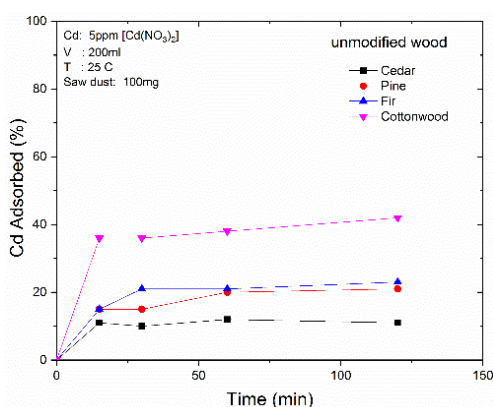


Figure 7: Cd^{2+} adsorption by sawdust from cedar, pine, fir and cottonwood.

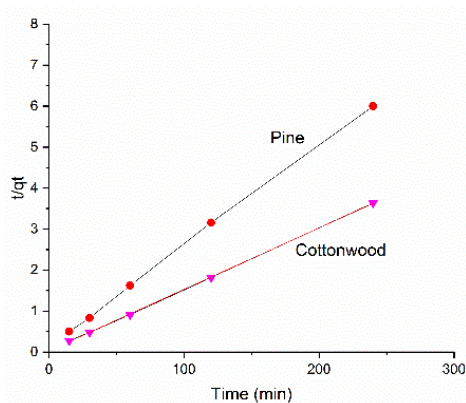


Figure 8: Pseudo-2nd order model for adsorption of lead on cottonwood and pine.



One of the most detrimental ions with respect to its tendency to occupy the adsorption sites is iron. When designing a new ion exchange resin, or a solvent extractant, the ultimate test for the design success is its selectivity against iron. In the present case, it was found that esterified wood was not selective against iron at all as both ferrous and ferric iron were almost completely removed from the solutions under given conditions. However, the loading capacity of esterified wood appears to be high enough to accommodate both, Cu and Fe, ions. In a practical application, because the concentration of iron in mine waters is orders of magnitude higher than the toxic heavy metals, iron would have to be removed in a preceding treatment step.

3.2.2 Adsorption of heavy metals from actual mine waters

Because of encouraging results in Fig. 9 and Fig. 10, it was decided to test the esterified wood with respect to its heavy metal adsorption capabilities from real mine waters. Due to a small amount of absorbent being used in adsorption experiments, 100 mg per 100 ml of solution, the original mine waters had to be diluted. The dilutions were 20X for water from Berkeley Pit Mine, 10X for Bunker Hill Mine and 10X for water from Blackbird Mine. All three mine waters are acidic in nature, but of different pH. Knowing that the initial pH is the most important parameter to adsorption, to avoid the effect of pH all three waters were adjusted to the same initial value, pH=4.

The adsorption of Cu, Zn and Mn from Berkeley pit water is shown in Fig. 11. Copper removal was about 60%, while Zn and Mn were removed to a lesser extent. The lower extraction values were due to the presence of large concentrations of other metals (Fe, Ca, Al, Mg, etc.) in this water. The pH change was from initial pH 4.06 to final pH 3.78.

The most significant elements in Bunker Hill Mine waters are Zn and Mn. About 60% of each metal was absorbed on esterified cottonwood within one hour, Fig. 12. As during the adsorption from Berkeley Pit Mine water, the pH of solution stayed about the same; pH=3.93 was the final value.

Blackbird Mine is the only cobalt ore deposit in the USA. Now abandoned, the mine releases large concentrations of Cu (123 mg/l) and Co (26.7 mg/l) into adjacent water streams as tributaries to Salmon River. Removal of Cu and Co from Blackbird Mine water by esterified wood was very successful, with close to 100% efficiency, Fig. 13. pH of solution did not change during the adsorption.

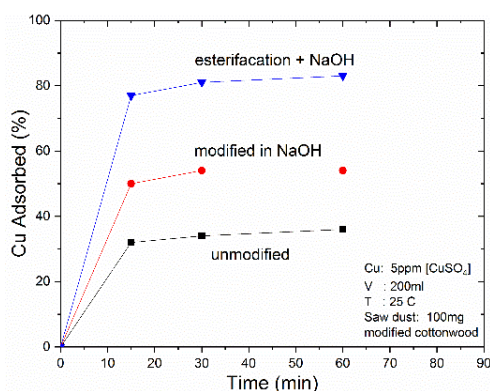


Figure 9: Importance and effectiveness of a method of esterification.

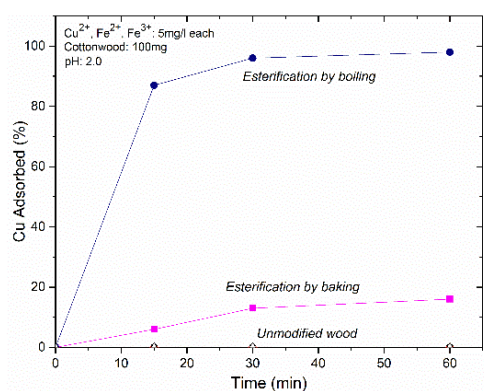


Figure 10: Adsorption of copper even in the presence of iron species.

3.3 Potential for practical application

Excellent adsorption results and inexpensiveness of the natural-based-on-wood biosorbents open numerous pathways for development of methods for heavy metal removal from mine, and industrial, waters. One of the approaches would be to fill the porous bags with sawdust biosorbents for placement along the mine creek banks, or to use them as artificial water dams. Upon saturation, the bags would be replaced with those containing fresh adsorbent. The bags loaded with heavy metals could be disposed-of on the sites specifically designed for storage of hazardous waste. Or, the sawdust could be dried, and burned for recovery of particular heavy metals from the resulting ash.

Depending on conditions such as water composition, concentration, volume, terrain, etc. one could readily develop various other approaches for heavy metal removal, as long as the sorbent is efficient and inexpensive. Natural biosorbents are promising candidates toward that goal.

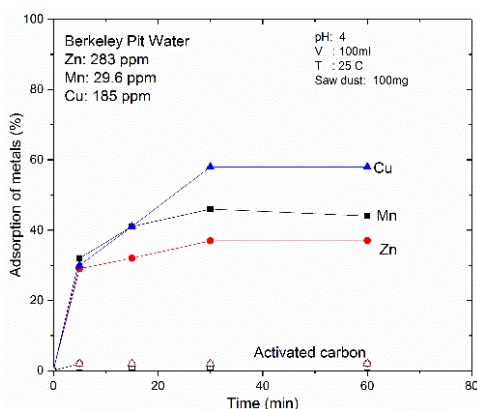


Figure 11: Removal of Cu, Mn and Zn from Berkeley Pit water by adsorption on sawdust modified by esterification.

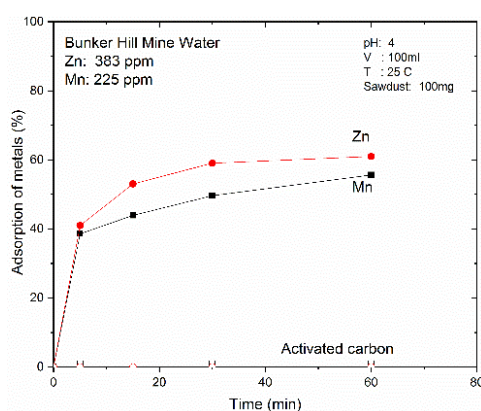


Figure 12: Removal of Mn and Zn from Bunker Hill water by adsorption on sawdust modified by esterification.

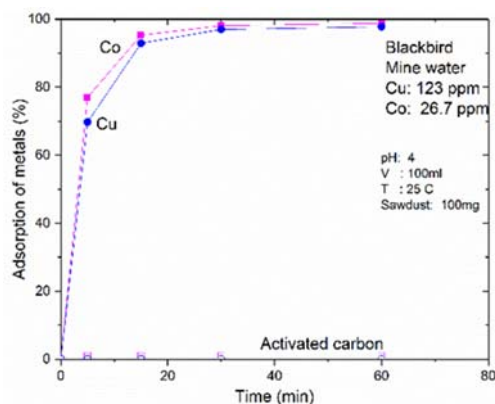


Figure 13: Removal of Cu and Co from Blackbird Mine water by adsorption on sawdust esterification modified.



4 CONCLUSIONS

Wood in its native form is a heavy metal biosorbent. This property is derived from the presence of numerous hydroxyl groups on the cellulose backbone molecule. The hydroxyl groups are also present on two other main wood constituents, hemicellulose and lignin. Adsorption capabilities of wood materials can further be enhanced by chemical modification, such as esterification, by introduction of ion exchange, and/or chelating functional groups.

Thermodynamic and kinetic studies on adsorption of cadmium were done from synthetic solutions. The cellulose source was the sawdust from cottonwood. Initial pH of solution was an important parameter, as cadmium uptake increased by increase of pH. Temperature was not an important parameter for the equilibrium of adsorption, but it was for the initial kinetics. Cadmium loading capacity of cottonwood was 7.09 mg per gram of sawdust.

Native sawdust does not have good loading capacity for uptake of heavy metals from actual mine waters. However, upon modification by esterification, the kinetics and loading capacity dramatically improved, as verified by successful removal of Cu, Co, Zn, and Mn. For comparison purpose, activated carbon removed barely measurable amount of these metals. Esterification was achieved by phosphoric acid and urea mixture. Particular sequence of esterification is an important parameter.

Chemically modified wood offers a pathway for development of technologies for treatment of industrial waters and mitigation of mine sites.

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