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Adsorption of Heavy Metals by Bio-Chars Produced from Pyrolysis of Paper Mulberry from Simulated Industrial Wastewater

S. Adil[1], A. Mashiatullah[2*], M. Asma[1], A. Ghaffar[2], S. Khan[2] and J. Abid[2]

[1]Department of Environmental Science, International Islamic University, Islamabad, Pakistan

[2]Isotope Application Division, Directorate of Technology, PINSTECH, Islamabad, Pakistan

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Paper mulberry bio-char (by-product of pyrolysis) was evaluated for the removal of heavy metals (Cd, Cr, Cu, Zn and Pb) from simulated industrial waste water. The surface properties and surface area of the bio-char was found suitable for metal adsorption. Batch sorption studies for adsorption potential of paper mulberry bio-char for Cd, Cr, Cu, Pb and Zn were investigated under different experimental conditions of pH, temperature and contact time. Maximum removal efficiency of Cd, Cu, Pb and Zn was 97.8, 76.8, 85.6, and 82.2 % respectively at pH 12 while maximum removal of Cr was recorded (98%) at pH 2. The removal efficiency showed different behaviour at different contact times. Maximum removal efficiency of Cd, Cr, Zn was 81, 86, 61.4% at contact time of 3 hr. The maximum removal of Cu was 64.2% observed at a contact time of 4 hours while the maximum removal of Pb and Zn was 85% at contact time of 2 hr. The values of the thermodynamic parameters, enthalpy ΔH^o, Gibbs free energy ΔG° of sorption and entropy ΔS^o were calculated to define endothermic or exothermic behavior of the sorbent used. Negative value of ΔG° for Cd, Cu, Cr and Pb indicated paper mulberry bio-char as a feasible sorbent for the efficient removal of Cd, Cu, Cr and Pb. Negative value of ΔH° was observed for Cd and Pb indicating that the adsorption process is exothermic while positive value of ΔH° was calculated for Cu, Cr and Zn showed that the adsorption is endothermic. The results obtained showed that plant residue bio-char can act as an effective sorbent for the removal of heavy metals from aqueous solutions.

Keywords: Bio-char, Adsorption, Heavy metals, Thermodynamics, Endothermic, Exothermic, Wastewater

1. Introduction

Heavy metals are discharged into water bodies from domestic and industrial effluents such as metal plating industries, tanneries and mining, etc. These contaminants from water bodies may then enter into the surrounding soil, surface water and groundwater. When this polluted water is consumed by living organisms, these toxic heavy metals can accumulate in their bodies and cause harm [1]. Human health and ecological systems are therefore threatened by industrial effluents. The heavy metal concentration in water bodies is increasing day by day due to rapid industrial and agricultural development together with rapid population growth, [2]. It is therefore, necessary to remove these toxic heavy metals from industrial waste water before they enter into the environment. Several methods have been developed to solve this issue. Conventional water treatment technologies, such as coagulation and flocculation, precipitation, electro-coagulation, ion exchange, membrane filtration, electrochemical filtration and packed-bed filtration were found to be effective in lowering heavy metal concentrations [3]. Most of these technologies, however, may have high operating cost and/or sludge disposal problems [1]. These disadvantages increase the need for developing alternative and economical water treatment methods for heavy metal elimination. Adsorption is considered a simple and efficient method. Biosorbents have been suggested as potential candidates to remove toxic metals from wastewater [4]. Some biosorbents are broad ranged, bind and collect most heavy metals with no specificity, whereas others are specific for certain heavy metals. Agricultural by-products like bio-char if appropriately modified can be used for treating both industrial and municipal wastewater containing heavy metals. Great efforts have been made to use economically efficient and unconventional adsorbents produced from agricultural/ plant wastes, aquatic plants, and industrial by products [5-7].

Bio-char is a fine-grained, porous, carbon rich material similar to charcoal produced by the combustion of biomass under limited oxygen supply. The term bio-char was originally related with a specific type of production process, generally known as ‘slow pyrolysis” in which oxygen is absent, heating rates are slow and peak temperatures are also relatively low. However, the term bio-char has now been extended to pyrolysis products, resulted even at higher temperatures, known as fast pyrolysis and novel techniques such as microwave conversion. Pyrolysis is the thermal

* Corresponding author: mashiatullah@gmail.com

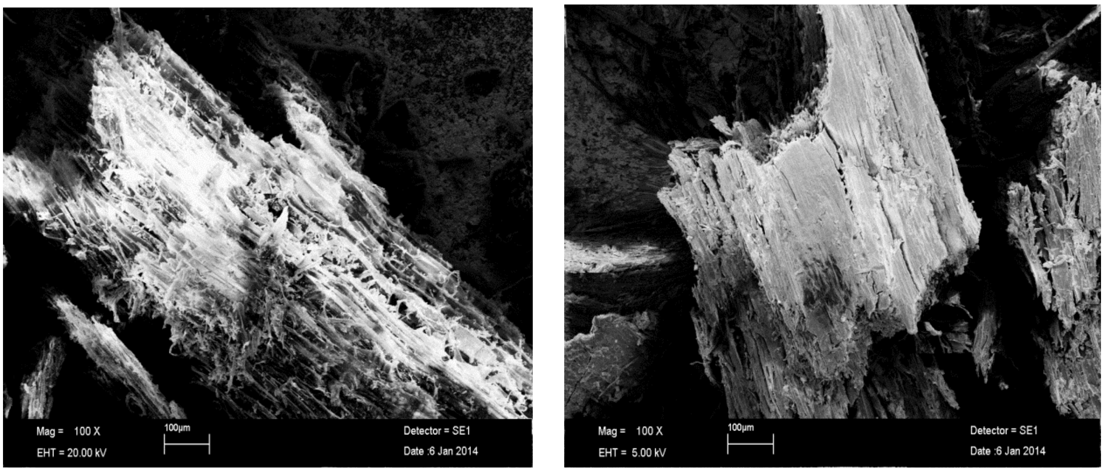

Figure 1. Paper mulberry bio-char micrographs.

conversion of biomass at elevated temperatures, forming high carbon solid (bio-char), liquid (bio-oil) and gas product. The distribution of products depends upon heating rate, temperature, surrounding atmosphere and residence time [8]. Bio-char is currently being used as a low-cost sorbent for the removal of metallic contaminants from aqueous solutions [9, 10]. Bio-chars produced from animal waste, agricultural residues and wood materials have been investigated for their capability to adsorb various heavy metals, including cadmium, copper, lead and nickel [10, 11]. The present study is conducted to investigate the applicability of adsorptive treatment by developing low cost paper mulberry wood bio-char for the effective removal of heavy metals from industrial wastewater.

2. Materials and Methods

2.1 Raw Material and Bio-char Preparation

Paper mulberry *(Broussonetia papyrifera)* is a fast growing tree or shrub of the Moraceae family. This species commonly found in various environments in the Asia and Pacific region [12]. Due to its large biomass and rapid growth either from root, stem cuttings or seeding it usually takes few months to attain the harvest size of 300- 400 cm height [12]. Once the plants are cut, the species grow faster and biomass is increased than newly planted ones. With the rapid development of domestic livestock and the enormous global demands for forage, value of wild plant resources such as mulberry are of intense interest [13].

Paper mulberry wood/bark used in this study was obtained from different sectors of Islamabad, Pakistan. 5 Kg of bark was collected. Air and oven dried bark were crushed and ground into small pieces in a rotary cutting mill. The resultant powder was sieved to obtain an average size of 0.00141 mm (1.4um). Pyrolysis experiments of paper mulberry wood/bark biomass were carried out in a Helium Diffusion Furnace (SLM-1) at 350◦C and finally 2kg of porous bio-chars was obtained.

2.2 Bio-char Characterization

Surface area of the char was calculated from Nitrogen gas physisorption method at 77 K over the relative pressure range of P/P0 = 0.05-0.30. SEM micrographs of the prepared bio-char samples were recorded using Scanning Electron Microscope SEM (Model: Leo 440). SEM micrographs clearly show the amorphous and heterogeneous nature of paper mulberry bio-char (Figure 1). Scanning electron microscopy also revealed that internal pores and cracks /mesopores are present in bio-chars materials. These pores are of importance in many liquid-solid sorption processes

2.3 Batch Adsorption Experiments

Artificial wastewater was prepared by dissolving accurately weighted ($CdCl_2.H_2O$), ($CuCl_2.2H_2O$), (K_2CrO_7), ($PbCl_2$) and ($ZnSO_4.7H_2O$) in distilled water to prepare solutions of 1000 mg/l concentrations. Mixtures of these heavy metals solutions were prepared by taking 500 ml of each solution in a volumetric flask. Batch equilibrium adsorption experiments were performed using a volume of 30 ml from mixture of solution. After the sorption process, the sorbent was separated from the sample by filtering and the filtrate was analyzed using Voltammeter (VA 797 Computrace) for Pb, Cd, Cu and Zn and UV spectrophotometer for Cr

To investigate the effects of adsorption parameters such as, pH (2, 4, 8, and 12), temperature (28, 32, 36, 40 and 42 ^{o}C) and contact time (4, 3 and 2 hr) the solutions were studied in batch mode.

The removal efficiency of the contaminants (Pb, Cr, Cd, Cu and Zn) was calculated using the following formula.

Removal efficiency= $(C_f - C_i)/ C_f \times 100$ (1)

Where

C_i Quantity of metals before adsorption experiment

C_f Quantity of metals after adsorption experiment

Where C_i is the initial metal ion concentration (mg/L), C_f is the equilibrium concentration of the metal ion (mg/L).

3. Results and Discussion

3.1 Properties of Bio-char

Table 1 shows the surface area, total pore volume and average pore diameter of the paper mulberry bio-chars produced. Single point BET surface area of the bio-chars was determined by the nitrogen sorption method. Paper mulberry bio-char has surface area of 1.84 m^2g^{-1}, total pore volume of 5.37×10^{-3} and average pore diameter of 11.7 nm. There is an inverse relationship between surface area and average pore diameter.

Table 1. Physical properties of bio-chars.

Char samples	$^aS_{BET}$ (m^2g^{-1})	^bV_T (cm^3/g)	^{c} av (nm)
Paper mulberry	1.84	5.37×10^{-3}	11.7

a (S_{BET}: BET surface area; b (v_T: Total pore volume); c (average pore diameter)

3.2 Effect of pH on Heavy Metals Removal

pH of the solution is one of the most significant parameter effecting the removal of heavy metals from aqueous solution. The pH of the solution has the capacity to affect the surface charges of the biosorbent, the concentration of the opposing ions on the functional groups of the biosorbent, the degree of ionization of the biosorbent during biosorption, and the forms of the metal ions in aqueous solutions [14- 16]. The effect of initial pH on the adsorption of heavy metals was studied at pH of 2, 4, 8, and 12 and the results are given in Figure 2. It is seen from this figure that the adsorption amount increased as pH increased to 12 for Cd, Cu, Pb and Zn ions. Due to lower pH, the surface holds more positive charges and therefore significantly repels the cations present in solution i.e. metal ions competing with H^+ ions for sorption sites. Thus hydrogen ions would preferentially adsorb over adsorbent surface hindering various positively charged metal ions from reaching the binding sites of the adsorbent. Whereas, more negatively charged surface becomes available as the pH increases, thus facilitating greater metal removal.

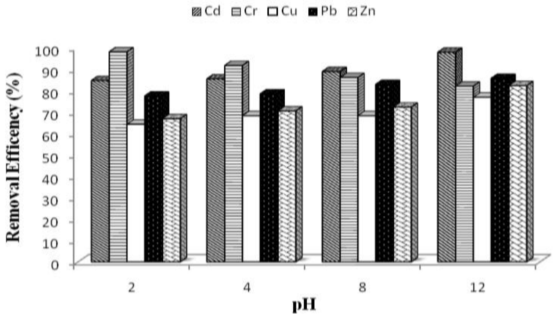

Figure 2. Removal efficiency of paper mulberry bio-char at different pH.

Cr adsorption decreases with increasing pH due to fact that the metal surface becomes more protonated in acidic conditions and favours the uptake of anionic Cr. With the increase in pH of the solution surface protonation of adsorbent decreases slowly leading to decreased in Cr adsorption. Dissociation of the functional groups on adsorbent influences pH dependence of metal adsorption. Moreover, there is competition between OH^- and chromate ion as the pH of solution increases due to the fact more OH^- ions are released at higher pH values. Adsorption capacity of sorbent is reduced due to weakening of the electrostatic forces between adsorbent and metal ions as the net positive surface potential of the adsorbent decreases at higher pH.

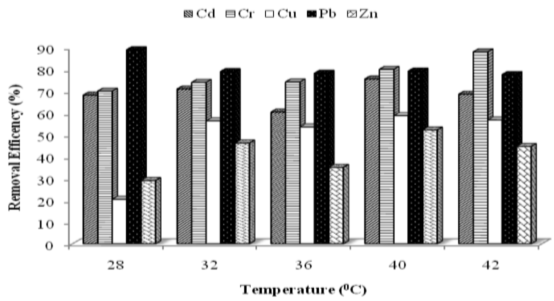

Figure 3. Removal efficiency of paper mulberry bio-char at different temperatures.

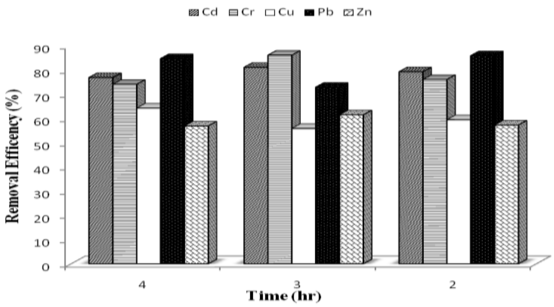

Figure 4. Removal efficiency of paper mulberry bio-char at different contact time.

Table 2. Thermodynamic parameters of adsorption of heavy metals on paper mulberry bio-char.

Thermodynamic parameters	Temperature (°C)	ΔG°				
		Cd	Cu	Cr	Pb	Zn
	28	-1.230	-0.387	-2.167	2.274	-0.096
	32	-1.246	-0.392	-2.195	-2.304	-0.097
	36	-1.262	0.397	-2.224	2.334	-0.098
	40	-1.279	-0.402	-2.253	-2.334	0.100
	42	-1.287	-0.405	-2.267	-2.379	-0.100
ΔH°		-0.132	0.078	0.54	-0.038	0.037
ΔS°		414.7	251.03	186.4	112.1	116.5
R^2		0.505	0.599	0.765	0.644	0.463

3.3 Effect of Temperature on Heavy Metals Removal

Temperature of the medium also effects adsorption efficiency [17]. Therefore the sorption of Cd, Cu, Pb and Zn on paper mulberry bio-char was studied at 28, 32, 36, 40 and 42°C. Effect of variation in temperature on the removal efficiency of paper mulberry bio-char for Cd, Cr, Cu, Pb, and Zn is shown in Figure 3. Removal efficiency of (Cd, Cr, Cu, and Zn) was found to increase by increasing temperature. Maximum adsorption of heavy metals by paper mulberry bio-char was recorded at temperature 40 and 42 °C. The increase in the sorption capacity of paper mulberry with temperature indicates an endothermic process [18]. The increased adsorption of heavy metals with temperature may be attributed to either increase in the number of the active surface sites available for adsorption on the adsorbent or the de-solvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases [19]. While adsorption of (Pb) has found to decrease with increase in temperature after which it remains stable, but resulted in desorption of some of the metal ions from the adsorbent surface due to the decreased surface activity, and the biosorption process was observed to be exothermic in nature [20].

3.4 Effect of Contact Time on Heavy Metals Removal

Effect of variation in contact time on the removal efficiency of paper mulberry for Cd, Cr, Cu, Pb and Zn at contact times of 2, 3, 4 hours are shown in Figure 4. Highest removal efficiency of paper mulberry for Cd, Cr, and Zn were observed at contact time of 3 hours. Maximum removal efficiency of paper mulberry for Pb was observed at contact time of 2 hours while the maximum adsorption of Cu by paper mulberry bio-char was observed at contact time of 4 hours. The percentage of metal ions removed approached equilibrium within 180 min (3 hours) for Cd^{+2}, Cr^{+2} and Zn^{+2},120 min (2 hours) for Pb^{+2} and 240 min (4 hours) for Cu^{+2}. The following trend was observed Cr^{2+}>Pb^{2+}>Cd^{2+}> Cu^{2+}>Zn^{+2}, after which further increase in time did not bring about any further improvement but resulted in desorption of some of the metal ions (Cadmium and Zinc) from the adsorbent surface. This experiment shows that different metal ions attained equilibrium at different times.

3.5 Thermodynamic Modeling

In order to determine spontaneous nature of a reaction, thermodynamic calculations should be taken in to account. Modeling temperature dependence of the adsorption process is associated with several thermodynamic parameters. Enthalpy ΔH°, entropy ΔS° and Gibbs free energy ΔG° of sorption are useful thermodynamic parameters in concluding endothermic or exothermic nature of a reaction. Change in Gibbs free energy indicates spontaneity of a reaction. To determine the Gibbs free energy of a chemical reaction two factors must be considered i.e., energy and entropy [21]. Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and the entropy change (ΔS°) can be estimated using the variation of equilibrium constants with temperature. Following equation gives change in Gibbs free energy of an adsorption processes:

$$\Delta G° = -RT \ln KL \quad (2)$$

In the equation, R = gas constant having value of 8.314 J/mol K, KL = equilibrium constant and T = absolute temperature in Kelvin. The KL value was calculated with the help of the given equation:

$$KL = qe/Ce \quad (3)$$

Where qe = equilibrium concentration of metal ions on adsorbent (mg/g), and Ce = equilibrium concentration of metal ions in the solution (mg/L). ΔH° ΔS° and ΔG° relationship can be determined by following equations:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (4)$$

Eq. (6) can be written as

$$\ln KL = -\Delta G°/RT = -\Delta H°/RT + \Delta S°/R \qquad (5)$$

According to Eq. (5), ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of lnKL versus 1/T, respectively. Possibility of sorption at higher temperatures decreases with the decrease in ΔG◦ values. Positive value of ΔH° indicates that the nature of the adsorption process is endothermic in all cases. It means that at elevated temperatures sorption process are increased. Values of enthalpy (ΔH°), Gibbs free energy change (ΔG° and entropy (ΔS° of the study are presented in Table 2. Thermodynamic feasibility and spontaneous nature of adsorption process by PMB is indicated by negative ΔG° values. Exothermic and endothermic nature of process is indicated by negative and positive values of enthalpy change (ΔH° respectively. Increased in randomness at the solid–solution interface during the sorption process is shown by positive value of ΔS°.

4. Conclusion

In this study bio-char, a by-product of the pyrolysis process was evaluated as an alternative low-cost adsorbent for the removal of Cu, Cd, Cr, Zn and Pb ions from aqueous solution. Optimum adsorption conditions were determined as a function of temperature of solution, contact time and pH for Cd, Cr, Cu, Pb and Zn removal. The thermodynamic parameters ΔG°, ΔH° and ΔS° show a chemically favoured, spontaneous and endothermic adsorption. It can be concluded that paper mulberry bio-char is an effective, alternative, and economically feasible precursor for heavy metal removal from aqueous solutions.

References

[1] D. Sud, G. Mahajan and M. P. Kaur, Bioresource Technol. **99** (2008) 6017.

[2] A. K. Meena, K. Kadirvelu, G.K. Mishraa, C. Rajagopal and P. N. Nagar, J. Hazard. Mater. **150** (2008) 619.

[3] A. K. Rao and S. Ikram, Desalination **277** (2011) 390.

[4] A. Demirbas, J. Hazard. Mater. **167** (2009) 1.

[5] Y. Li, X. Ding, Y. Guo, C. Rong, L. Wang, Y. Qu and Z. Wang, J. Hazard. Mater. **186** (2011) 2151.

[6] S. Karagöz, T. Tay, T. Ucar and M. Erdem, Bioresource Technol. **99** (2008) 6214.

[7] E. Apaydin-Varol, E. Pütün and A.E. Pütün, Fuel **86** (2007) 1892.

[8] M. Ahmad, A. U. Rajapaksha, J. E. Lim, M. Zhang, N. Bolan, D. Mohan and Y. S. Ok, Chemosphere **99** (2014) 19.

[9] L. Beesley and M. Marmiroli, Environ. Pollut. **159** (2011) 474.

[10] M. Uchimiya, S. Chang and K.T. Klasson, J. Hazard. Mater. **190** (2011) 432.

[11] X.D. Cao, L. Ma, B. Gao and W. Harris, Environ. Sci. Technol. **43** (2009) 3285.

[12] R. N. Malik and S. Z. Husain, Pak. J. Bot. **39** (2007) 1045.

[13] G. Habib, Mater. Res. Dev. **24** (2004) 106.

[14] A. Özer and H. B. Pirincci, J. Hazard. Mater. **137** (2006) 849.

[15] A. Özer, J. Hazard. Mater. **141** (2007) 753.

[16] J-X. Yu, L-Y. Wang, R-A. Chi, Y-F. Zhang, Z-G. Xu and J. Guo, Appl. Surf. Sci. **268** (2013) 163.

[17] O.D. Uluozlu, A. Sari and M. Tuzen, Chem. Eng. J. **163** (2010) 382.

[18] F. Ghomri, A. Lahsini, A. Laajeb and A. Addaou, Larhyss J. **12** (2013) 1112.

[19] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal and P.N. Nagar, J. Hazard. Mater. **122** (2005) 161.

[20] Ş. Taşar, F. Kaya and A. Özer, J. Environ. Chem. Eng. **2** (2014) 1018.

[21] H. Ucun, Y.K. Bayhan and Y. Kaya, J. Hazard. Mater. **153** (2008) 52.