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Heavy Metal Removal Efficiency of Paper Mulberry Biochar and Commercially Available Silica Powder from Simulated Industrial Wastewater

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Abstract: Paper mulberry bio-char produced was characterized and evaluated for heavy metals removal from simulated industrial wastewater in compare to silica powder. The batch adsorption study was conducted under different conditions like, the effects of solution pH, contact time and temperature. The paper mulberry bio-char (PMB) was more effective and exhibited a higher adsorption potential for cadmium, copper, chromium, lead and zinc than commercially available silica powder. Experiments conducted with an initial metal concentration of 50 mg/l at pH 2, 4, 8, 12. Maximum removal of cadmium, copper, chromium, lead and zinc by PMB was higher than silica powder. Contact time of 2, 3, 4 h showed maximum removal of cadmium, copper, chromium, lead and zinc removal for PMB and was found higher than that of silica powder. The thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated for predicting the nature of sorption. The results showed that plant-residue bio-char can act as effective alternative sorbent instead of silica powder for the removal of heavy metal ions from industrial wastewater.

INTRODUCTION

The pollution of surface and underground water has been gradually increased; that is worldwide concern due to the disposal of heavy metals for last few decades [1]. Heavy metals coming from municipal waste and agriculture runoff to the earth's surface from industrial process can pollute surface water and underground water. Heavy metals are usually released into water bodies from industrial/domestic effluents such as metal plating industries, mining and tanneries, etc. Heavy metals from polluted water bodies can then diffuse into the surrounding soil, surface water and groundwater. When the polluted water is consumed by living organisms, the toxic heavy metals can accumulate and become harmful [2]. The human health and ecological systems are threatened to get worse. Harmful heavy metals are abundant in the water bodies due to the rapid industrial and agricultural development together with

the population growth [1]. It is necessary to remove heavy metal from industrial sources before they enter to environment. Many processes are developed to address these stringent environmental regulations which necessitate removal of heavy metal compounds from wastewater.

Common contaminants removal processes are known as chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical filtration, etc. [3-5]. Most of these processes are difficult to implement on large scale due to expensiveness and ineffectiveness at low concentration (<100 mg/l) and production of toxic sludge and other waste products that also need disposal [6, 7]. The disadvantages have increased the need of developing alternative and low-cost water treatment technologies for treatment of heavy metal contaminants. Among these technologies for the removal of heavy metal, adsorption is considered as simple, user-friendly technique and efficient method. Adsorption is a fundamental process in the

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physiochemical treatment of wastewaters because of its relative low cost.

Great efforts have been made to use the economically efficient and unconventional adsorbents to adsorb heavy metals from aqueous solutions, such as aquatic plants, plant wastes, agricultural and industrial by-products. Therefore, especially assessment of biomass is getting increased attention in all over the world as it is renewable, widely available, cheap and environmental friendly. There are a number of biomass sources, such as forest residues, low grade plants, agricultural residues and municipal solid wastes, which can be utilized for activated carbon precursor. Biomass is a renewable energy resource and has a growing interest as a chemical feedstock source [8, 9].

Bio-char is a fine-grained, carbon rich material and porous substance, similar in its appearance to charcoal produced by natural burning which results from combustion of organic materials under oxygen-limited conditions (Pyrolysis). Because of its high surface-to-volume ratio and strong affinity for non-polar substances biochars can be a potential sorbent for organic pollutants and pesticides, particularly planar aromatic compounds [10, 11]. The distribution of products depends upon heating rate, temperature, surrounding atmosphere and residence time. Bio-char is extensively used for water treatment process, adsorption potential of almond shell bio-char for Ni and Co removal from aqueous solution. Characterization and investigation of bio-chars produced through pyrolysis of hardwood for the removal of Cu and Zn from aqueous solution. The ability of bio-chars converted from anaerobically digested biomass to sorb heavy metals used in a range of laboratory sorption and characterization experiments [13-15].

The primary objective of this study was to investigate the ability of paper mulberry derived biochar in comparison with commercially available silica powder for the removal of heavy metals (cadmium, copper, chromium, lead, zinc) from simulated industrial wastewater.

MATERIALS AND METHODS

Adsorbates: The adsorbates in this study were cadmium, copper, chromium, lead and zinc by dissolving cadmium chloride ($CdCl_2.H_2O$), copper chloride ($CuCl_2.2H_2O$), potassium dichromate (K_2CrO_7), lead chloride (PbCl2) and zinc sulphate ($ZnSO_4.7H_2O$) salts in 1000ml of distilled deionized water used as stock solution concentrations of 1000 mg/l of each metal. Mixture of cadmium, copper, chromium, lead, zinc solutions were prepared by taking 50ml (50ppm) of each solution in 500ml

volumetric flask and make volume by distilled water.

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

Removal efficiency= $(C_f - C_i)/ C_f$ X 100

Where, C_i is quantity of metals before adsorption experiment; C_f is quantity of metals after adsorption experiment. In addition, C_i is the initial metal ion concentration (mg/l), C_e is the equilibrium concentration of the metal ion (mg/l).

Adsorbents: The adsorbents that were studied were: PMB biochar; commercially available silica powder (SP).

PMB Biochar Preparation: Paper mulberry *(Broussonetia papyrifera)* locally grown in Pakistan, were obtained from a plantation in Islamabad, Pakistan was used for producing bio-char. Bark/wood thoroughly washed in water to remove any dust, sand, leaves, dirt and adhesive insoluble materials. Conversion of paper mulberry to biochar was conducted in a high Helium Diffusion Furnace (SLM-1). Air and oven dried samples were crushed and ground small particles in electric grinder to obtain homogenous powder and the resultant powder was sieve to a size no larger than 0.00141 mm (1.4μm) in size. Sieved sample of paper mulberry biomass were pyrolyzed in a tube furnace at 350°C. The biochar was then air dried and held for further characterization.

Biochar Characterization
SEM Analysis: For SEM analysis PMB biochar samples were processes by compacting bio-chars sample in the locally designed pellet press to make discs (diameter= 9mm, thickness= 3mm) to fit in the especially fabricated Aluminum (Al) stubs (O.D= 10 mm, I.D= 9mm, depth= 3mm) to make the surface of bio-char samples conductive before scanning electron microscopy. The maximum thickness of Au coating ranged from 10-20 μM. The conductive layer helps in passing of electron charge through the sample. A series of electron micrographs were recorded of each sample at various magnifications SEM (Model: Leo 440I).

BET Surface Area Measurement: The method of Brunauer, Emmett and Teller (BET) is commonly used to determine the total surface area of materials. One gram of bio-char samples was degassed at 350°C for 24 hours under pressure of 7 Pa before adsorption measurements. The degassed samples were introduced in an automated nitrogen adsorption apparatus at 77 K. The equilibrium

points inside the 0.00-0.22 P/P0 range were determined by the BET equation to calculate the surface area of the bio-char samples [16]. The porosity of the bio-char such as pore diameter and pore volumes was also determined from BET analysis.

RESULTS AND DISCUSSION

Effect of pH on Adsorption: pH of the solution is one of the most important parameters in the removal of heavy metals from aqueous solution. The pH of the solution has an ability to affect the surface charges of the biosorbent, the degree of ionization of the biosorbent during biosorption and the forms of the metal ions in aqueous solutions [17-19]. The effect of pH on heavy metals (Cd, Cr, Cu, Pb and Zn) ions by PMB bio-char and silica powder were evaluated at four pH levels viz 2, 4, 8 and 12 (Figures 1 and 2). Cadmium, copper, lead and zinc adsorption increased with increase in pH. Maximum removal efficiency of these metals were recorded at pH of 12 (see Figures 1 and 2). One of the potential factors for the considerable low adsorption capacity at pH 2.0 is the H^+ ions compete with metal cation for the exchange sites in the system; thereby partially releasing the later. The heavy metal cations are completely released under circumstances of extreme acidic conditions [20, 21]. However removal efficiency of chromium was decreased as the pH is increased and maximum removal efficiency was achieved in acidic pH. This is because of the fact under acidic condition the metal surface is highly protonated that favors the uptake of Cr in anionic form. By increasing the pH of the solution surface protonation of adsorbent gradually reduces and hence adsorption decrease.

Effect of Contact Time on Adsorption: Contact time is another important factor in batch sorption process [22]. The effect of contact time on the sorption of Cd, Cu, Cr, Pb, Zn was determined at three contact times viz 2, 3 and 4hours (Figures 3 and 4). For adsorption of Cd, Cr and Zn, PMB bio-char reached to near asymptotic removal within 3h. Maximum removal of Cu and Pb by PMB bio-char observed at contact time of 4h and 2h, respectively. While, removal efficiency of Cd and Cu by SiO_2 was below 50% at contact time of 3h. Maximum removal efficiency for Zn was 12.6% at contact time of 4h. Removal efficiency of cadmium, copper, chromium, lead and zinc by paper mulberry biochar were higher than commercially available silica powder.
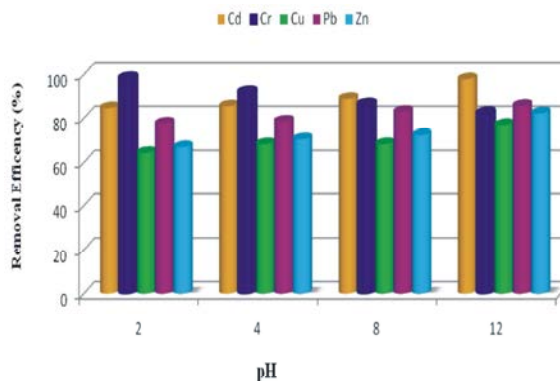

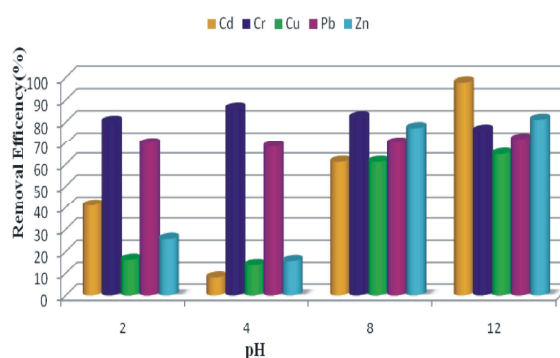Fig 1: Removal efficiency of PMB bio-char at different pH

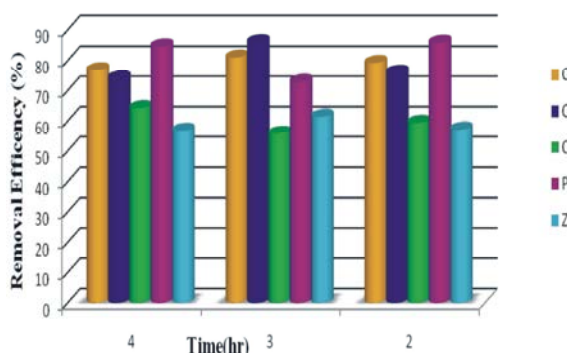Fig 2: Removal efficiency of Silica at different pH

Fig 3: Removal efficiency of PMB bio-char at different contact time
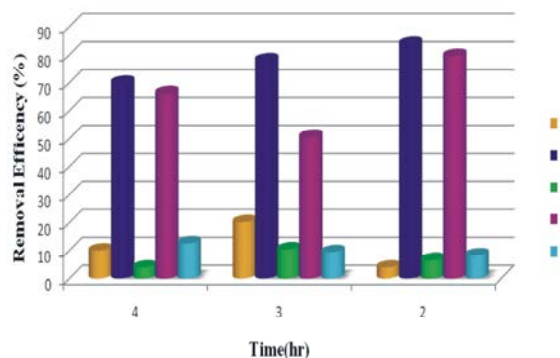

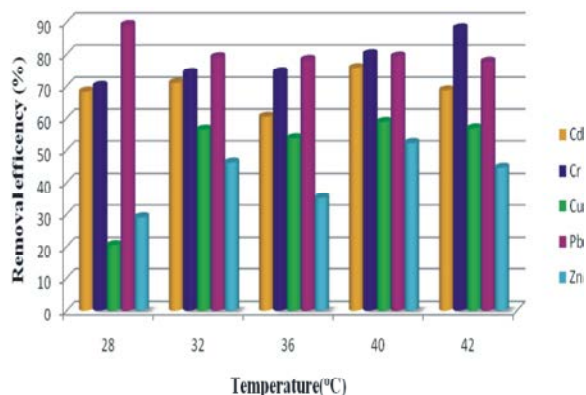Fig 4: Removal efficiency of silica at different contact time

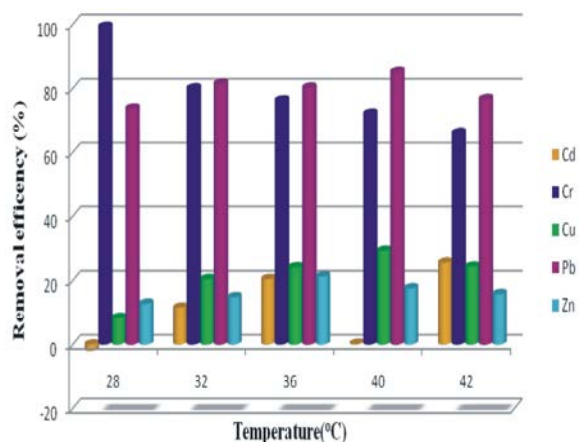Fig 5: Removal efficiency of PMB bio-char at different temperature

Fig 6: Removal efficiency of silica at different temperatures

Effect of Temperature on Adsorption: The effect of temperature variation on the sorption of Cd, Cu, Cr, Pb and Zn was determined at four temperature levels viz 28, 32, 36, 40 and 42°C (Figures 5 and 6). For cadmium, copper, zinc PMB showed maximum heavy metal removal of 75.6, 58.8 and 52.2% at 40°C; that was far greater than heavy metal removal at 42, 40 and 36°C. For chromium maximum removal efficiency of SiO_2 was (99%) at 28°C; that is greater than the adsorbed on PMB (88%) at 42°C. Maximum removal of Pb by paper mulberry was 89%. An increase in removal of metals by PMB with increasing temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation 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 [23].

Table 1: Physical properties of bio-chars

Char samples	$^aS_{BET}$ (m^2g^{-1})	^bV_T (cc/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)

Since diffusion is an endothermic process, greater adsorption will be observed at high temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperature. While sorption of chromium was recorded to be decreased with an increase in temperature and show maximum removal of 99% at 28°C, after which further increase in temperature did not bring about any further improvement for the metal ions, but resulted in desorption of some of the metal ions from the adsorbent surface.

Biochar Characterization
Scanning Electron Microscope and Bet Surface Area:
Table 1 shows 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 $1.84m^2g^{-1}$, total pore volume of 5.37×10^{-3} and average pore diameter of 11.7nm. There is an inverse relationship between surface area and average pore diameter.

Figure 7 shows scanning electron microscopy (SEM) images of paper mulberry bio-char. Morphological analysis was performed by scanning electron microscopy. SEM micrographs clearly show the amorphous and heterogeneous nature of paper mulberry bio-char. Scanning electron microscopy revealed that internal pores and cracks /mesopores are present in bio-chars materials. Due to importance of mesopores to many liquid-solid sorption processes these pores are of importance to many liquid-solid sorption processes [24].

Thermodynamic Model: Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The thermodynamic parameters, the values of enthalpy $\Delta H°$ and entropy $\Delta S°$ and Gibbs free energy $\Delta G°$ of sorption are useful in defining whether sorption is endothermic or exothermic. Modelling temperature dependence of the adsorption process is associated with several thermodynamic parameters. Thermodynamic considerations of an adsorption process are necessary
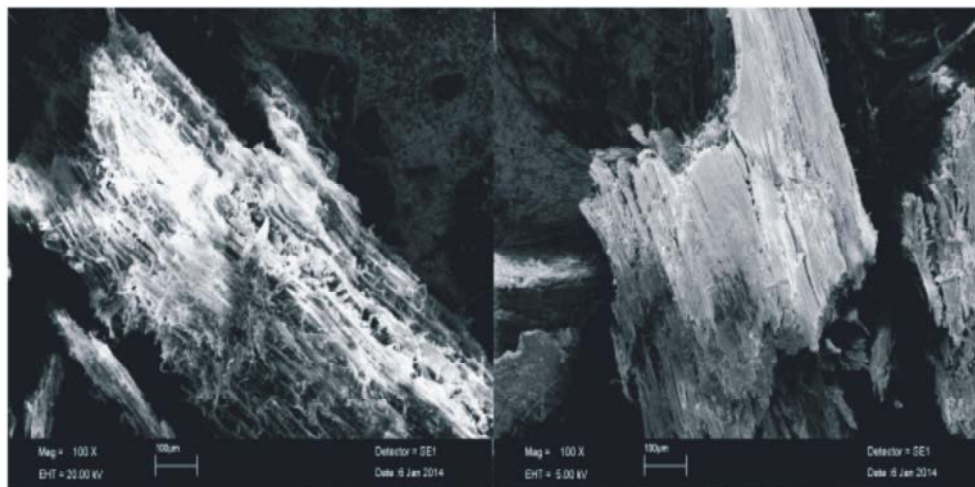
Fig 7: Paper mulberry bio-char micrographs.

to conclude whether the process is spontaneous or not. The Gibbs free energy change is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process [25]. Thermodynamic parameters such as Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and the entropy change ($\Delta S°$) can be estimated using equilibrium constants changing with temperature. The Gibbs free energy change of the adsorption reaction can be determined from the following equation.

$$\Delta G° = -RT \ln K_L \qquad (4)$$

Where R is gas constant (8.314 J/mol K), K_L is equilibrium constant and T is absolute temperature (K). The K_L value was calculated using the following equation:

$$K_L = q_e / C_e \qquad (5)$$

Where q_e and C_e is the equilibrium concentration of metal ions on adsorbent (mg/g) and in the solution (mg/l), respectively. Relation between $\Delta G°$, $\Delta H°$ and $\Delta S°$ can be expressed by the following equations

$$\Delta G° = \Delta H° - T\Delta S° \qquad (6)$$

Eq. (6) can be written as

$$\ln K_L = - \Delta G°/RT = - \Delta H°/RT + \Delta S°/R \qquad (7)$$

According to Eq. (7), $\Delta H°$ and $\Delta S°$ parameters can be calculated from the slope and intercept of the plot of ln K_L versus 1/T, respectively [25-27]. Moreover, the decrease in $\Delta G°$ values with increase in temperature shows a decrease in feasibility of sorption at higher temperatures. The positive value of $\Delta H°$ indicates that the nature of adsorption process is endothermic in all cases. This behavior indicates that higher temperatures are more preferred for higher sorption. The positive

Table 2: Thermodynamic parameters of adsorption of heavy metals on PMB

Thermodynamic parameters	Temperature (°C)	$\Delta G°$				
		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
$\Delta H°$		-0.132	0.078	0.54	-0.038	0.037
$\Delta S°$		414.7	251.03	186.4	112.1	116.5
R^2		0.505	0.599	0.765	0.644	0.463

Table 3: Thermodynamic parameters of adsorption of heavy metals on silica powder

Thermodynamic parameters	Temperature (°C)	$\Delta G°$				
		Cd	Cu	Cr	Pb	Zn
	28	-1.172	-0.963	-4.997	-1.903	1.428
	32	-1.187	0.976	-5.063	-1.929	1.447
	36	1.203	0.989	-5.130	-1.954	1.466
	40	1.218	1.002	-5.196	-1.979	1.485
	42	1.226	1.008	-5.229	-1.992	1.494
$\Delta H°$		-0.166	0.069	-0.188	0.0168	0.0174
$\Delta S°$		557.0	212.2	595.3	65.8	43.0
R^2		0.254	0.732	0.715	0.192	0.31

value of $\Delta S°$ shows the increased randomness at the solid-solution interface during the sorption process [13]. The calculated values of Gibbs free energy change ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) are given in Tables 2 and 3.

The negative $\Delta G°$ values indicate that the process is thermodynamically feasible, spontaneous and corresponding to a chemical. The negative value of $\Delta H°$ (Tables 2 and 3) indicates that the nature of adsorption process is exothermic. While positive value of ($\Delta H°$) shows that the nature of adsorption process is endothermic. The positive value of $\Delta S°$ shows the increased randomness at the solid-solution interface during the adsorption of metal ions on PMB bio-char and silica powder. The increase in adsorption capacity of sorbents at higher temperature may be attributed to the enlargement of pore size or activation of the adsorbent surface [28].

CONCLUSION

The ability of activated PMB bio-char to remove heavy metals from simulated industrial wastewater was demonstrated through a series of batch experiments examining the influence of solution pH value, contact time and temperature. Comparison with commercially available silica powder was also conducted in present study. This work showed that paper mulberry biochar was more effective alternative and low cost sorbent precursor of silica powder in removing Cd, Cr, Cu Pb, Zn, from multi-metal solutions. Heavy metals often coexist in contaminated water, their association and interactions with one another will influence their removal. Therefore, the competitive sorption issue should be taken into account before what biochars can be relied upon as sorbents for treating mixed wastewaters.

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