RESEARCH ARTICLE

Removal of Lead and Cadmium from Aqueous Solutions by Banana Peel Biochar

Khan Agha Shenwari[1], S.Priyatharshini[2], P.Dhevagi[2], T. Chitdeshwari[3] and S. Avudainayagam[2]
[1]Ministry of Agriculture, Irrigation and Livestock - Nangarhar Canal Project – Afghanistan
[2]Department of Environmental Sciences
[3]Department of Soil Science & Agricultural Chemistry
Tamil Nadu Agricultural University, Coimbatore – 641 003

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ABSTRACT

Heavy metals are ubiquitous environmental pollutants to influence on changing the different environmental compartments including air, water and soil. Due to the toxicity, persistence and bioavailability status, metal contamination is a serious issue for environment especially in terrestrial and aquatic systems. Biosorption of heavy metals is the physicochemical removal process of heavy ions or their compounds, from wastewater by using biosorbents. In this point of view, to remove lead and cadmium by eco-friendly manner banana peel biochar powder based biosorbents has been taken for the present investigation, and used Atomic Adsorption Spectrophotometer for metal estimation. Different electrochemical and biochemical characterizations such as pH, EC, CEC, particle size, zeta potential, organic carbon, crude protein, moisture content, dry matter, ash content and elemental composition of banana peel biochar was analyzed through standard methods. The SEM images determined that banana peel biochar contain irregular porous surface area, and also the FTIR peaks showed that banana peel biochar has C-H, =CHand C-Cl functional groups which has important role in adsorption of metals. The batch experiment was conducted to the effect of pH, metal ion concentration and contact time. The highest adsorption of Pb (83.45%) and Cd (89.87%) was observed at pH 7 and 75 ppm concentration, and the maximum adsorption of both elements recorded at 6 hours contact time. The banana peel biochar has high capacity of heavy metals adsorption from wastewater such as Pb (II) and Cd (II), but the adsorption efficiency of Cd was higher than Pb.

Keywords: *Lead, Cadmium, pH, Absorption - Banana peel biochar*

INTRODUCTION

Rapid industrialization leads to reduction in the availability of water, despite their potential abundance in the earth. There is an increasing demand for water on daily basis; the available water resources are gradually decreasing and also contaminated. Heavy metals have received a great deal of attention owing to their potential risks on health and environment. The heavy metals like arsenic, barium, chromium, lead, mercury, cadmium, selenium, and silver in larger amounts can be dangerous even though they occur at low level in the environment. Lead is being one of the three most hazardous metal, accumulates in the body causing severe damage to the central nervous system, kidney, bone marrow and liver (Tsoi *et al*., 2016). Recent studies indicate that the rise in mortality and systolic blood pressure are due to elevated lead levels in blood. Cadmium, the seventh most toxic metal as per ATSDR, (2007), on the other hand, instigates cancer, damage to bones, kidney and mucus membrane. It also causes vomiting and affects hormone secretion. The main source of lead and cadmium in water is the effluents of processing industries, i.e., electroplating, paint, pigment, basic steel work, textile industries, metal finishing and electric batteries (Anwar *et al*., 2010). There are several methods to remove the metals from wastewater. Conventional method includes, different technologies, such as adsorption, chemical precipitation, coagulation/flocculation, evaporation, membrane filtration, complexation, biological operations, ion exchange/solvent extraction and electrochemical operations, etc., have been employed in removing metals from contaminated water and wastewater, but adsorption is an economical metal removal method compared to other technologies.

*Corresponding author's e-mail: khanaghashenwari@yahoo.com

MATERIAL AND METHODS

Adsorbent preparation

The (*Musa paradisiac*) banana peel were collected from the banana chips industry in local market, Coimbatore - Tamil Nadu, India for experimental studies. The peels were washed and kept to sun light for drying for 6-8 days and then biochar was prepared through the process of slow pyrolysis at 400-600 °C temperature. The pyrolysis reactor consisted of two chambers namely combustion and pyrolysis chamber. A known quantity (10 kg) of dried banana peel was filled in the pyrolysis chamber and some quantity of charcoal is filled in the combustion chamber which was used as the combustion fuel. The pyrolysis process was initialized by combusting the fuel in the combustion chamber and the air supply for the combustion was provided from the bottom opening of the reactor. After the reaction time, the charcoal produced was taken out and cooled to atmospheric temperature, powdered, packed in an airtight covers and stored for further analysis.

Solution preparation

The Pb $(NO_3)_2$ and $CdCl_2.H_2O$ were used as the sources of Lead and Cadmium solutions. (0.159 g) of Pb $(NO_3)_2$ and (0.179 g) of $CdCl_2.H_2O$ was dissolved into (100 ml) Milli-Q water and prepared 1000 ppm stock solutions. Then different concentrations (25, 50, 75 and 100 ppm) were prepared from stock solution using the formula: $V_1 N_1 = V_2 N_2$, where; V_1 is the volume of stock solution (ml), V_2 is the desired volume of solution (ml), N_1 is Initial concentration (ppm) (stock solution) and N_2 is the final concentration (ppm) (working standard solution).

Characterization of adsorbents

The different characterization of banana peel biochar such as electrochemical properties, biochemical components and elemental composition were analyzed as per the standard procedure (Jackson,1973;Sadasivam and Manickam,2009).

Scanning electron microscope (SEM) with energy dispersive X-ray (EDX)

Scanning electron microscope (M/s. FEI – Quanta 250, Czech Republic) was used to observe the morphological characteristic of banana peel biochar samples (Ucar *et al.,* 2014). The samples were grounded to nanosize and spreaded on double sided conductive carbon tap fixed on the stub. After attaining high vacuum the filament was turned on and adjusted to various required parameters like electron beam, intensity, spot size, voltage, emission current then the SEM images were captured and pore space was measured to study the adsorption properties of banana peel biochar. The SEM was also equipped with EDX analyzer which determined the elemental parameters of banana peel biochar.

Fourier transform infrared spectroscopy (FTIR)

The banana peel biochar sample was analyzed by FT-IR spectroscopy before and after adsorption of Pb and Cd and determined the functional groups. FTIR spectra were recorded with 0.5 mg of sample embedded in potassium bromide (0.1 wt % KBr) and then pressed into pellets separately and observed in a FTIR (Model 8400S of Shimadzu, Japan) using Attenuated Total Reflectance (ATR) technique having wavelength source (400-4000 cm^{-1}) (Trakal *et al.,* 2014).

Batch adsorption

One gram of banana peel biochar powder (0.5 mm size) was added to 100 ml of the metal ion solutions with different initial concentrations (25 ppm, 50 ppm, 75 ppm and 100 ppm). After mixing different pH of the solutions(4, 5, 6, 7 and 8) were adjusted by drop-wise addition of 0.1N NaOH and 0.1N HCl, and equilibrated in room temperature. After equilibration time the solutions were filtered through whatsmann No. 42 filter paper, and final metal ion concentration was measured by Atomic Adsorption Spectrophotometer. The removal efficiency was calculated using the formula: Removal efficiency (%) = $(C_i - C_f)/ C_i \times 100$, Where; Ci is the initial concentration of metal ion in solution before sorption (mg L^{-1}) and Cf is the final metal ion concentration after the sorption analysis (mg L^{-1}).

RESULTS AND DISCUSSION

Electrochemical, biochemical and elemental characterization

The electrochemical, biochemical and elemental composition of banana peel biochar are given in table 1 and 2.

Table 1. Electrochemical and biochemical characterization of banana peel biochar

Parameter	Result	Parameter	Result
pH	9.96	Organic carbon (%)	20.32
EC (dSm^{-1})	2.95	Crude protein (%)	15.31
CEC (cmol + kg^{-1})	10.4	Moisture content (%)	7.50
Particle size (nm)	11315.60	Dry matter (%)	92.50
Zeta potential (mV)	-0.20	Ash content (%)	17.00

The pH of banana peel biochar was 9.96 in (1:10) ration. The alkaline pH may be effected by the release of alkali salts from feedstock during pyrolysis. The EC and CEC of banana peel biochar was 2.95(dSm^{-1}) and 10.4 (cmol + kg^{-1}) respectively, which was higher compared to raw banana peel, hence biochar is an effective adsorbent for the removal of metal ions. Gomez-Eyles *et al*., (2013) mentioned that the reason for high CEC in biochar might be due to increase in surface area after pyrolysis and also increase in charge density on the surface.

Table 2. Elemental composition of banana peel biochar

Parameter	Result (mg g^{-1})	Parameter	Result (mg g^{-1})
Total Nitrogen	15.2	Sodium	25.65
Total Phosphorus	5.51	Iron	0.18
Total Potassium	36.42	Manganese	42.14
Calcium	12.43	Zinc	0.13
Magnesium	10.87		

The particle size was 11315.6 nm and the zeta potential was negatively charged (-0.2), which indicates stability of the particles. Organic carbon and crude protein was estimated 20.32%and 15.31%, but moisture content, dry matter and ash content was observed7.5%, 92.5% and 17%respectively. The higher dry matter

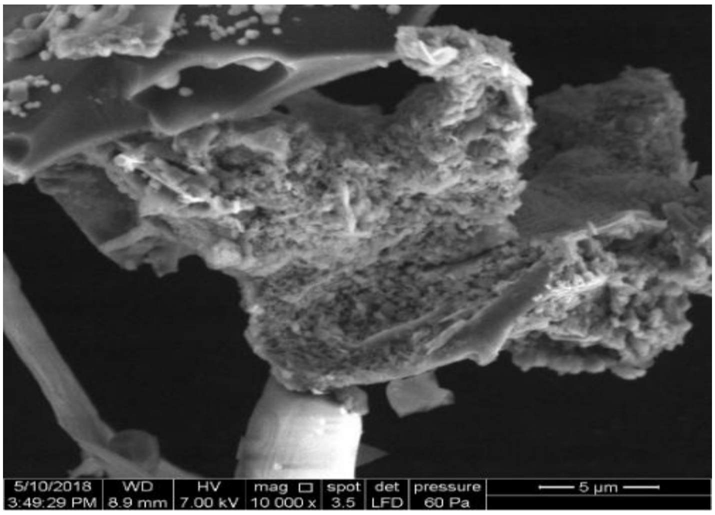

Figure 1. SEM image of banana peel biochar before adsorption

content is may be due to the changes that occurred during the pyrolysis. The ash content in raw banana peel powder was seen 10.65% which is approximately same with the report of Anhwange and Joseph, (2009) who observed 8.50%, but Raymundo *et al.,* (2014) noted 19.98% of ash content in banana peel. Thetotal nitrogen, phosphorous and potassium content of banana peel biochar was estimated 15.2, 5.51 and 36.42 mg g^{-1}, but the calcium and magnesium was observed 12.43 and 10.87 mg g^{-1} respectively. Pannraphat (2014) was reported very low calcium content (1.246 %), and higher magnesium (21.540 %) in banana peel biochar, this may be due to the differences in the banana varieties, method of peel removal as well as pyrolysis temperature. The total Na, Fe, Mn and Zn content of banana peel biochar was 25.65, 0.18, 42.14 and 0.13 mg g^{-1} respectively. The recorded higher Na content but lesser Fe, Mn and Zn in banana peel biochar compared to our result.

Surface characteristics of banana peel biochar

The surface morphology of banana peel biochar before and after adsorption of Pb and Cd was studied under Scanning Electron Microscope (Fig.1, 2, 3). The images showed irregular porous, shape and size on the external surface of the banana peel biochar. The smooth surface might have promoted the adsorption of metal

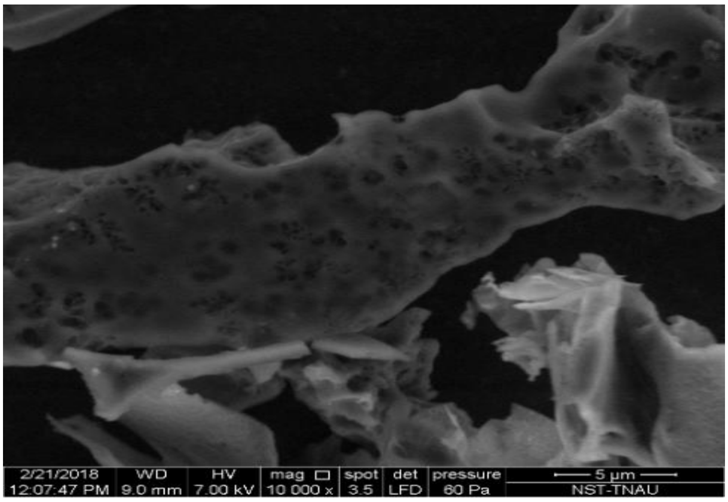

Figure 2. SEM image of banana peel biochar after adsorption of Pb ions

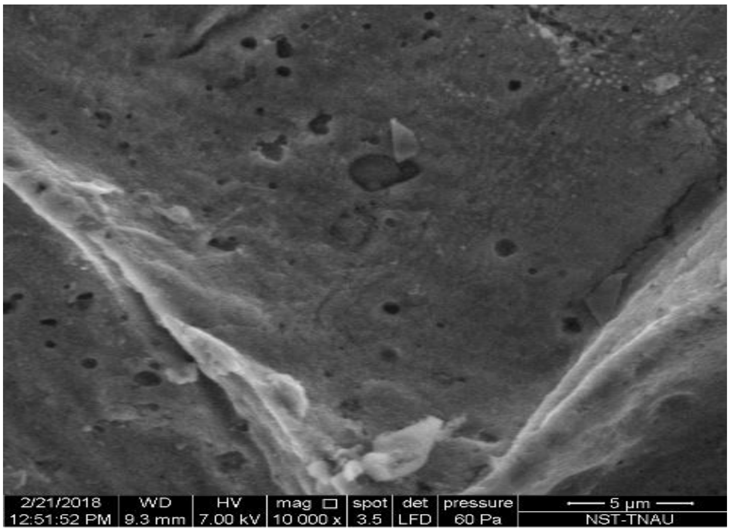

Figure 3. SEM image of banana peel biochar after adsorption of Cd ions

ions. The surface pores are open before adsorption and after the adsorption of Cd and Pb it was occupied by metal ions. In addition to smaller particle size, micro porous structure and surface area of biochar may be the reason for higher Pb and Cd adsorption.

Table 3. Chemical composition of banana peel biochar before and after adsorption of Pb and Cd ions by EDX analyzer

Element	Wt. before adso. (%)	Wt. after Pb adso. (%)	Wt. after Cd adso. (%)	Element	Wt. before adso. (%)	Wt. after Pb adso. (%)	Wt. after Cd adso. (%)
C	68.78	67.68	70.71	P	0.00	0.79	0.34
N	03.66	3.25	7.23	S	0.00	0.25	0.00
O	24.61	22.06	15.84	Cd	1.12	-	2.21
Na	0.36	0.74	0.00	Pb	0.00	1.82	0.33
Mg	0.19	0.87	0.54	Cl	0.14	0.62	0.23
Al	0.23	0.48	0.22	K	0.70	-	1.29
Si	0.21	1.00	0.62	Zn	0.36	0.44	0.00

SEM images of biochar and activated carbon that activation has the main role in the development of porosity which is largely responsible for increasing the surface area and adsorption capacity. SEM image of charcoal showed holes which spaced out on the surface with smooth edges. Hence, the pore space and agglomeration of biochar particles could enhance metal uptake and encourage mass transport of heavy metals through the inside of the sorbent.

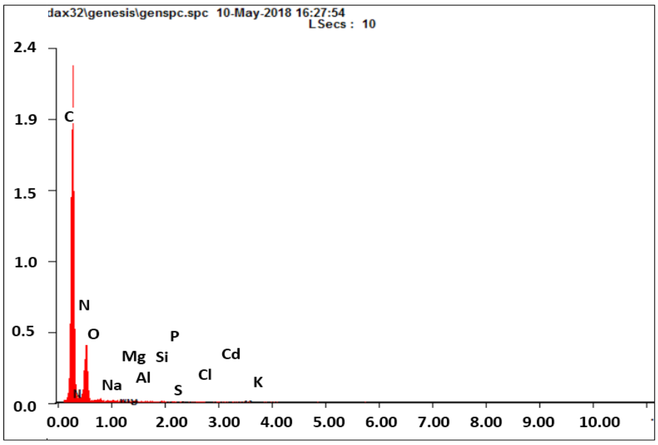

Figure 4. EDX micrograph of BPB before adsorption

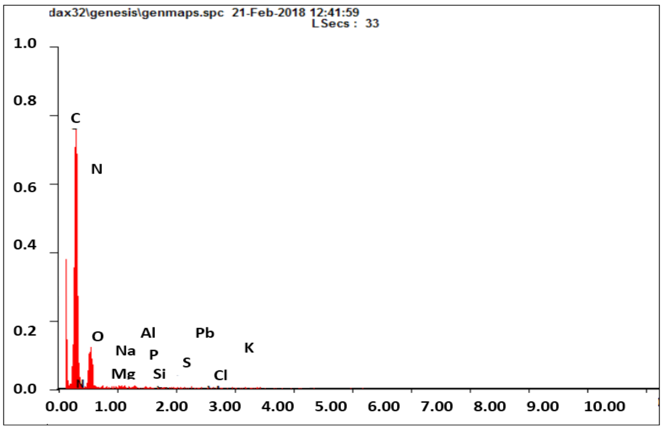

Figure 5. EDX micrograph of BPB after Pb adsorption

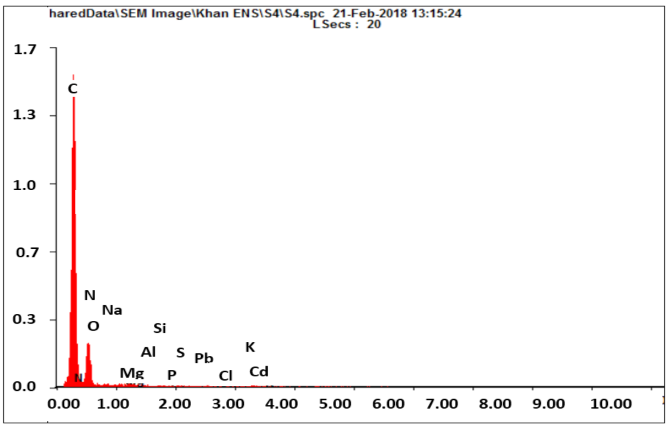

Figure 6. EDX micrograph of BPB after Cd adsorption

EDX analysis

The chemical composition on the surface of banana peel biochar was observed by EDX before and after adsorption. The percentage weight of chemical elements in banana peel biochar is given in table 4, and the micrographs have been represented in (Fig. 4, 5, 6).

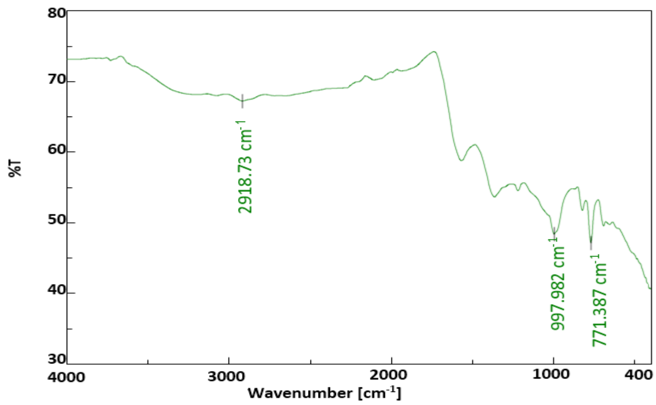

Figure 7. FTIR analysis of banana peel biochar before adsorption

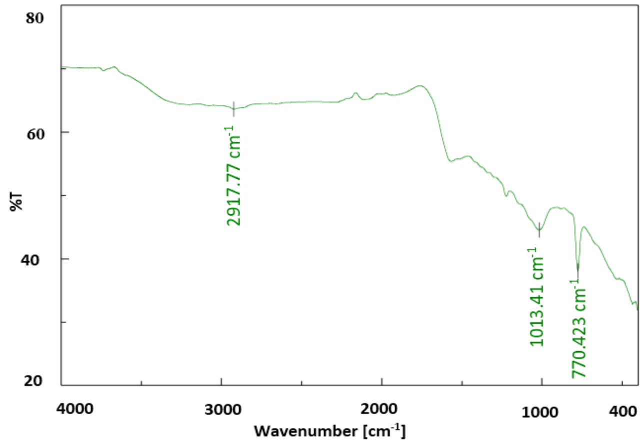

Figure 8. FTIR analysis of banana peel biochar after Pb adsorption

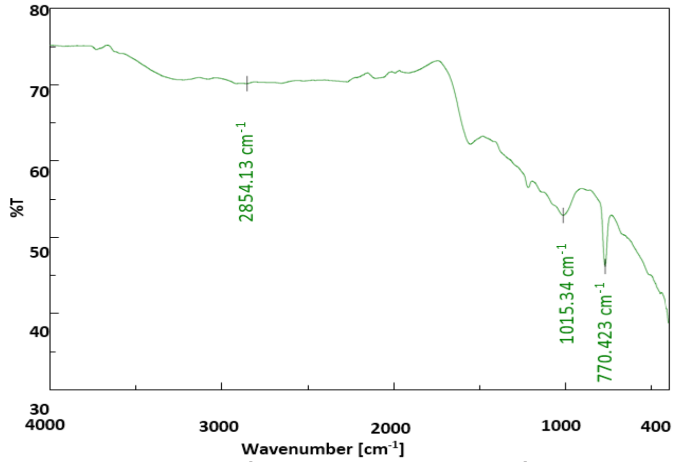

Figure 9. FTIR analysis of banana peel biochar after Cd adsorption

Functional characteristic of banana peel biochar

The FTIR spectrum peaks was observed within 4000-400 cm^{-1} wavelength; which was only a sign of the complex chemical nature (Fig 7, 8, 9). The presence functional groups in banana peel biochar before and after adsorption are given in table 5. Before adsorption the alkane functional group with (C-H) band was detected at 2918.73 cm^{-1} frequency but after adsorption of Pb and Cd, it was decreased to 2917.77 cm^{-1} and 2854.13 cm^{-1} respectively and similar C-H stretching vibration functional group before and after adsorption of Cd. Alkene functional group with (=C-H) band was observed at 997.982 cm^{-1} frequency before adsorption, and after adsorption of Pb and Cd changed to ether (C=O) at 1013.41 cm^{-1} and 1015.34 cm^{-1} frequencies respectively. There were no changes in alkyl halide functional group before and after adsorption. In case of Pb adsorption there was no change in C-H and C-Cl, and =C-H stretch becomes C-O functional group, but in case of Cd adsorption, C-H group is reduced, =C-H increased and without change in C-Cl. The functional groups detected in the biochar also increased the potential for adsorbing the metal cations.

Table 4. Functional groups in banana peel biocharbefore and after adsorption of Pb and Cd

Functional group	Biochar before absorption (cm^{-1})	Biochar after Pb absorption (cm^{-1})	Biochar after Cd adsorption (cm^{-1})	Type of Vibration	Intensity
C-H (Alkane)	2918.73	2917.77	2854.13	stretch	strong
=C-H (Alkene)	997.982	-	-	bending	strong
C-O (Ether)	-	1013.41	1015.34	stretch	strong
C-Cl (Alkyl Halide)	771.387	770.423	770.423	stretch	strong

Adsorption parameters

Effect of pH

The pH is one of the main variable affect the adsorption process, influencing not only the speciation of the metal ions, but also the surface charge of the metal ions, surface charge of the sorbent and the degree of ionization of the adosorbate during the reaction. In the present study the effect of pH on Pb and Cd adsorption

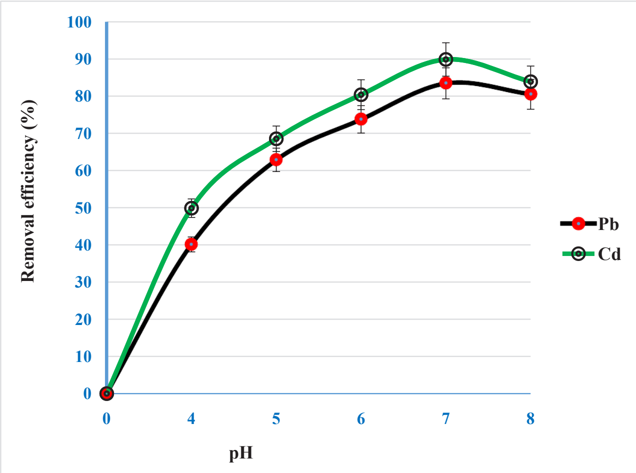

Figure 10. Effect of pH on adsorption of Pb and Cd

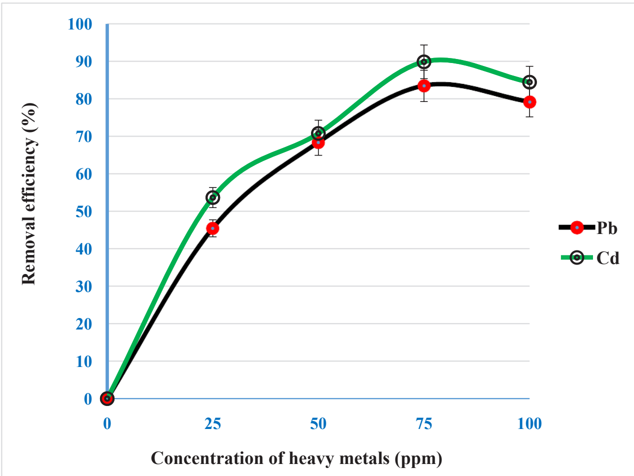

Figure 11. Effect of concentration on adsorpion of Pb and Cd

was studied from pH 4 to 8 (Fig 10). The adsorption capacity of banana peel biochar increased with the increasing of pH from 4 to 7 then decreased. The highest removal percentage of Pb (83.45) and Cd (89.87) was observed at pH 7, and the lowest removal percentage (45.45) and (53.65) respectively was recorded at pH 4. Similar observations of higher adsorption at higher pH > 6 was reported by Ucar *et al,* (2014). At lower pH, the surface functional groups (mainly oxygen containing groups) bind to the H^+, making these inaccessible for Pb ions. With increasing pH, the deprotonating functional groups provided the chance to co-ordinate with Pb and Cd ions resulting in higher removal percentage. The less removal percentage of Pb and Cd in high acidic condition may be due to the high mobility and high concentration of H^+, because H^+ ions are adsorbed in more amount compare to metal ions. Abbasi *et al*. (2013) also reported that adsorption of Ni^{+2} and Co^{+2} by banana peel increased with the increasing pH form 1.0 to 6.0. The much lowered pH (H_3O^+), the hydrogen doing competition with Cu^{2+} for binding onto adsorbent sites results in decreased adsorption capacity of biosorbents. Shafaghat *et al.* (2012) also had opinion that under high acidic condition, the adsorption capacity of biosorbents are lower.

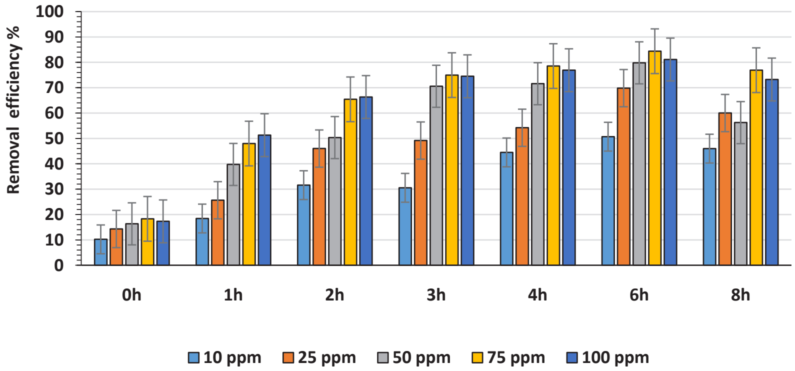

Figure 12. Removal % of Pb by banana peel biochar based on contact time

Effects of metal ions concentration

The effect of metal ion concentration on the adsorption of Pb and Cd by banana peel biochar was determined for (25, 50, 75 and 100 ppm) concentration solutions (Fig 11). The removable efficiency of both Pb and Cd increased with the increasing of metal concentrations from 25 to 75 ppm, after that it showed decreasing trend. The highest adsorption of Pb (83.45%) and Cd (89.87%) was observed at 75 ppm and the lowest was recorded at 25 ppm. Anwar *et al.*, (2010) reported the same result from Co^{+2} and Ni^{+2} adsorption by banana peel, but Priyanka, (2017) reported that the removable efficiency of Pb (II) decreases with increasing initial concentration from 10 to 100 mg L^{-1}.

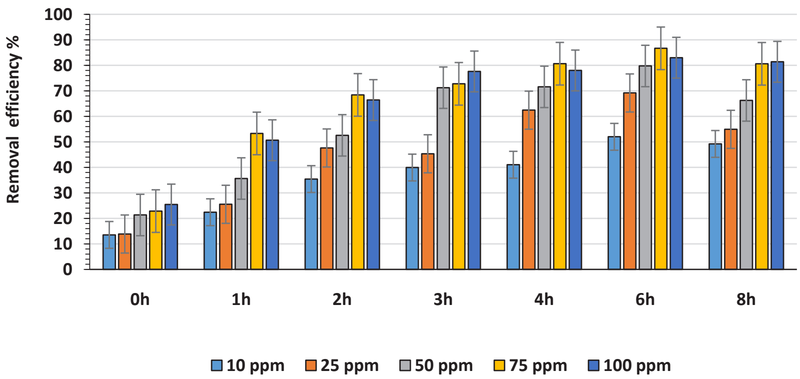

Figure 13. Removal % of Cd by banana peel biochar based on contact time

Effect of contact time

The adsorption of Pb and Cd by banana peel biochar was analyzed based on contact time (Fig 12, 13). It ranged from 0-8 hours under shaking at 250 rpm. Adsorption percentage of Pb and Cd by banana peel biochar increased with the increase in contact time from 0-6hours, after that decreased with increase of time. The highest adsorption of Pb (84.39%) and Cd (86.69%) was recorded at 6 hours, and the lowest adsorption (10.23%) and (13.54%) respectively was observed at 0hour equilibration period. Present study is well correlated with the observation of Anwar *et al*. (2010) who determined that adsorption of Pb and Cd by banana peel increases with increase in contact time. The adsorption of metal ions gradually decreases as time progressed. This might be due to ions have to pass through the deeper surface of the pores, which encounter substantial resistance leading to decreased adsorption during the later phase of the study. And also the transportation rate of ions from the exterior to the interior sites of the adsorbent particles actually determines the adsorption rate of later phase. The Cd adsorption efficiency by banana peel biochar was more compared to Pb adsorption. This is due to the cadmium apparent energy of sorption (0.04L g^{-1}) and for lead (0.11L g^{-1}) even though both the elements have same charges (+2). Hence the higher apparent energy of sorption for Pb due to larger radius than Cd (Anwar *et al.*, 2010).

CONCLUSION

Lead and Cadmium are the most hazardous metals accumulate in the human body causing severe damage. To avoid health hazards it must be remove from waste water before its disposal. Hence biosorption is one of the economically method for the removal of heavy metals from waste water compared to other techniques. Based on the results and discussion concluded that banana peel biochar is an effective adsorbent for the removal of Pb (II) and Cd(II), and the removal efficiency of Cd was higher than Pb. The present study also determine that instead of chemical, we can use pectin rich agricultural waste materials as heavy metal removers from wastewater to overcome water pollution.

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