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SORPTION OF METALS BY TREE BARK FROM SYNTHETIC CONTAMINATED WATER

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Large quantities of metals and other chemicals are emitted from different industries that result in contamination of water and soils. In Pakistan, majority of the industries discharge wastewater without any treatment and such wastewater is considered the main source of contaminants including several metals like Lead (Pb) and Cadmium (Cd). The plant residue/bark was used as metal sorbent for the removal of metals namely Pb and Cd from synthetic contaminated water in this study. Eucalyptus bark proved to be a cheap sorbent for certain contaminants in previous research studies. The different concentration levels of both metals in solution were 5, 10 and 20 mg L^{-1} with one gram bark (2-5 mm particle size) per treatment. The highest Pb sorption capacity (almost 100%) was recorded at 10 mg Pb L^{-1} while that of Cd increased linearly with an increase in influent concentration. This study demonstrated that the application of Eucalyptus bark as sorbent for Pb and Cd metals from contaminated water is cost- effective and environmental friendly technique. It donot involve any hazard associated with its final disposal and economic crisis regarding production and processing as filter. There was an increase in Pb and Cd sorption with progress in contact time (more during the first 80 mins). The Langmuir Isotherms fitted well to Cd sorption data than Freundlich one.

Keywords: Cadmium, lead, *contaminated water*, bark, langmuir isotherm.

INTRODUCTION

Large quantities of metals and chemicals are generated from industry in Pakistan. Most of the known industries with waste generation containing metals include metallurgical, steel, tannery and textiles (Davis *et al.,* 2000). Since there is almost no effluent treatment at industry, thereby disposal is causing contamination of waters and soils (Wuana and Okieimen, 2011). The concentration of pollutants needs to be decreased according to the legislative standards for the safety of human and environment. According to World Health Organization (WHO), some toxic metals require immediate attention such as cadmium, lead, iron, copper, mercury, manganese, nickel, cobalt, chromium and aluminium (Ghodbane *et al.,* 2008). Among these, lead (Pb) and cadmium (Cd) are potential hazardous heavy metals polluting not only the operational site but also the environment in vicinity of area Kazmi *et al*., 2015). Lead is a hazardous pollutant emitted from fossil fuels burning like petrol and plastics, paints, alloys, batteries, ammunition, pigments, cables, and the glass industry. This pollutant is usually concentrated around road sides in herbage, soil and waters due to emissions from vehicular traffic. The occurrence of Pb in drinking water is shown to cause serious health problems (Ahmedna *et al.,* 2004) like accumulation in the body organs (e.g. brain) leading to plumbism and even death. It also leads to anorexia, loss of memory, nausea, and insomnia. The kidneys, gastrointestinal tract and central nervous system are also affected by Pb exposure (Wuana and Okieimen, 2011). Different studies demonstrated that organic forms of Pb are more poisonous as compared to inorganic forms, which act as enzyme inhibitor and metabolic poison. Application of some phosphatic fertilizers unintentionally adds Cd and certain other potentially toxic elements to the soil, including Hg and Pb (Raven *et al.,* 1998). High levels of Cd can be found in ceramics, metal plating, mining, metallurgical alloying and other industrial operations (Davis *et al.,* 2000). The toxic effects of heavy metals on plants (Kabata-Pendias and Pendias, 2001) and humans (Ali *et al.,* 2013) are discussed in detail in literature. Lead and Cadmium are some of the non-essential most toxic and carcinogenic heavy metals that could cause serious environmental and health problems to humans and the ecosystem through direct contact with metal contaminated soils.

In Pakistan, majority of the industries discharged their wastewater without any treatment and this toxic wastewater may contaminate surface water, ground water and agricultural soils. These elements may enter into organisms by means of plants ingestion, foods, water, soils and can generate serious health problems. The soil pollutants are harmful to ecosystems and agricultural practices as well as a serious threat to human wellbeing. Several techniques are used to remediate contaminated waters and soils which include physical, chemical, biological treatments, integrated remediation, phyto-remediation and bio-remediation (Lee *et al*. 2008). Some other cost-effective techniques (GWRTAC, 1997) for removal of heavy metals from soil and waters are bio-sorption, immobilization and soil washing. Techniques like ion-exchange, membrane filtration, evaporation, chemical precipitation, adsorption biological treatment and reverse osmosis are also used extensively nowadays (Hina, K.??? 2013). Recently, attention has been given to the development of cost-effective and environmental friendly technologies, which may have the ability to sorb contaminants and metals. Natural materials or certain agricultural wastes can be used as potential adsorbents. A number of agricultural by-products have been used as adsorbent by several researchers for their capacity for removal of metals such as pine bark (Al Asheh and Duvnja, 1997), rice husk (Kumar, 2006), tree fern, sawdust (Taty Costodes *et al.,* 2003), grain and modified corn cobs. The cations removal capacity of the sorbents was reported to be dependent on (i) the wastewater loading rate, (ii) type of wastewater, (iii) particle size and (iv) contact time between the wastewater and sorbent particles (Nguyen and Tanner, 1998). Eucalyptus bark has been successfully used for the treatment of wastewater containing chromium and reactive dyes (Morais *et al.,* 1999).

The aim of the current study was to evaluate the tree bark as potential filter for removal of metals from contaminated water. The effect of different concentration levels of metals (Cd and Pb) and contact time will be assessed in batch study. The effectiveness of different treatments will be evaluated by plotting Langmuir and Freundlich Isotherms. The characterization of the sorbent will be done using parameters like FTIR (Fourier transform Infrared spectroscopy), EDX (energy dispersive X-ray spectroscopy) and SEM (scanning electron microscope) analysis. It is proposed that end use of this bark could be an active filter for removing contaminants from waste streams and thereby disposal to waste management sites.

MATERIALS AND METHODS

Preparation and characterization of adsorbent: *Eucalyptus Camaldulensis* is one of the commonly distributed tree species in arid and semi-arid regions of Pakistan like Gujrat and large quantity of its bark could be available for use as filter in current study..Eucalyptus bark was obtained from "Jalal Pur Jattan region (32° 38′ 31.0″N 74° 12′ 11.9″E)" located near University of Gujrat, Punjab, Pakistan. The peel was freshly taken from the trees, thoroughly washed with distilled water to remove dust and dirt and then was oven-dried at 65ºC for 24 hours. It was cut into small pieces, crushed and grinded to obtain particle size range of 5-10 mm. For the characterization of sorbent, the Fourier Transform Infrared Spectroscopy (FTIR) (Model: FTIR Spectrum 100 PerkinElmer), Scanning Electron Microscopy (SEM) and Energy Dispersive X Ray Spectroscopy (EDX) Analysis was done. The bark pH was determined using method reported by Calvelo Pereira *et al.* (2014).

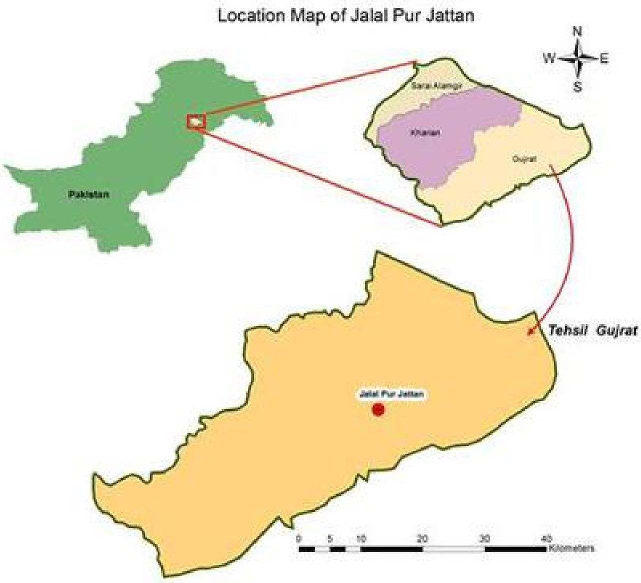

Figure 1. Sample collection site of Jalal Pur Jattan, Gujrat region, Pakistan.

Synthetic solution preparation: For determination of sorbent capacity of the bark, simulated wastewater was prepared using $CdSO_4.8/3H_2O$ and $Pb(NO_3)_2$ for Cd and Pb, respectively. Three levels of Cd and Pb (10, 15, 20 mg L^{-1}) were prepared in double distilled water. The batch experiment was conducted in triplicate. Analytical grade chemicals were used in this study.

Batch sorption experiment: For the sorption studies, one gram bark was added in 250 mL flasks with 20 mL solution of different treatments, i.e. levels of Cd and Pb. The flasks were covered with aluminium foil to prevent spillage of sample and kept for shaking at 100 rpm for 8 hrs on horizontal shaker. After shaking, solutions were filtered using Whatman filter paper No. 42. The Cd and Pb content of supernatant was analysed at Atomic Absorption Spectrophotometer (AAS). The sorption of metals in relation with time was also assessed by changing shaking time (5 to 1000 min) at same influent concentration (20 mg L^{-1}) of Cd and Pb. The Cd adsorption isotherm (Langmuir) was plotted in the range of 5-20 mg L^{-1}. In this study, the pH of the solutions of Cd and Pb containing bark was set to 8.5. The batch adsorption studies were conducted at room temperature (25°C) while keeping the pH of solutions constant. This pH was selected based on the previous studies

(Mohan *et al.,* 2015, Solisi *et al.,* 2008) on heavy metals sorption. For example, it was reported that optimum pH for Pb sorption was 6.0 to 8.5 or higher in practice with energy cane biochar and magnetic energy cane biochar (Mohan *et al.,* 2015) and optimum pH for Cd adsorption was 8.0 with *Ochrobactrum anthropi*. Therefore, a uniform pH of 8.5 was adjusted for sorption of both metals in current study.

***pH sorption study*:** The 20 mL of contaminated solutions were put in conical flasks with 1 g bark and pH of each solution in flasks was adjusted to 3, 5, 7 and 10 by adding 0.1 M HCl or 0.1 M NaOH solutions. The conical flasks were kept on shaking for 5 hrs. Later, the flasks were kept for 24 hrs to reach equilibrium at 25°C and then filtrates were analyzed for Pb and Cd to determine the metal sorption by difference method.

***Statistical analysis*:** The comparison between different treatments and error bars were placed using Minitab Statistical Software.

RESULTS

***Characterization*:** Fourier Transform Infrared Spectroscopy of Eucalyptus bark was conducted in the range of 4,000- 450 cm^{-1} (Fig. 2). The spectrum of FTIR spectra revealed that eucalyptus bark has functional groups required for the metal sorption. The FTIR spectra showed features of G type of lignin (Faix *et al.,* 1988), i.e. peaks at 1621 and 1051 cm^{-1}. In addition, a band at 1318 cm^{-1} was evident indicating C–O stretching vibrations which were similar to springy ring (Wang *et al.,* 2009). The presence of acidic functional groups responsible for adsorption are depicted in the spectrum with bands of 1051 and 1621 cm^{-1} showing C=O stretching and C=O stretching conjugation to the aromatic ring, respectively. A band at 3428 cm^{-1} showed the presence of H bonded with OH groups (Hina, K. 2013). These functional groups indicated that the removal of the heavy metals may get affected by the presence of these metal ions binding with functional groups.

The SEM analysis showed the presence of well-defined holes in the range of 490 to 750 nm (Fig. 3). The EDX (energy dispersive X ray spectroscopy) analysis showed rough surface of the bark depicting enhanced surface area sites of sorption.

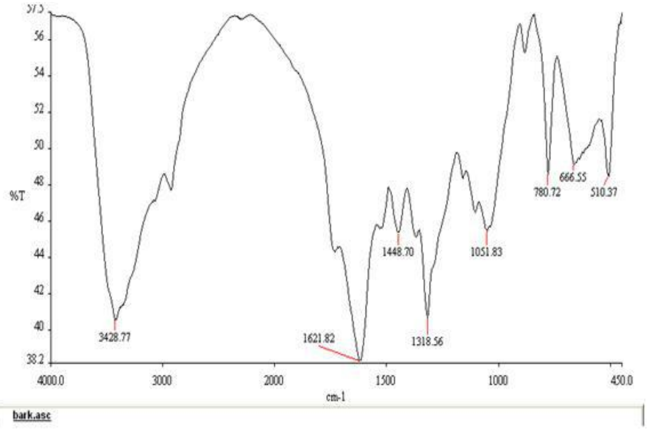

Figure 2. The FTIR spectra of Eucalyptus bark.

***Batch sorption studies*:** The sorption of Cd on bark at different levels of metals is shown in Figure 4. The sorption of Cd increased with an increase in influent concentration, i.e. 0.087 mg g^{-1} < 0.193 mg g^{-1}<0.32 mg g^{-1} at 5, 10, 20 mg L^{-1}, respectively, which was statistically significant at 0.05 P value. In this study, bark significantly removed Cd ($p < 0.05$)

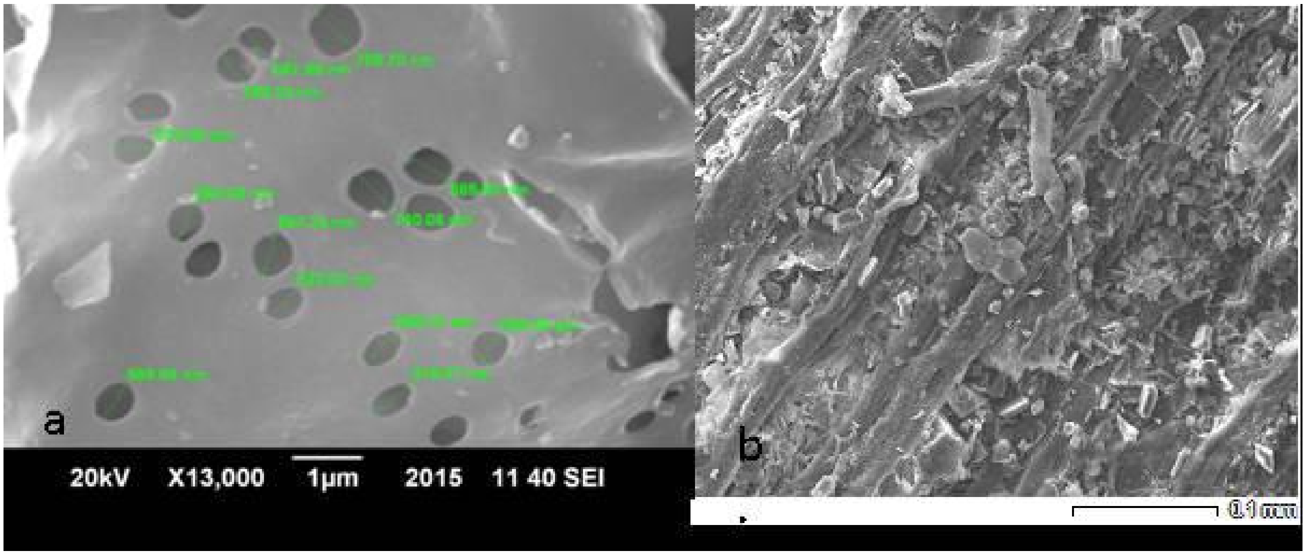

Figure 3. The (a) Scanning Electron Microscopy (SEM) and (b) Energy Dispersive X Ray Spectroscopy (EDX) of Eucalyptus bark.

linearly with increase in target metal in solution. The error bars are placed on graphs using statistical software with calculation of standard error and standard deviation.

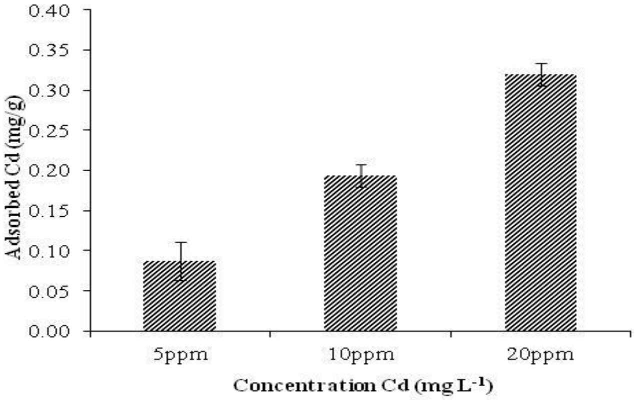

Figure 4. Amount of Cd sorbed (mg g^{-1}) by Eucalyptus bark at different influent Cd concentrations.

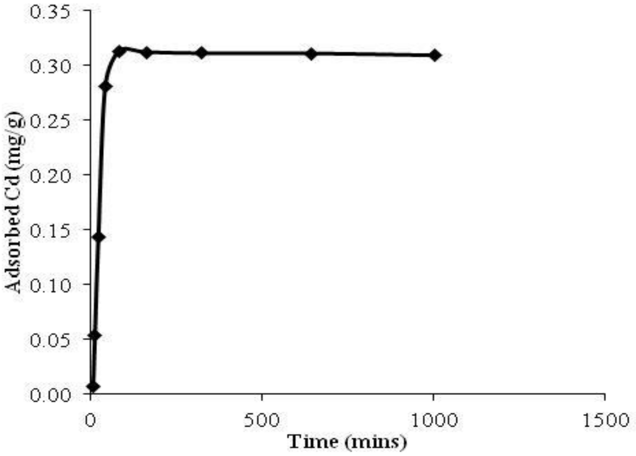

Figure 5. Sorption of Cd on Eucalyptus bark in relation with time.

The results for Pb from the batch sorption study are represented in Figure 6 and 7. The maximum sorption (≈100 %) was recorded at 10 mg Pb L^{-1}. The rate of Pb removal was found to be in dose dependent fashion such as 20 mg L^{-1} > 10 mg L^{-1} > 5 mg L^{-1}. It is very interesting to note that the percent removal of Pb ranged from 100, 99 and 72% at influent Pb concentrations of 10, 20 and 5 mg L^{-1}, respectively. The percent removal of Cd was different than that of Pb and it increased linearly with an increase in influent concentration (Fig. 4). It is already reported that different sorbents significantly removed Pb from aqueous solution (Ayyappan *et al.,* 2005). It showed that Eucalyptus bark has good affinity to sorb Pb and Cd. The mechanism involved in metals sorption on organic waste or bark needs further investigation and research studies.

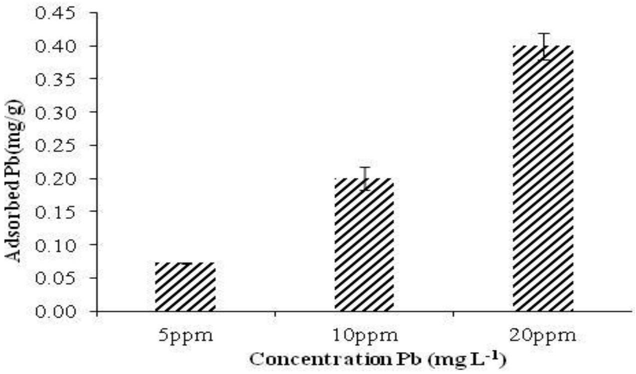

Figure 6. Amount of Pb sorbed by Eucalyptus bark at different influent Pb concentrations.

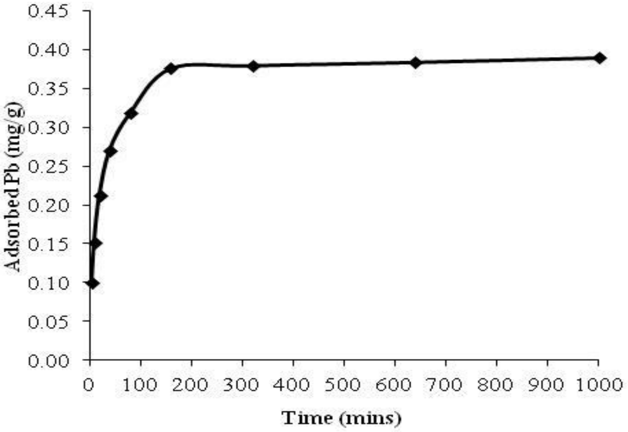

Figure 7. Sorption of Pb on Eucalyptus bark in relation with time.

***pH dependent sorption study*:** The removal of Pb and Cd at highest concentration level and under four pH levels (3, 5, 7, 10) were evaluated in a batch study. The highest removal of Cd and Pb was recorded at pH 10 and 7, respectively (Fig. 8).

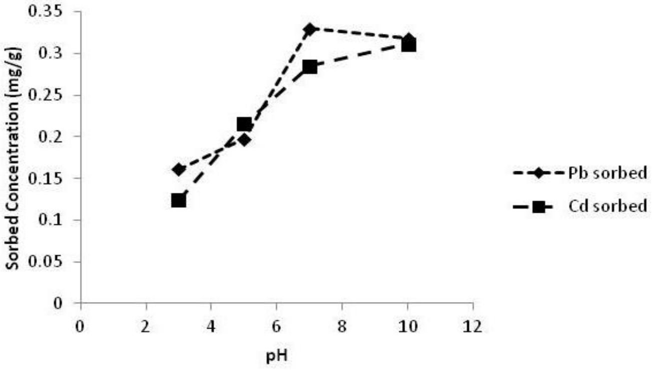

Figure 8. Adsorption of Pb and Cd on Eucalyptus bark in relation with pH.

DISCUSSION

The characterization of the bark showed presence of acidic functional groups in FTIR analysis. They gave binding sites for sorption of cations and metals.

In batch sorption study, the maximum removal of Cd (0.32 mg g^{-1}) was found at 20 mg L^{-1} influent metal concentration. Ghodbane *et al.* (2008) reported that the adsorption capacity of Eucalyptus bark increased at certain levels due to the availability of more exchangeable sites. The maximum sorption of Cd with respect to time was recorded up to initial 80 mins (Fig. 5) and decreased with the increase of time. The sorption capacity of Pb was found to be increased with increase in concentration level.

***Sorption isotherm*:** The sorption data was treated with Langmuir Isotherm (though difficult to interpret at 3 concentration levels) to determine the equilibrium of metals sorption on Eucalyptus bark using following equation (Eq.1).

Ce/qe = Ce/qm + 1/Kaqm ------------(Eq. 1)

Where, Ce = equilibrium concentration of metals (mg L^{-1}), qe = amount of metals sorbed per unit mass of Eucalyptus bark (mg g^{-1}), qm = maximum amount of metals sorbed per unit mass of Eucalyptus bark (mg g^{-1}); Ka = adsorption equilibrium constant (L (mg)$^{-1}$) related to the adsorption energy

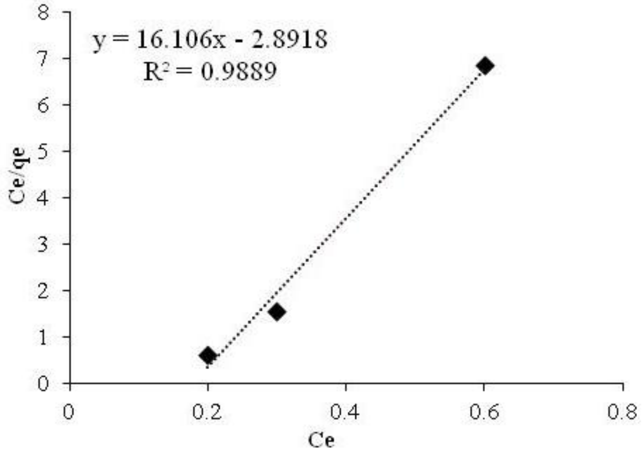

Figure 9. Adsorption equilibrium of Cd on Eucalyptus bark (Langmuir Isotherm).

SThe sorption data for Cd satisfactorily fitted to Langmuir Isotherm (Figure. 9) where the positive values for maximum adsorption were obtained (R^2 =0.99). The fitness of data to Langmuir Model indicated that adsorption sites on Eucalyptus bark were homogeneous in the form of monolayer coverage. The maximum adsorption capacity (qm) calculated from the Langmuir isotherm for Cd was 3.894 mg g^{-1}. The results revealed that Pb showed ≈ 100% sorption and achieved zero concentration at equilibrium for two points (10 and 20 mg L^{-1}). The Freundlich isotherm for Cd sorption is plotted in Figure 10. The Freundlich equation is given as:

In qe = In K_F + 1/n In Ce-----------(Eq. 2)

Where Ce= equilibrium concentration of F (mg/L), K_F and n = Freundlich constants (KF is related to the F adsorption capacity).

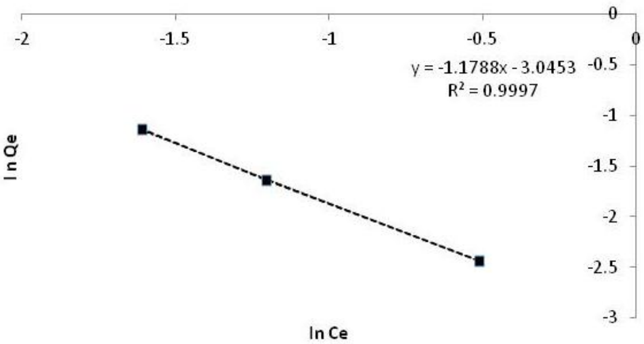

Figure 10. Adsorption equilibrium of Cd on Eucalyptus bark (Freundlich Isotherm).

According to Langmuir and Freundlich Equation, the sorption becomes zero or infinite at Ce = 0. Therefore, the Langmuir and Freundlich isotherms were not plotted over the data with Pb in current study. Another reason for data ambiguity on Pb could be limitations in instrument detection for Pb in equilibrium solution at lower levels.

***Conclusions*:** This study demonstrated that the application of Eucalyptus bark as sorbent for Pb and Cd removal from wastewater is efficient and environmental friendly technique. The relation of adsorption of metals with time showed promising results for Pb and sorption increased linearly with time up to contact time of 160 mins. The FTIR analysis confirmed the presence of acidic functional groups in Eucalyptus bark responsible for metals sorption. It also showed potential of bark as filter for contaminants removal from water. The equilibrium studies showed that sorption of Cd and Pb was significant on Eucalyptus bark. The Langmuir model fitted well for the Cd sorption on bark with correlation factor of 0.99, while the model was not applied to Pb sorption study due to limitation of zero equilibrium concentration of metal at two points. Therefore, it can be concluded that Eucalyptus bark obtained locally from Pakistan can be used as a natural filter for the removal of hazardous cations and heavy metals from wastewaters and industrial effluents. But proper filter must be developed and replaced time to time to keep contaminated water remediation on the go.

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