



Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions

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ABSTRACT

The potential to remove Cu^{2+} and Pb^{2+} ion from aqueous solutions through biosorption using barley straw (BS) was investigated in batch experiments. The main parameters influencing Cu^{2+} and Pb^{2+} ion sorption on BS were: initial metal ion concentration, amount of adsorbent, contact time and pH value of solution. The influences of initial Cu^{2+} and Pb^{2+} ion concentration (0.1–1 mM), pH (2–9), contact time (10–240 min) and adsorbent amount (0.1–1.0 g) have been reported. Equilibrium isotherms have been measured and modelled. The percent adsorption of Cu^{2+} and Pb^{2+} ions increased with an increase in pH and dosage of treated BS. The biosorptive capacity of the BS was dependent on the pH of Cu^{2+} and Pb^{2+} ion solution. Adsorption of Cu^{2+} and Pb^{2+} ion was in all cases pH dependent showing a maximum at equilibrium pH value at 6.0. The equilibrium sorption capacities of Cu^{2+} and Pb^{2+} after 2 h were 4.64 mg/g and 23.20 mg/g for BS, respectively. The adsorption data fit well with the Langmuir isotherm model and the experimental result inferred that complexation on surface, adsorption (chemisorption) and ion exchange is one of the major adsorption mechanisms for binding Cu^{2+} and Pb^{2+} ion to the sorbents.

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1. Introduction

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Today, with the rapidly increasing urban population and water resources becoming more and more scarce, there is a strong need to reconsider our consumption patterns and the way we use our water resources. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products [1]. The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Developing countries suffers from water pollution; the high costs of contents and treatments make the major problems in these countries. Search for a cheaper alternative, reveals that utilizing natural materials significantly reduce high cost of water treatment.

Pb^{2+} ion is among hazardous materials that are most commonly found in an industrial wastewater, thus its removal is of utmost importance. Lead has many different uses. Its most important use is in the production of some types of batteries. It is also used in the production of ammunition, in some kinds of metal products (such as sheet lead, solder, some brass and bronze products, and pipes), and in ceramic glazes [2]. Lead causes plant and animal death

as well as anemia, encephalopathy, cognitive impairment, brain damage, mental deficiency, anorexia, kidney damage, behavioural disturbances, vomiting and malaise in humans [3].

Copper and its compounds are widely used in many industries and there are many potential sources of copper pollution. The continued intake of copper by human beings leads to necrotic changes in the liver and kidney, mucosal irritation, wide spread capillary damage, depression, gastrointestinal irritation, and lung cancer [4]. According to Safe Drinking Water Act the permissible limit of copper in drinking water is 1.3 mg/L [5]. Excessive copper concentrations can lead to weakness, lethargy and anorexia, as well as damage to the gastrointestinal tract [6].

Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, refining ores, paint and pigments, tanneries, chloralkali, sludge disposal, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc. [7]. The conventional methods used to remove toxic metals from aqueous effluents include membrane filtration [8], chemical precipitation [9], ion exchange [10], and adsorption [11]. In the major part of cases the use of these methods in the remediation processes is precluded due to high costs involved [12]. Conventional methods for the removal of heavy metals from wastewaters, however, are often cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/L [13]. For this reason, low cost adsorbents have been evaluated for the removal of heavy metals from aqueous solutions.

Biosorption is a promising technique for the removal of heavy metals from aqueous environments especially when adsorbents

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are derived from lignocellulosic materials [14]. The search for new technologies to remove toxic metals from wastewaters has directed attention to biosorption, which is based on metal binding to various biological materials. Biosorption is a fast and reversible reaction of the heavy metals with biomass. Laszlo and Dintzis [15] have shown that lignocellulosics have ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. Agricultural by-products vary greatly in their ability to remove metals from solution. The ability of biological materials to adsorb metal ions has received considerable attention for the development of an efficient, clean and cheap technology for wastewater treatment at metal concentrations as low as 1 mg/L [16].

Several materials are derived from natural resources, plant wastes or industrial by-products such as peat, wood, barley, rice husk, plant straw, rice bran, peanut straw, almond straw, hazelnut straw, algal biomass, banana pith, soybean, cottonseed hulls, humic acids, tree bark, sugar beet pulp, leaves, green algae, activated carbon fibers, coconut waste, wood and straw have all been investigated for their ability to sequester trace metals from water. The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as tea waste and coffee [17], hazelnut straws [18], peanut hull [5], sawdusts [19], pinus bark [20] and different bark samples [21], husk [22], Ponkan mandarin peels [23], modified cellulosic materials [24], corncobs [25], apple wastes [26], wool fibers [27], tea leaves [28], banana and orange peels [29], sugarcane bagasse [30], papaya wood [31], maize leaf [32], leaf powder [33], grape stalk wastes [34] and different agricultural by-products [35,36] were used and investigated.

Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. The aim of this study was to find out the effectiveness of less expensive material that could be used as sorbent for the removal of Cu^{2+} and Pb^{2+} ions from aqueous solution. The Cu^{2+} and Pb^{2+} ion retention on BS has been carried out batchwise where the influence of physico-chemical key parameters such as the solution pH, the initial metal concentration, contact time, and ionic strength has been considered.

2. Materials and methods

2.1. Adsorbent

The BS was obtained from a farm in the vicinity of Konya, Turkey, were ground using a with a grinding machine (Retsch RM 100) and the resulting powdered straws were sieved to obtain particle size under $75\ \mu\text{m}$. Before their use, BS powder was washed thoroughly with deionized water and oven dried at 100°C for 24 h. All chemicals were of an analytical grade. Test material solutions were prepared by dilution of copper nitrate, $\text{Cu}(\text{NO}_3)_2$ and lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (Merck, Germany) with double distilled water.

2.2. Apparatus

The pH measurements were performed with a pH meter (Orion 900S2). A thermo stated shaker (GFL 3033) and magnetic stirrer (IKAMAG-RO15) were used for the sorption experiments. An Atomic Absorption Spectrometer (AAS) (Unicam 929) operating with an air-acetylene flame was used to analyze the Cu^{2+} and Pb^{2+} ion concentration in the solution.

2.3. Batch adsorption

The initial pH of the metal solution was adjusted to values in the pH range of 2–9 by the addition of 0.1 M HCl or 0.1 M NaOH prior to experiment. The addition of KNO_3 solution into the mixture changed the ionic strength. Samples of the sorbents (0.5 g by dry weight) were equilibrated with certain volume of metal solutions at varying concentrations (0.1–1 mM), pH values (2–9), and ionic strengths (0.01–0.1 M). The concentration decay curves and equilibrium sorption capacities were determined in batch experiments by shaking, at predetermined times, sealed test tubes containing 0.5 g of sorbent and 80 mL of 10^{-3} M metal solution. The sorbents and solution were separated by filtration through a membrane filter ($0.45\ \mu\text{m}$). Sorption of metal ion by the filter was controlled by washing the filter twice with diluted HCl and analyzing the filtrate for the remaining metal ion concentration. The metal ion concentration in the original solution and left in bulk solution were determined by the AAS technique. Blank test for reference solution (distilled water) was repeated during every sample measurement. Experiments and analysis have been carried out three times and the relative standard deviation was $\pm 0.9\%$.

Time dependent experiments were carried out by shaking the adsorption mixture at various predetermined intervals and analyzing the metal ion content at the end of the contact time. The amount of the metal adsorbed (mg) per unit mass of biomatrix was obtained by using the equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t is the adsorbed metal (mmol/g adsorbent) on the sorbent, m is the weight of sorbent (g), V is the volume of metal solution (L), C_0 is the initial metal concentration (mmol/L), and C_t is the metal concentration (mmol/L) at any time. When t is equal to the equilibrium contact time, then the amount of metal ion sorbed at equilibrium, q_e , is calculated using Eq. (1).

3. Results and discussion

3.1. Effect of pH on Cu^{2+} and Pb^{2+} ion removal

The pH influences the protonation or deprotonation of the adsorbent. The pH dependence of equilibrium adsorption data of metal ions in solution is shown in Fig. 1. The results of these experiments showed that solution pH increased slightly after reaching equilibrium where a maximum increase in solution pH of 0.4 was

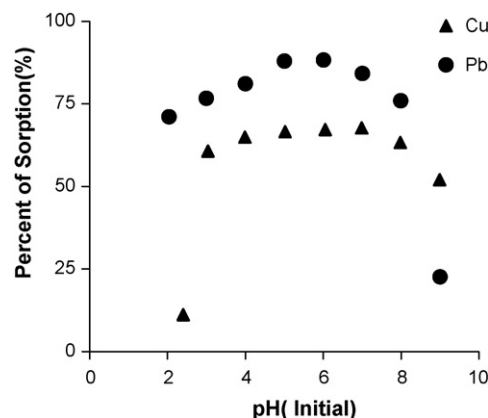


Fig. 1. Effect of pH on the adsorption of Cu^{2+} and Pb^{2+} using BS. Adsorption conditions; initial concentration of metal: 1.0 mM, 0.5 g sorbent, 20 mL of adsorption medium, temperature: $25 \pm 1^\circ\text{C}$.

obtained with biosorbent mass of 0.50 g. For that reason pH of the equilibrium solution was accepted as the initial solution pH values. The percent sorption of Cu^{2+} increased with increase in pH and reached maximum 65.2% for 1 mM initial concentration at pH 6.0. The percentage Cu^{2+} removal increased from 60.0% to 69.0% with an increase of pH from 3.0 to 6.4 and thereafter removal decreased from 69% to 50% with an increase of pH from 6.4 to 9.0. The percentage sorption of Pb^{2+} increased with increase in pH and reached maximum 88.0% for 1 mM initial concentration at pH 6.0. The percentage Pb^{2+} removal increased from 70.0% to 88% with an increase of pH from 2.5 to 6.0 and thereafter removal decreased from 88% to 25% with an increase of pH from 6.0 to 9.0.

One of the important factors in biosorption studies is the effect of the acidity of the medium. At very low pH values, the binding sites on the BS are likely to be protonated resulting in poor metal binding levels. An optimum pH range usually between pH 4.0 and pH 6.4 leaves the binding sites unprotonated and metal binding is maximised. As can be seen from Fig. 1, the maximum of biosorption for both metallic ions took place at about pH ranges 5.0–6.4. The biosorption of metal ions increased from 2.0 to 5.0 and for pH values higher than 6.4, the amount of metallic ions uptaken was decreased.

It is also known that heavy metal cations are completely released under circumstances of extreme acidic conditions. Metal biosorption is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include adsorption (chemisorption), complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption [37]. A possible explanation to this observation for metallic ion biosorption could be attributed that at lower pH values, the dissociation of the carboxylic acids leading to the formation of carboxylate groups plus H^+ will be precluded, since the pK_a of carboxylic acids ranges from 3.8 to 5.0 [23]. Therefore, an increase in the pH value from 2.0 to 5.0 will lead to a remarkable increase in the amount of metallic ion biosorbed. A decrease in adsorption, pH values higher than 6.4, was due to the formation of soluble hydroxyl complexes and leads to a decrease of biosorption process, as already observed for other biosorbent containing carboxylic acids [38].

3.2. Effect of time on the removal of metal ions

Fig. 2 illustrates the effect of sorption time on sorption efficiency. The equilibrium time was found to be 60 min and independent of initial metal concentration. The plots indicate that the metal ions

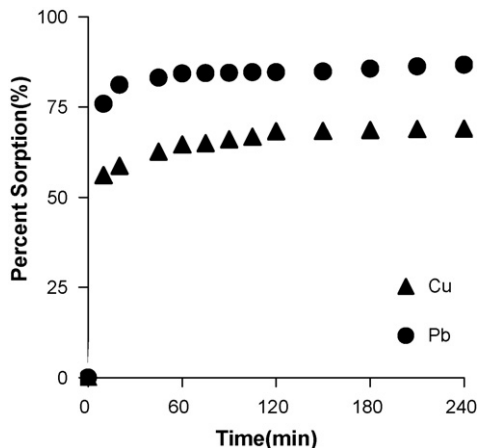


Fig. 2. Effect of contact time on the sorption of Cu^{2+} and Pb^{2+} by BS. Adsorption conditions; initial concentration of metal: 1.0 mM, 0.5 g sorbent, 20 mL of adsorption medium, temperature: $25 \pm 1^\circ\text{C}$, pH 6.

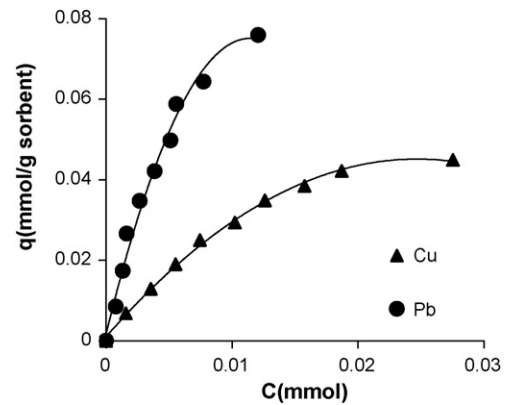


Fig. 3. Sorption isotherm of Cu^{2+} and Pb^{2+} ion on BS as a function of initial metal concentration (0.1–1 mM) at pH 6.0; 0.5 g sorbent, 80 mL of adsorption medium, temperature: $25 \pm 2^\circ\text{C}$.

adsorbed increase rapidly in the beginning and become very slow in the end. The majority of metal ion in adsorption equilibrium was achieved in between 15 and 50 min for Cu^{2+} ion and the sorption tends toward saturation at 90 min. The majority of metal ion in adsorption equilibrium was achieved in between 10 and 50 min for Pb^{2+} ion and the sorption tends toward saturation at 60 min. The initial faster rate of metal sorption may be explained by the large number of sorption sites available for adsorption. For the initial bare surface, the sticking probability is large, and consequently adsorption proceeded with a high rate. The slower adsorption rate at the end is probably due to the saturation of active sites and attainment of equilibrium.

3.3. Effect of initial metal ion concentration

The effect of metal concentration on the sorption by the BS was investigated by varying the metal concentration (0.1–1 mM) at a pH of 6.0 for 60 min equilibrium time (Fig. 3). The percentage of sorption is highly dependent on the initial concentration. The removal curves are single smooth and continuous suggesting the formation of monolayer of adsorbate on the surface of sorbent. The percent metal ion removal of BS increased with increasing metal ion concentration. This is obvious that for higher initial concentrations, more efficient utilization of sorption sites is expected due to a greater driving force by a higher concentration gradient.

Isotherms studies provide information on the capacity of sorbent, which is a most important parameter for a sorption system. Characterisation of the adsorption process is often carried out using a number of isotherm models. These include the most common Langmuir (Eq. (2)) and Freundlich (Eq. (3)) isotherms. These isotherms relate metal uptake per unit weight of resin q_e to the equilibrium metal ion concentration in the bulk fluid phase C_e .

The Langmuir model has eventually been empirically most often used since it contains the two useful and easily imaginable parameters (K_b and A_s) which are more easily understandable since they reflect the two important characteristics of the sorption system [36,37,39,40]. The general form of both these models are:

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_s} + \frac{C_e}{A_s} \quad (2)$$

where A_s (mol/g) and K_b (L/mol) are the coefficients, q_e is the weight adsorbed per unit weight of adsorbent and C_e is the metal concentration in bulk solution at equilibrium.

Table 1
Freundlich and Langmuir adsorption isotherm parameters.

Metals	Freundlich isotherm method			Langmuir isotherm method		
	K_f^a	n	R^2	K_b	A_s^a	R^2
Cu	0.662	1.444	0.974	67.087	0.073	0.978
Pb	0.846	1.858	0.976	169.420	0.112	0.987

^a mmol/g dry sorbent.

Freundlich equation:

$$q = K_f C_e^n \quad (3)$$

where n is the Freundlich constant and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent and C_e is the equilibrium metal concentration in fluid.

Since the correlation coefficients were high for each metal–sorbent equilibrium condition as seen from Table 1, the Langmuir-type sorption isotherm was suitable for equilibrium studies. Cu^{2+} sorption capacity was 4.64 mg/g and Pb^{2+} sorption capacity was 23.20 mg/g for BS (Table 1). A wide range of low-cost sorbents has been studied worldwide for Cu^{2+} and Pb^{2+} removal and adsorption capacities were given in Table 2 [41–49].

3.4. Effect of ionic strength

The effect of the interfering ion KNO_3 on the sorption of metal ions was evaluated. Increasing ionic strength influenced aqueous phase equilibrium between metal ion and BS. Metal sorption decreased with increasing ionic strength of the aqueous solution. The electrostatic attraction at low ionic strength appears to play a negligible role in the removal of Cu^{2+} and Pb^{2+} for sorbents. The results indicated that there was no significant decrease in the removal of metal ion for the interval of (0.01–0.1 M) KNO_3 ionic concentration.

3.5. Effect of amount of sorbent

The effect of variation of sorbent amount on the removal of metal ions by BS is shown in Fig. 4. Amount of sorbent was varied from 0.1 to 1 g and equilibrated for 60 min at an initial metal ion concentration of 1 mM. It is apparent that the metal ion concentration in solution decreases with increasing sorbent amount for a given initial metal concentration. This result was anticipated because for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area.

Table 2
Metal sorption capacities of some sorbents reported in literature.

Adsorbent	Sorption capacity (mg/g)	Reference
For copper ion		
Sour orange residue	21.70	[42]
Banana peel	4.75	[43]
Sawdust	1.79	[44]
Barley straw	4.64	This study
For lead ion		
Sphagnum moss peat	30.70	[45]
Tree fern	40.00	[46]
Sawdust	21.05	[47]
Rice husk	11.40	[41]
Chitosan	8.31	[49]
Barley straw	23.20	This study

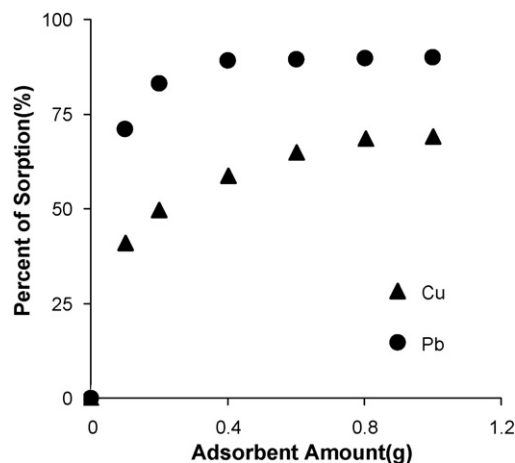


Fig. 4. Effect of sorbent dosage on the sorption of Cu^{2+} and Pb^{2+} on BS. Adsorption conditions; initial concentration of metal: 1.0 mM, 0.1–1 g sorbent, 20 mL of adsorption medium, temperature: $25 \pm 1^\circ\text{C}$.

3.6. Desorption studies

The reversibility of the adsorption process was also investigated. Desorption studies are helpful to explore the possibility of recycling the adsorbents and recovery of the metal resource. Desorption studies were conducted by mixing approximately 1 g of BS with 25 mL of 1 mM metal ion concentration. Desorption studies were carried out using 0.1 M HCl solution as stripping agents. Metal loaded biosorbent obtained from our sorption experiments was transferred to the vessels and shaken with 50 ml of each acid for 24 h. In order to determine the reusability of the sorbents after sorption process, the sorbents were taken out from the solution and washed with deionized water. The filtrate was analyzed for desorbed metal ion. Concentration of the desorbed ion corresponded to the amount released and enabled the determination of the percentage fraction of desorption. Consecutive biosorption–desorption cycles were repeated three times by using the same sorbents. The total loss-amount of metal ion released from sorbents varied from 20.0 to 25.0%.

4. Conclusion

BSs can be an alternative sorbent for the removal of Cu^{2+} and Pb^{2+} from aqueous solution. Cu^{2+} removal is built up; equilibrium conditions were attained after 90 min of mixing of the solution. Pb^{2+} removal is built up, equilibrium conditions were attained after 60 min of mixing of the solution. The metal ion removal was a function of solution pH. The results indicate that the optimum pH for the removal of metal ions by BS is pH 6.0 and 6.6 for Cu^{2+} and Pb^{2+} , respectively. Maximum uptake capacities by the BS were found to be, 69.0 and 88.0% for Cu^{2+} and Pb^{2+} , respectively. Isothermal data of metal sorption on straws can be modelled by both Freundlich and Langmuir isotherms. The data in the linearized forms (Langmuir equation) gave satisfactory correlation coefficients for a part of the covered concentration range. The equilibrium sorption capacities

of Cu^{2+} and Pb^{2+} after 2 h were 4.64 mg/g and 23.20 mg/g for BS, respectively.

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