RESEARCH ARTICLE

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Equilibrium and Kinetic Studies of Adsorption of Cd^{2+} and Pb^{2+} Ions from Aqueous Solution by Citric Acid Modified Maize Fibres

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Abstract
Maize fibres were pre-treated and chemically modified with 0.05 M citric acid. The adsorption of Cd^{2+} and Pb^{2+} ions onto the citric acid modified maize fibres was studied in batch experiment at ambient conditions. The study showed that the adsorption of Cd^{2+} and Pb^{2+} ions depends on metal ion concentration, adsorbent dosage and contact time. Langmuir and Freundlich adsorption models were used to model the equilibrium data. Based on linear regression value r^2, the adsorption fits Langmuir adsorption model well compared that of Freundlich. The maximum binding capacity of the metal ions as obtained from the Langmuir fit were 4.93 and 4.88 mg g^{-1} for Cd^{2+} and Pb^{2+} ions, respectively. The value of Freundlich constants, n and k_F, obtained from Freundlich fit were 2.63 mg g^{-1} and 0.60 for Cd^{2+} and 2.79 mg g^{-1} and 0.68 for Pb^{2+}. The rate constant and r^2 values as obtained from pseudo first-order, pseudo second-order and intra-particle diffusion plots were 2.6×10^{-2} min^{-1}, 0.997; 9.7×10^{-2} g mg^{-1} min^{-1}, 0.985 and 2.6×10^{-2} min^{-1}, 0.997, respectively, for Cd^{2+}, while those for Pb^{2+} were 2.6×10^{-2} min^{-1}, 0.993; 7.1×10^{-2} g mg^{-1} min^{-1}, 0.990 and 2.6×10^{-2} min^{-1}, 0.993, respectively. The r^2 values showed that the metal ion adsorption onto citric acid modified maize fibres follows pseudo first-order kinetics and is controlled by intra-particle diffusion. This study suggests that citric acid modified maize fibres can be used in simple water treatment units to remove Cd^{2+} and Pb^{2+} ions.

Keywords: Maize fibres; adsorption; adsorption isotherms; chemical modification.

1. Introduction

Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters. The day-by-day increment of stringent regulations on portable water demands for new technologies for heavy metal removal from wastewater to attain today's toxicity-driven limits [1]. Cadmium and lead have gained the attention of environmentalists because of their toxic nature. Significant amount of cadmium enters the environment through waste streams via activities such as metal plating and the deposition of other substances like batteries, television phosphors, pigments, plastic stabilisers, semiconductors, alloys and fungicides that often contain it in the environment [2]. Although cadmium is a possible essential trace element in some organisms, it is toxic (a cumulative poison in mammals). Adverse health effects due to cadmium are well documented. It has been reported to cause renal disturbances, lungs inefficiency, bone lesions, cancer and hypertension in humans [3, 4].

The environmental load of lead is also by the deposition of substances such as batteries, water pipes, solder, paints, putty, caulk and matches containing it in the environment [2]. Lead is toxic (a cumulative poison). As with other heavy metals strongly bound by biological complexion agents, lead is a cumulative poison and can act through long-term ingestion of relatively small quantities. Lead can be retained in the body for long periods, especially in the bones, where it can replace some of calcium. Lead poisoning in children by ingestion of paint fragments is well known [5].

Considerable research has been carried out in developing cost-effective heavy metal removal techniques. A number of physicochemical methods, such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, application of membrane technology and evaporation traditionally employed for heavy metal removal are either extremely expensive or ineffective, especially at relatively low concentrations (around 1–100 mg mL^{-1}) [6, 7]. Methods employing adsorption principles have become the most promising alternative for this

purpose. The use of biological materials, especially waste agricultural residues, for recovering heavy metals from contaminated industrial effluent has emerged as a potential alternative method to conventional techniques [8]. Recently, research has revealed that application of low-cost or no-cost adsorbents derived from waste agricultural biomass, such as bone meal, corn cobs, barely husk, shear butter seed husk, sunflower stalk, cassava waste, rice husk and walnut shells [9], has given favourable result. Previous studies have reported the use of many agricultural residues in metal adsorption, but none has reported the use of maize fibres. This work seeks to investigate the adsorption of Cd^{2+} and Pb^{2+} ions in aqueous solution onto citric acid modified maize fibres.

2. Methods

Stock cadmium solution (1000 mg L^{-1}) was prepared by dissolving the required amount of $CdCl_2 \cdot H_2O$ (Sigma–Aldrich) in distilled water. Cadmium solutions of desired concentration were prepared by adequate dilution of the stock solution with distilled water. Stock lead solution was prepared, in a similar way, using $PbCl_2$ (Sigma–Aldrich), and other concentrations were prepared from it. The maize fibres were obtained from a local market as solid waste. The fibres were dried in air and sieved to eliminate adhering starch particles and non-fibre materials and thereafter dried in air again. The fibres were chemically modified by treatment with 0.05 M citric acid using the method described by Marshall *et al.* [10].

2.1. Effect of adsorbent dosage

The amount of Cd^{2+} and Pb^{2+} ions adsorbed by the citric acid modified maize fibres was studied at different adsorbent doses at a fixed concentration (50 mg L^{-1}) of the metal ions. To aliquots (30 mL) of the metal ions in separate conical flasks, the required amounts (0.2–1 g) of the adsorbent were added. Each flask was corked and shaken on a mechanical shaker for 30 min and then filtered. The concentration of Cd^{2+} and Pb^{2+} ions in the filtrate was determined using atomic absorption spectroscopy (AAS) (model 210/200A).

2.2. Effect of contact time

The required volume (30 mL) of metal ion solutions (50 mg L^{-1}) was pipetted into separate conical flasks. The flasks were corked after addition of 1 g of citric acid modified maize fibres and shaken mechanically at varying intervals of 5–90 min, respectively. At the end of the contact period, the residual concentration of the metal ions in the solutions was determined using AAS (model 210/200A).

2.3. Effect of metal ion concentration

Varying initial concentrations (50–300 mg L^{-1}) of the metal ions were used for this study. Citric acid modified maize fibres (1 g) were dispersed into 30 mL of the separate metal ion solutions. The mixture of each solution was shaken mechanically on a shaker for 2 h at room temperature. Each mixture was filtered and the residual concentration of metal ions in the filtrate was determined using AAS (model 210/200A).

3. Results and Discussion

3.1. Effect of adsorbent mass

The relationship between adsorbent dosage and the percentage of Cd^{2+} and Pb^{2+} ions removed from aqueous solution by the adsorbent is shown in Figure 1. The percentage of the metal ions removed increased with increase in the mass (6.67–33.33 mg mL^{-1}) of the adsorbent. However, more Pb^{2+} ions were removed compared with Cd^{2+}. The increase in adsorption efficiency with increase in mass of citric acid modified maize fibres can be attributed to increase in adsorption sites as the mass of the adsorbent increased.

3.2. Equilibrium modeling

Figure 2 represents the relationship between the amount of the metal ions adsorbed and the corresponding concentrations in the bulk aqueous phase at equilibrium. Within the range 50–300 mg L^{-1}, of the metal ion concentration studied, the amount of the metal ions adsorbed initially increased with increase in equilibrium concentration (C_{eq}) of the metal ions, but became constant (ca. 4 mg g^{-1}) at $C_{eq} \geq 120$ mg L^{-1}. This corresponds to complete coverage of adsorption sites on the adsorbent. These curves belong to the L-type according to the classification of equilibrium adsorption in solution [11].

Equilibrium data are very fundamental in the design of adsorption systems. Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational

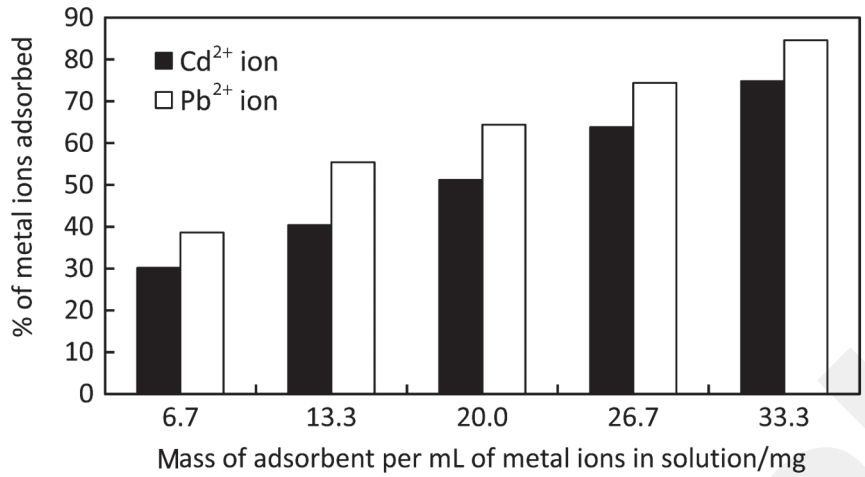

Figure 1: Effect of adsorbent dosage on the amount of Cd^{2+} and Pb^{2+} ions removed from aqueous solution by citric acid modified maize fibres.

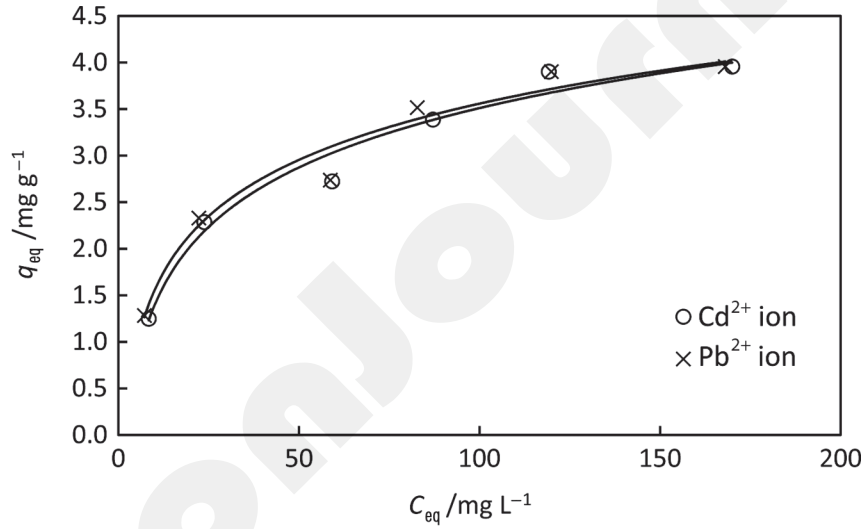

Figure 2: Equilibrium adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres.

conditions and to design and optimise an operating procedure [12]. Several isothermal equations have been used for equilibrium modeling of adsorption systems. Among these, two are commonly used (i.e., Langmuir and Freundlich adsorption isotherms).

Langmuir isotherm models a single coating layer on adsorption surface. This model supposes that the adsorption takes place at a specific adsorption surface. The attraction between molecules decreases as they get closer to the adsorption surface [13]. The empirical and linearised forms of Langmuir equation are given by Eqs. 1 and 2 [14], respectively.

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \tag{1}$$

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{b q_{max}} + \frac{C_{eq}}{q_{max}} \tag{2}$$

where q_{max} (mg g^{-1}) is the maximum amount of metal ions adsobed per unit weight of adsorbent to form a complete monolayer, C_{eq} (mg L^{-1}) is the equlibrium concentration of the solution and q_{eq} (mg g^{-1}) is the amount of metal ions adsorbed per unit mass of adsorbent. Eq. 2 was used to obtain the values of b and q_{max} from the experimental data by plotting C_{eq}/q_{eq} versus C_{eq}, as shown in Figure 3.

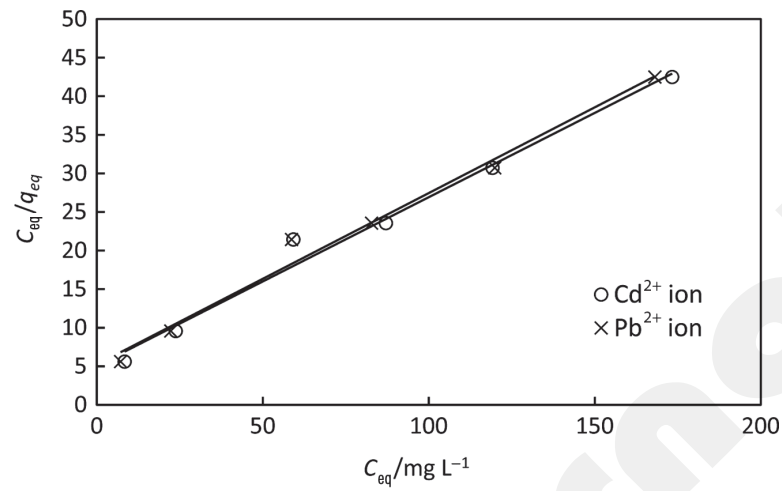

Figure 3: Langmuir fit for adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres.

Freundlich isotherm is used for modeling adsorption on heterogeneous surfaces. The emperical and linearised forms of this isotherm are given by Eqs. 3 and 4 [14], respectively.

$$q_{eq} = k_F C_{eq}^{1/n} \tag{3}$$

$$\ln q_{eq} = \ln k_F + \frac{1}{n} \ln C_{eq} \tag{4}$$

where k_F and n are the Freundlich constants characteristic of the system and are indicators of adsorption capacity and adsorption intensity, respectively. Eq. 4 was applied to the experimental data to obtain k_F and n from the plot of ln q_{eq} versus ln C_{eq} (Figure 4).

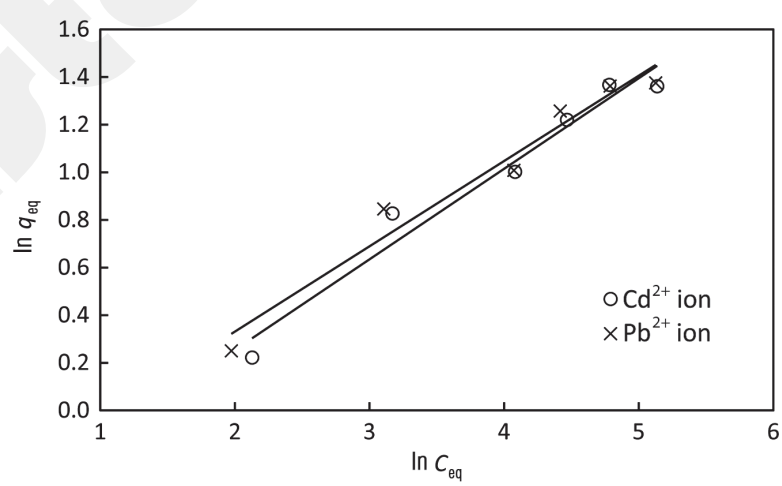

Figure 4: Freundlich fit for adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres.

Within the range of concentration, 50–300 mg L^{-1} of the metal ions studied, Langmuir isotherm appeared to be a good model for the adsorption process. This is evident by the value of r^2 given in Table 1.

Table 1: Isotherm parameters for adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres.

Models	Cd^{2+}			Pb^{2+}		
Langmuir	r^2	q_{max} (mg g^{-1})	b (L mg^{-1})	r^2	q_{max} (mg g^{-1})	b (L mg^{-1})
	0.989	4.93	0.021	0.985	4.88	0.023
Freundlich	r^2	n	k_F ($mg^{1-1/n}L^{1/n}g^{-1}$)	r^2	n	k_F ($mg^{1-1/n}L^{1/n}g^{-1}$)
	0.962	2.63	0.60	0.963	2.79	0.68

3.3. Kinetic modeling

The amount of the metal ions removed from aqueous solution by the adsorbent depends on the contact time, as shown in Figure 5. This effect may be attributed to the fact that the metal ions had more time to interact with the adsorption sites as the time prolongs and hence more got adsorbed.

Adsorption kinetics are used in order to explain the adsorption mechanism and characteristics. The pseudo first-order and pseudo second-order kinetic models were applied to the adsorption data. The adsorption rate constant proposed by Lagergreen [15] and Ho [16] using first-order reaction kinetics is given by Eq. 5.

$$\frac{dq_t}{dt} = k_1\left(q_{eq} - q_t\right) \tag{5}$$

where k_1 is the adsorption rate constant for first-order adsorption, q_t (mg g^{-1}) the amount of metal ions adsorbed at time t and q_{eq} (mg g^{-1}) the amount of metal ions adsorbed at equilibrium or saturation. Eq. 6 is the integrated form of Eq. 5.

$$\ln\left(q_{eq} - q_t\right) = -k_t t + c_1 \tag{6}$$

where c_1 is the integration constant for first-order reaction kinetics. If it is supposed that $q_t = 0$ at $t = 0$, then Eq. 6 transforms to Eq. 7.

$$\ln\left(q_{eq} - q_t\right) = \ln q_{eq} - k_1 t \tag{7}$$

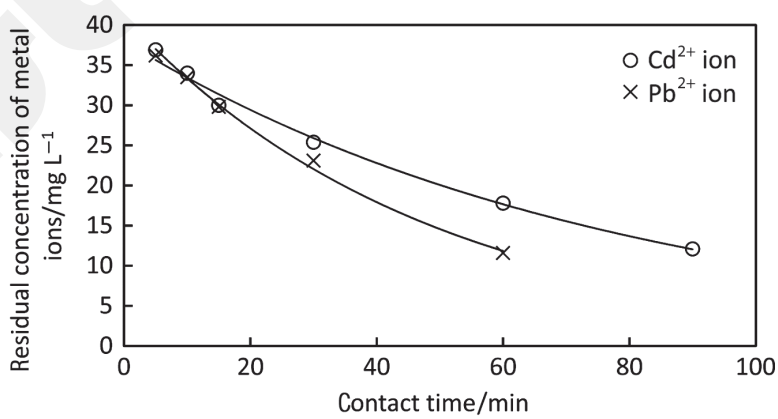

Figure 5: Residual concentration of Cd^{2+} and Pb^{2+} ions at different contact times, the concentration of a metal ion solution is 50 mg mL^{-1}.

Based on of Eq. 7, $\ln(q_{eq}-q_t)$ was plotted against t (Figure 6) and the value of k_1 was obtained from the slope.

The adsorption rate proposed by Ho and McKay [17] using pseudo second-order reaction kinetics is given by Eq. 8.

$$\frac{dq_t}{dt} = k_2\left(q_{eq} - q_t\right)^2 \tag{8}$$

where k_2 is the rate constant for pseudo second-order reaction kinetics. With an algorithmic arrangement, Eq. 9 can be obtained from Eq. 8.

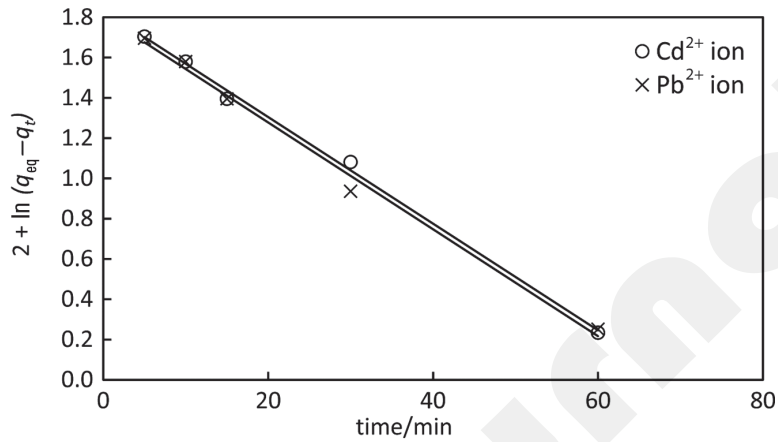

Figure 6: Pseudo first-order plot for adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres. Concentration of metal ions: 50.0 mg L^{-1}, adsorbent dose: 1 g 30 mL^{-1} and temperature: 29 ± 1°C.

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \tag{9}$$

Eq. 9 was used to model the adsorption data by plotting t/q_t against t.

For particle-diffusion-controlled (Figure 7) adsorption process, Eq. 10 [18, 19] allows determination of the rate constant k_p (Figure 8). The result of the kinetic study is summarised in Table 2.

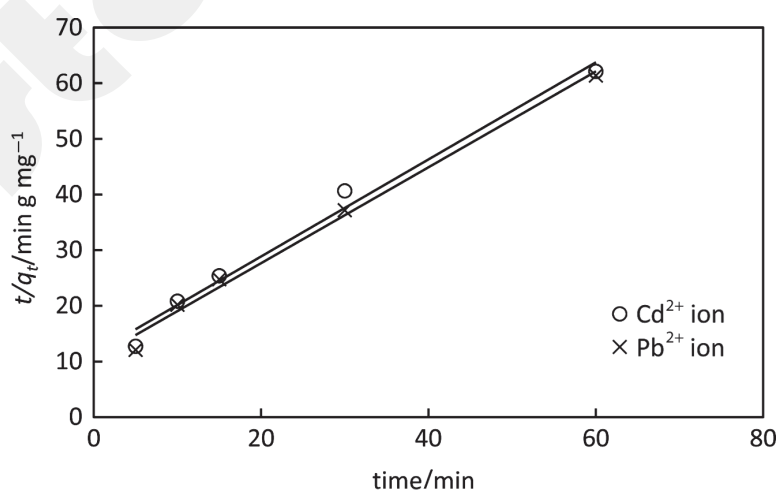

Figure 7: Pseudo second-order plot for adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres. Concentration of metal ions: 50 mg L^{-1}, adsorbent dose: 1 g 30 mL^{-1} and temperature 29 ± 1°C.

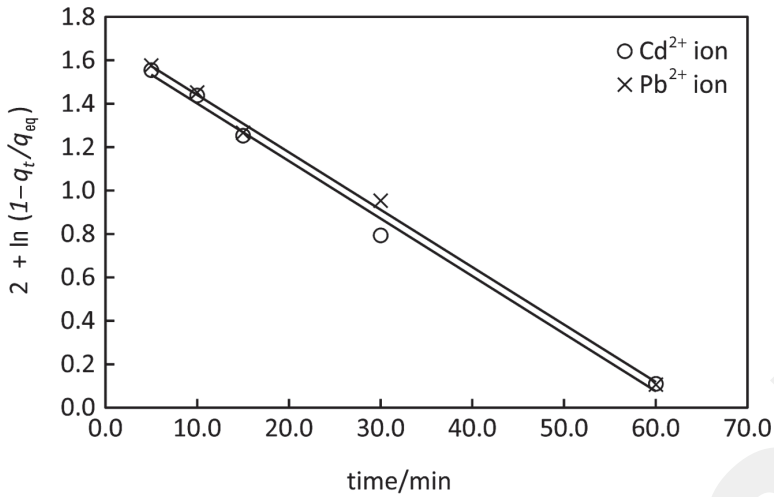

Figure 8: Intra-particle diffusion plot for adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres.

Table 2: Kinetic parameters for adsorption of Cd^{2+} and Pb^{2+} ions onto citric acid modified maize fibres.

Models	Cd^{2+}		Pb^{2+}	
Pseudo first-order	r^2	k_1 (10^{-2} min^{-1})	r^2	k_1 (10^{-2} min^{-1})
	0.997	2.6	0.993	2.6
Pseudo second-order	r^2	k_2 (10^{-2}g mg^{-1} min^{-1})	r^2	k_2 (10^{-2}g mg^{-1} min^{-1})
	0.985	9.7	0.990	7.1
Intra-particle diffusion	r^2	k_1 (10^{-2} min^{-1})	r^2	k_1 (10^{-2} min^{-1})
	0.997	2.6	0.993	2.6

$$\ln\left(1-\frac{q_t}{q_{eq}}\right) = -k_p t \tag{10}$$

The values of q_{max} obtained from the Langmuir fit of the metal ions differed appreciably from some of those reported with other types of adsorbents in the literature given in Table 3. These values suggest that although citric acid modified maize fibres may not effectively remove Cd^{2+} and Pb^{2+} ions from aqueous solution they may be used in single contact applications particularly where contaminated wastewater requires pre-treatment before exposure to more sensitive adsorbents and in cases where quantitative recovery of adsorbed metals is desired.

Table 3: Adsorption capacity of some adsorbents reported in the literature.

Adsorbent	Cd^{2+}	Pb^{2+}	References
Shells of hazelnut	5.42	16.23	[20]
Shells of almond	3.18	5.43	[20]
Barks of larix	–	21.06	[21]
Sawdust	15.27	15.77	[22]
Rice hulls	21.4	11.4	[23]
Stem of *Quercus ilex* L.	0.36	0.75	[24]
Citric acid modified maize fibres	4.93	4.88	Present study

4. Conclusion

The potential of citric acid modified maize fibres to remove Cd^{2+} and Pb^{2+} ions from aqueous solution has been studied. The adsorption followed pseudo first-order kinetics and Langmuir isotherm models and it is controlled by intra-particle diffusion. The findings of this study suggest that maize fibres can be used in simple water treatment units to remove Cd^{2+} and Pb^{2+} ions to enhance the quality of water and/or wastewater.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

FE developed the project; JO worked on the project under the supervision of FE and AT; AT also prepared the manuscript.

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