



Competitive adsorption of Pb^{2+} and Cd^{2+} onto activated carbon produced from municipal organic solid waste

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ABSTRACT

Competitive adsorption of cadmium (Cd^{2+}) and lead (Pb^{2+}) was investigated using activated carbon (AC) produced from municipal organic solid waste. The effect of pH, contact time, metal concentration and adsorbent dosage on the performance of the adsorption process was investigated using synthetic binary metal solutions. The results showed that optimum removal efficiency of both metals from binary metal solutions could be achieved at a pH value of 5 and a contact time of 120 min. Moreover, the results showed that, for both metal ions, the increase in the initial metal concentration led to an increase in adsorption capacities and decrease in removal efficiencies. At a Cd^{2+} concentration of 100 mg/L, the removal efficiency of Cd^{2+} was found to decrease from 21.42% to 6.79% (68.3% decrease), when Pb^{2+} concentration was increased from 25 to 300 mg/L, respectively. On the other hand, the increase in the AC dosage was found to result in decreasing the adsorption capacity from 19.65 to 10 mg/g and from 61 to 12 mg/g when AC dosages were increased from 25 to 400 mg, for Cd^{2+} and Pb^{2+} , respectively. The experimental results of both metals were found to fit non-linear Freundlich adsorption isotherm and pseudo-second-order kinetic models.

Keywords: Adsorption kinetics; Isotherm models; Adsorbent dosage; pH effect; Metal binary solution; Surface characteristics

1. Introduction

Globally, discharges of wastewater containing heavy metals to receiving environments are increasing due to increases in industrial activities. However, proper and adequate treatment to such wastewater must be provided in order to protect the receiving environments and secure an unconventional source of water [1]. In addition to the different and various treatment techniques that have been implemented to remove metals from water and wastewater streams, adsorption was reported to be relatively simple in design and can be used to remove various contaminants [2]. Moreover, Park et al. [3] reported that adsorption is a fast process and low in cost.

The use of conventional or commercial activated carbon (AC) as sorbent is costly; therefore, alternative sources of AC

have been investigated for their suitability as adsorbents of metals from water and wastewater streams. Generally, industrial streams contain more than one metal ion; therefore, the main objective of competitive adsorption studies is to investigate adsorption behavior of metals ions from aqueous solutions. Moreover, displacement of an adsorbed metal by another metal during the adsorption process is of great interest to researchers.

Recently, Park et al. [3] investigated the competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. The main objective of the investigation was to compare between single-metal and multi-metal adsorption behaviors and capacities of Cd^{2+} , Cr^{3+} , Cu^{2+} , Pb^{2+} and Zn^{2+} . The results showed that maximum adsorption capacities of Pb^{2+} , Cd^{2+} , Cr^{2+} , Cu^{2+} and Zn^{2+} were 102, 86, 65, 55 and 34 mg/g, respectively, in single-metal adsorption isotherms. However, in multi-metal adsorption isotherms, maximum adsorption

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capacities of Pb^{2+} , Cd^{2+} , Cr^{3+} , Cu^{2+} and Zn^{2+} were 88, 5, 21, 40 and 7 mg/g, respectively. They concluded that Freundlich and Langmuir adsorption models of multi-metal adsorption isotherms differ from those of single-metal, which was attributed to competition. Ma et al. [4] investigated the competitive adsorption of Cr^{3+} , Cu^{2+} , Pb^{2+} and Zn^{2+} ions on carbon nanotubes (CNTs). The investigators assessed the adsorption/desorption performances of the four metal ions on oxidized CNTs using synthetic biofluids. Kinetics and adsorption isotherms of the metal ions were determined in single-metal and multi-metal adsorptions. The investigators concluded that CNTs had significant adsorption capacities for Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} , where Pb^{2+} showed the highest adsorption capacity in both single-metal and multi-metal (competitive) assessments. They reported that adsorption capacities of metal ions were found to decrease by 41.6%, 15.6%, 81.5% and 89.7% for Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} , respectively. Bediako et al. [5] investigated the removal of heavy metals from aqueous phases using chemically modified waste Lyocell fiber, where single and tertiary metal solutions were used. With single-metal adsorption isotherms, the results showed that maximum uptakes of Pb^{2+} , Cd^{2+} and Cu^{2+} were 531.29 ± 0.28 , 505.64 ± 0.21 and 123.08 ± 0.26 mg/g, respectively. In ternary metal systems, Cu^{2+} was found to attain maximum uptake, which was attributed to the good selectivity of the sorbent toward Cu^{2+} than Pb^{2+} and Cd^{2+} . Li et al. [6] and Abollino et al. [7] reported that Cu^{2+} has higher stability constant with its complexes than Pb^{2+} and Cd^{2+} , which could suggest that the metal complex formed between Cu^{2+} and the adsorbent was more stable than that of Pb^{2+} and Cd^{2+} . Zhang et al. [8] investigated the competitive adsorption of radioactive strontium (^{90}Sr) and cobalt (^{60}Co) from nuclear power plant wastewater onto tin antimonite (SnSb) in single and binary components. The investigators studied the effect of pH and presence of non-radioactive materials on the performance of the adsorption process. The results showed that the adsorbent was having good affinity to both Sr^{2+} and Co^{2+} ions over a wide range of pH values (2–12) and in the presence of various non-radioactive ions. Moreover, although Co^{2+} was having more affinity to the adsorbent, Sr^{2+} was found to inhibit the adsorption of Co^{2+} . A pseudo-second-order equation was found to describe the kinetic performance of both metal ions well. More studies on competitive adsorption of various metal ions can be cited in the published literature [9–15].

Competitive adsorption of different metals onto AC, in multi-component systems, depends on AC properties such as surface properties, structure and functional groups. In addition, competitive adsorption is highly affected by properties of metal ions including concentration, molecular structure, ionic size, ionic charge, electronegativity and ionic weight. Moreover, chemical characteristics of solution such as pH and ionic strength have great effects on competition between metal ions [16]. Onundi et al. [17] investigated the removal of Cu^{2+} , Ni^{2+} and Pb^{2+} from mixed synthesized semiconductor industrial wastewater by granular AC (GAC). They reported that adsorption capacities were in the following order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. They related the competition to the presence of sulfate functional groups on the AC surface, which possess higher affinity to Pb^{2+} than Cu^{2+} and Ni^{2+} . Depci et al. [18] investigated competitive adsorption of Zn^{2+} and Pb^{2+} from aqueous solutions and reported that adsorption affinity sequence of metal ions is attributed to electronegativity,

ionic potential and softness. They found that Pb^{2+} has higher adsorption capacity than Zn^{2+} due to its higher electronegativity. Mohan et al. [19], who studied competitive adsorption of Cu^{2+} and Cd^{2+} from binary and ternary systems, reported that Cu^{2+} has higher adsorption capacity due to its higher electronegativity. Furthermore, hydrated radius of Cu^{2+} is smaller than that of Cd^{2+} ; therefore, it is easier to get into the narrow pores of the AC. It was also reported that although Cd^{2+} has higher ionic potential, it has lower adsorption capacity, which was attributed to the weak interaction between Cd^{2+} and the AC. Ricordel et al. [20] studied competitive adsorption of Pb^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} on AC produced from peanut. They reported that adsorption capacities were in the following order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$, which was attributed to the difference of ionic radii, where ions with higher ionic radii have higher adsorption capacities. However, Faur-Brasquet et al. [21], who studied the removal of the same metals on AC cloths, reported contradictory explanations with respect to the effect of ionic radii. Adsorption capacities were found to be in the following order: $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+}$. They related the low adsorption of Pb^{2+} to its high ionic radius when compared with Ni^{2+} and Cu^{2+} , which resulted in quick saturation of adsorption sites due to overcrowding. The difference of affinity order for the same metal ions on different adsorbents indicates that competition of metal ions depends on the properties of both adsorbates and adsorbents [22].

Based on the above discussion, it is very clear that several studies have investigated the adsorption of heavy metals from multi-solute systems using AC prepared from different single waste material. However, and up to the knowledge of the investigators, very few studies reported results on competitive adsorption of heavy metals using AC produced from mixed waste material. Moreover, there is a lack of information, in the published literature, on competitive adsorption of metals onto AC produced from municipal organic solid waste (MOSW). Therefore, the main objective of the current investigation is to study the mechanism of competitive adsorption of Pb^{2+} and Cd^{2+} from binary solutions using AC produced from MOSW. Effects of pH (3–7), contact time (5–1,920 min), metal concentration (25–300 mg/L) and adsorbent dosage (25–400 mg per 50 mL of metal solution) on the competition between the two metal ions were investigated.

2. Materials and methods

2.1. Chemicals

All solutions were prepared using deionized water, where nitrate salts (BDH Laboratory Supplies, UK) were used to prepare Cd^{2+} and Pb^{2+} ions stock solutions by dissolving 2.744 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 1.598 g of $\text{Pb}(\text{NO}_3)_2$, respectively, in 1,000 mL of deionized water. Before making up to 1,000 mL, the prepared stock solutions were acidified by adding HNO_3 to a pH value of less than 2. Proper dilutions were made to prepare metal solutions of different concentrations of Cd^{2+} and Pb^{2+} from the prepared stock solutions.

2.2. Production of AC from MOSW

Al-Malack and Basaleh [23] reported the production process of AC from MOSW in details.

2.3. Characterization of prepared AC

As reported by Al-Malack and Basaleh [23], the produced AC was characterized using Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FTIR).

2.4. Methods of analysis

In order to obtain reliable results, all isotherms were performed in duplicates. Moreover, blank samples were included in each run, where the produced AC was not added to the synthetic wastewater. Atomic absorption spectroscopy (AAS; PerkinElmer, USA, Analyst 700) was used to measure the initial and final concentrations of metal ions.

2.5. Effect of pH

The effect of pH on the adsorption process was investigated using pH values of 3, 4, 5, 5.5, 6, and 7, where pH values were adjusted using 0.1 N HNO₃ and 0.1 N NaOH. Batch isotherms were conducted using 50 mg of the produced AC per 50 mL of metal solution, metal concentration of 100 mg/L and contact time of 3 h. Samples were placed on a shaker having a constant shaking speed of 200 rpm at room temperature.

2.6. Effect of contact time

The effect of contact time on the removal efficiency of metal ions from binary aqueous solutions by the produced AC was investigated using contact time intervals of 5, 10, 15, 30, 120, 240, 480, 720, 1,440, and 1,920 min. The batch experiments were conducted using 50 mg of the produced AC per 50 mL of binary metal solutions, metal concentration of 100 mg/L and pH value of 5. Samples were placed on a shaker having a constant shaking speed of 200 rpm at room temperature.

2.7. Effect of initial metal concentration

To investigate the effect of initial metal concentration on the removal efficiency of Cd²⁺ and Pb²⁺ from binary solutions using the produced AC, batch experiments were performed at different initial concentrations, contact time of 180 min; pH value of 5 and adsorbent dosage of 50 mg per 50 mL of metal solution. Table 1 shows the investigated initial concentrations of metal ions during the competitive adsorption study.

2.8. Effect of adsorbent dose

To investigate the effect of the produced AC dosage on the removal efficiency of Cd²⁺ and Pb²⁺ in binary systems, batch experiments were performed using AC dosages of 25, 50, 100, 200, 300 and 400 mg per 50 mL of metal solution. During the investigation, initial metal (Cd²⁺ and Pb²⁺) concentration of 100 mg/L, contact time of 180 min and pH value of 5 were used.

3. Results and discussion

3.1. Characterization of prepared AC

The N₂ adsorption isotherms at 77° K showed that the produced AC has a BET surface area of 793 m²/g and an average pore width (D_p) of approximately 26.4 Å (2.64 nm). Functional groups present on the surface of the raw material and produced AC were investigated using FTIR. The results revealed that almost the same functional groups were found in both samples, which clearly indicate that the activation process has mainly enhanced the porosity of the produced AC and made insignificant changes to the surface chemistry. Crystalline structures of the raw material and produced AC were examined by XRD, where the results showed that sharp peaks were not observed, which clearly indicates that the structure is amorphous. The SEM micrographs of the raw material and produced AC samples clearly showed the formation of heterogeneous pores due to activation process. Al-Malack and Basaleh [23] reported and discussed surface characteristics of the raw material and produced AC in details.

3.2. Effect of operational factors

3.2.1. Effect of pH

The effect of pH on the removal efficiency of Cd²⁺ and Pb²⁺ ions from binary synthetic solutions using the produced AC is presented in Fig. 1. The results clearly showed that when pH values were increased, the removal efficiency of both metals was also increased. This is attributed to the fact that at low pH values there is a strong competition between hydrogen and metal ions; therefore, competition decreases with the increase in pH values due to the decrease in H⁺ (positively charged) and increase of OH⁻ (negatively charged) [24,25]. However, at high pH values, precipitation of metal ions as hydroxide takes place. Taty-Costodes et al. [26], who investigated the

Table 1
Initial concentrations of metal ions in binary solutions

| | | Pb ²⁺ (mg/L) | | | | | |
|-------------------------|-----|-------------------------|----------|-----------|-----------|-----------|-----------|
| | | 25 | 50 | 100 | 150 | 200 | 300 |
| Cd ²⁺ (mg/L) | 25 | (25,25) | (25,50) | (25,100) | (25,150) | (25,200) | (25,300) |
| | 50 | (50,25) | (50,50) | (50,100) | (50,150) | (50,200) | (50,300) |
| | 100 | (100,25) | (100,50) | (100,100) | (100,150) | (100,200) | (100,300) |
| | 200 | (200,25) | (200,50) | (200,100) | (200,150) | (200,200) | (200,300) |
| | 300 | (300,25) | (300,50) | (300,100) | (300,150) | (300,200) | (300,300) |

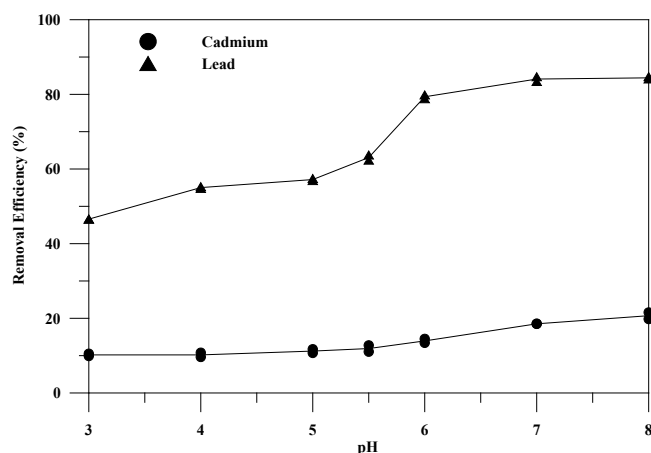


Fig. 1. Effect of pH on the removal efficiency of Cd^{2+} and Pb^{2+} from binary ion solutions.

Table 2

Properties of investigated metals (Cd^{2+} and Pb^{2+})

| Property | Pb^{2+} | Cd^{2+} |
|-----------------------------|------------------|------------------|
| Electronegativity (Pauling) | 2.33 | 1.69 |
| Hydrated ionic radius (Å) | 4.01 | 4.26 |
| Ionic radius (Å) | 1.19 | 0.95 |

effect of pH on the removal efficiency of Cd^{2+} and Pb^{2+} by sawdust, reported similar results to those obtained in the current study. The results also showed that the removal efficiency of Pb^{2+} was much higher than that of Cd^{2+} in competitive adsorption at all pH values under investigation, which can be attributed to competition between the two metal ions for active sites on the surface of the produced AC. Moreover, the attachment of Pb^{2+} to the produced AC is stronger than that of Cd^{2+} , which can be ascribed to its favored properties, as shown in Table 2. In addition to its higher electronegativity and ionic radius, Pb^{2+} has lower hydrated radius; consequently, Pb^{2+} can easily access microspores when compared with Cd^{2+} [27]. Qin et al. [28] studied the competitive adsorption of Cd^{2+} , Pb^{2+} and Cu^{2+} on peat. They reported that Pb^{2+} and Cd^{2+} had the highest and lowest removal efficiencies, respectively, which were attributed to the differences in electronegativity, ionic radius and hydrated ionic radius of both metal ions.

To avoid precipitation at higher pH values, batch isotherm experiments were carried out at pH values of 5. Bohli et al. [29], who studied the removal of Cd^{2+} , Pb^{2+} and Cu^{2+} from single and binary solutions on AC produced from olive stone, also reported an optimum pH value of 5.

3.2.2. Effect of contact time

Fig. 2 shows that the removal efficiency of both metals increased dramatically between 5 and 60 min of experiment period; however, between 60 and 120 min, the increase in removal efficiency started to slow down. The figure also shows that after 120 min of the experiment time, insignificant increase in removal efficiency was observed and equilibrium

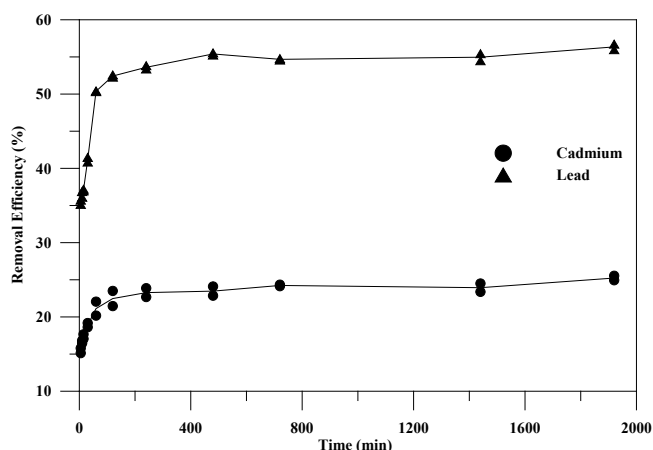


Fig. 2. Effect of contact time on the removal efficiency of Cd^{2+} and Pb^{2+} from binary ion solutions.

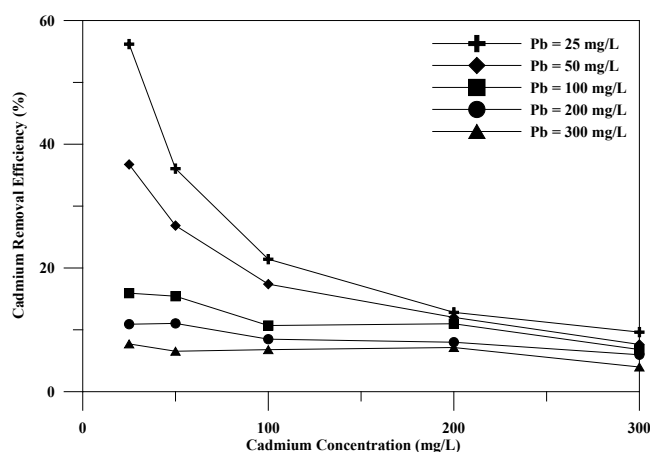


Fig. 3. Effect of Cd^{2+} initial concentration on the removal efficiency of Cd^{2+} at various Pb^{2+} concentrations.

occurred at 120 min for both metals. The fast adsorption rate observed within the first 60 min could be attributed to the high availability of surface area and active sites on the surface of the produced AC. Once active sites are filled, adsorption rate becomes slower until saturation is reached. The equilibrium time was obtained at 120 min, where adsorption of metal ions by the produced AC is equal to the desorption of those metal ions from the AC surface. However, adsorption experiments were carried out using a contact time of 180 min to ensure that equilibrium is reached.

3.2.3. Effect of initial concentration

The effects of initial concentration on the removal efficiency of Cd^{2+} and Pb^{2+} using the produced AC are presented in Figs. 3 and 4. Fig. 3 shows the effect of initial concentration of Cd^{2+} , in the presence of different concentrations of Pb^{2+} , on the removal efficiency of Cd^{2+} . On the other hand, Fig. 4 shows the effect of initial concentration of Pb^{2+} , in the presence of different concentrations of Cd^{2+} , on the removal efficiency of Pb^{2+} . The results showed that, for both metal ions, the increase in the initial concentration led to an increase in

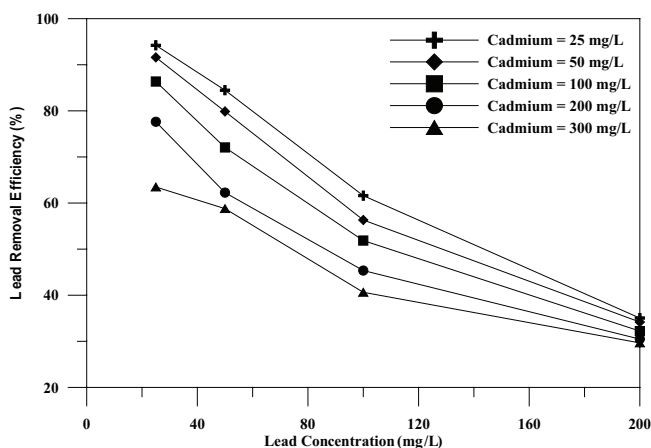


Fig. 4. Effect of Pb^{2+} initial concentration on the removal efficiency of Pb^{2+} at various Cd^{2+} concentrations.

the adsorption capacity and decrease in the removal efficiency. For example, at a Cd^{2+} concentration of 100 mg/L, the removal efficiency of Cd^{2+} was found to decrease from 21.42% to 6.79% (68.3% decrease), when Pb^{2+} concentration was increased from 25 to 300 mg/L, respectively. Similarly, at Pb^{2+} concentration of 100 mg/L, the removal efficiency of Pb^{2+} was found to decrease from 61.6% to 40.65% (34% decrease), when Cd^{2+} concentration was increased from 25 to 300 mg/L. However, it was observed that adsorption capacity of Cd^{2+} in competitive mode decreased sharply in the presence of Pb^{2+} . For example, the adsorption capacity of Cd^{2+} in single mode at initial concentration of 300 ppm was 56 mg/g, while the adsorption capacity in competitive mode at the same initial concentration was found to decrease to 28 mg/g, when Pb^{2+} was increased from 0 to 25 ppm. When Pb^{2+} increased from 25 to 50 ppm, a small decrease of Cd^{2+} adsorption capacity was noticed, while the behavior of adsorption capacity of Pb^{2+} in competitive adsorption was also found to decrease due to the presence of Cd^{2+} , which could be attributed to competition between the two metal ions for active sites. As mentioned before, the produced AC possesses definite number of adsorption sites that metal ions compete for, however, Pb^{2+} are attached more strongly to the produced AC when compared with Cd^{2+} . This can be attributed to the fact that Pb^{2+} has higher electronegativity, higher ionic radius, and lower hydrated ionic radius than Cd^{2+} . Consequently, the produced AC sites have stronger physical and chemical affinity to Pb^{2+} than Cd^{2+} , which is in consistence with results obtained on single adsorption [23]. Qin et al. [28], who studied the removal of Cd^{2+} and Pb^{2+} from single and binary solutions, reported similar findings. Moreover, the interaction forces between carbon and Cd^{2+} are weaker, and Cd^{2+} ions are attached to only surface centers that have high negative charge density as reported by Mohan et al. [19], who studied the removal of Cd^{2+} and Cu^{2+} from single and binary systems. Li et al. [30], who investigated the competitive adsorption of Cd^{2+} and Pb^{2+} by pretreated biomass, also reported similar results to those obtained from the current study. Mohan and Singh [31] studied multi-component adsorption of heavy metals by AC produced from bagasse. They reported that adsorption behavior of competitive systems was found to decrease, increase, or have no change, which depends on the

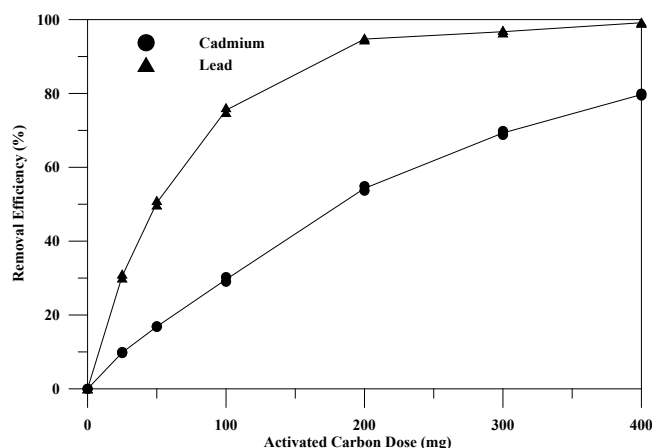


Fig. 5. Effect of AC dose on the removal efficiency of Cd^{2+} and Pb^{2+} from binary ion solutions.

ratio between $Q_{competitive}$ and Q_{single} according to the following categorization: $[Q_{competitive}/Q_{single}] > 1$ (increase), $[Q_{competitive}/Q_{single}] < 1$ (decrease) or $[Q_{competitive}/Q_{single}] = 1$ (no change). By applying this categorization to the results obtained from the current investigation for both metal ions, it was found that $[Q_{competitive}/Q_{single}]$ was less than 1; therefore, the results clearly indicate that adsorption capacities of Cd^{2+} and Pb^{2+} were suppressed by the presence of the other metal ions in the binary solutions.

3.2.4. Effect of adsorbent dosage

The effect of the produced AC dosage on the removal efficiency of Cd^{2+} and Pb^{2+} from binary synthetic solutions is illustrated in Fig. 5. The result showed that the removal efficiency of both metal ions increased gradually by increasing the dosage of the produced AC until specific value, after which insignificant effect was noticed. This can be attributed to the fact that by increasing the adsorbent dosage, the surface area, as well as adsorption sites, will increase, which will result in enhancing the removal efficiency of the metal ions. However, further increases in the dosage of the produced AC were found to have insignificant effect on the removal efficiency of both metal ions, which could be attributed to the equilibrium established between the residual concentration of metal ions in the solution and surface metal ions concentration [32]. On the other hand, the increase in the AC dosage was found to result in decreasing the adsorption capacity of both metal ions, where adsorption capacity was found to decrease from 19.65 to 10 mg/g and from 61 to 12 mg/g when AC dosages were increased from 25 to 400 mg, for Cd^{2+} and Pb^{2+} , respectively. For constant metal concentration, the results showed that at lower adsorbent dosages, all adsorption sites were found to become saturated; therefore, the adsorbed metal ion per gram of the AC was found to be relatively high. However, with increasing the AC dosage, the unsaturated adsorption sites were found to increase, thereby the adsorbed metal ion per gram of the AC decreased [33]. Moreover, the decrease of adsorption capacity could be attributed to the overlapping of the adsorption sites as a result of overcrowding of the AC particles [17]. Kumar and Gayathri [34], who investigated the

removal of Pb^{2+} by bael tree leaf powder, reported findings that are similar to those obtained from the current study. Furthermore, the results showed that strong competition between Cd^{2+} and Pb^{2+} for the produced AC sites takes place and since Pb^{2+} possesses higher electronegativity and ionic radius and lower hydrated ionic radius as explained before, large number of the AC adsorption sites were occupied by Pb^{2+} ions.

3.2.5. Adsorption equilibrium isotherms for Cd^{2+} and Pb^{2+} in competitive adsorption

The experimental data obtained from the current investigation was fitted to non-linear Langmuir and Freundlich adsorption isotherms using Eqs. (1) and (2), respectively. On the other hand, Eqs. (3) and (4) were employed to determine the models parameters, from which the relationship between concentrations of metal ions in solid phase (q_e) and liquid phase (C_e) was plotted at different initial concentrations of Cd^{2+} in presence of different concentrations of Pb^{2+} and vice versa.

$$q_e = \frac{K_L \times C_e}{1 + a_1 \times C_e} \tag{1}$$

$$q_e = K_f \times C_e^{\frac{1}{n}} \tag{2}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_1}{K_L} \times C_e \tag{3}$$

$$\log q = \log K + \frac{1}{n} \log C \tag{4}$$

Langmuir and Freundlich isotherms of Cd^{2+} adsorptions are shown in Figs. 6 and 7, respectively, while the parameters of both models are presented in Table 3. For Cd^{2+} ion, the correlation coefficients of both isotherms indicated that good fitting was obtained; however, Freundlich isotherm was fitted better with increasing the concentration of Pb^{2+} . The results also showed that the affinity factor for Langmuir isotherms (a_1) decreased with increasing the concentration of Pb^{2+} indicating that strong competition between both metal ions takes place for active adsorption sites. This is in consistence with the decrease in adsorption intensity factor of Freundlich isotherm (K_f) as concentrations of Pb^{2+} were increased. Mohan and Singh [31] and Mohan et al. [19], who studied the adsorption of Cd^{2+} from competitive solution onto Kraft lignin and AC produced from bagasse, respectively, reported similar findings of the current investigation. The results also revealed that, in Freundlich isotherm, values of n as shown in the Table 3 are between 2 and 10 indicate good adsorption characteristics. According to Aksu and Kutsal [35] who studied the removal of Pb^{2+} from wastewater, the adsorption characteristics based on values of n were classified into three categories: good for n values from 2 to 10, relatively good for n values between 1 and 2 and poor for n values of less than 1. Essential properties of the Langmuir model were determined by calculating the dimensionless separation factor R_L to define the favorability of adsorption as reported by Hall et al. [36]. The values of R_L in Table 3 were calculated using Eq. (5):

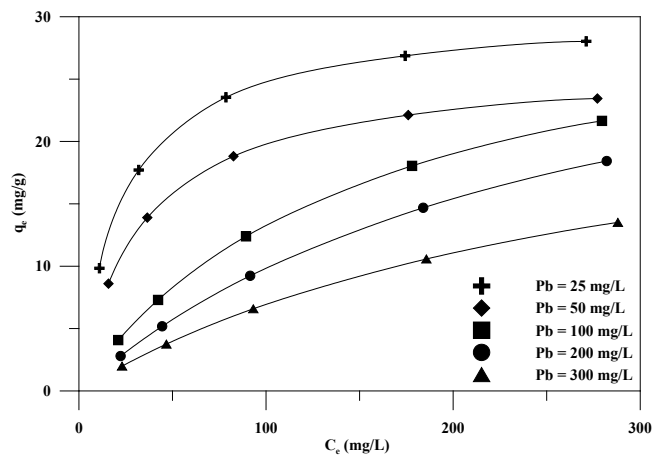


Fig. 6. Langmuir isotherm model of Cd^{2+} in competitive adsorption.

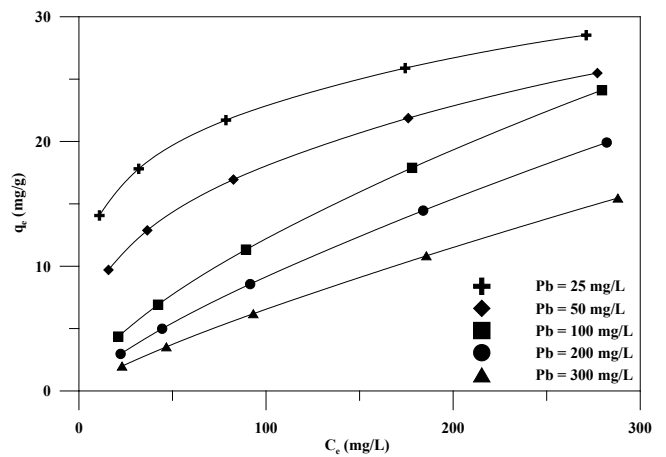


Fig. 7. Freundlich isotherm model of Cd^{2+} in competitive adsorption.

$$R_L = \frac{1}{1 + a_1 \times C_0} \tag{5}$$

where C_0 is the initial concentration, and a_1 is the Langmuir constant. The adsorption feasibility of Langmuir model depends on the value of R_L , according to the following categories: $R_L > 1$ means unfavorable; $R_L = 1$ means linear; $0 < R_L < 1$ means favorable and $R_L = 0$ means irreversible. The results revealed that the values of R_L are between 0.0 and 1.0, as shown in Table 3, which indicate that the adsorption is favorable. Similarly, the experimental results of Pb^{2+} adsorption in the presence of different concentrations of Cd^{2+} showed that correlation coefficients of both isotherms indicated good fits; however, Freundlich isotherm was found to have better fit with the increase in Cd^{2+} concentration. The results also showed that the affinity factor for Langmuir isotherms (a_1) decreased with increasing the concentration of Cd^{2+} , which indicates that there is a strong competition between metal ions for active adsorption sites. These results are in consistence with the decrease in adsorption intensity

Table 3
Parameters of Langmuir and Freundlich for Cd(II) and Pb(II) adsorption by AC

| Metal | | Isotherm | Parameters | | | | | Isotherm | Parameters | | |
|------------------|------------------|----------|----------------|----------------|----------------|----------------|----------------|------------|----------------|-------|----------------|
| Cd ²⁺ | Pb ²⁺ | model | R ² | K ₁ | a ₁ | Q ₀ | R _L | model | R ² | n | K _f |
| 25 | 25 | Langmuir | 0.992 | 1.328 | 0.044 | 30.40 | 0.124 | Freundlich | 0.998 | 4.539 | 8.302 |
| 50 | 50 | | 0.991 | 0.810 | 0.031 | 26.18 | 0.166 | | 0.960 | 2.967 | 3.827 |
| 100 | 100 | | 0.888 | 0.221 | 0.007 | 33.33 | 0.482 | | 0.954 | 1.512 | 0.581 |
| 200 | 200 | | 0.941 | 0.137 | 0.004 | 35.34 | 0.615 | | 0.984 | 1.334 | 0.290 |
| 300 | 300 | | 0.669 | 0.093 | 0.003 | 27.17 | 0.642 | | 0.946 | 1.233 | 0.156 |
| Pb ²⁺ | Cd ²⁺ | Langmuir | R ² | K ₁ | a ₁ | Q ₀ | R _L | Freundlich | R ² | n | K _f |
| 25 | 25 | | 0.978 | 7.257 | 0.083 | 87.72 | 0.0695 | | 0.972 | 4.029 | 23.17 |
| 50 | 50 | | 0.980 | 5.534 | 0.064 | 86.21 | 0.0875 | | 0.985 | 3.730 | 19.85 |
| 100 | 100 | | 0.976 | 3.899 | 0.046 | 84.03 | 0.1174 | | 0.991 | 3.273 | 15.37 |
| 200 | 200 | | 0.966 | 2.420 | 0.028 | 86.21 | 0.1793 | | 0.997 | 2.701 | 10.31 |
| 300 | 300 | | 0.978 | 1.744 | 0.020 | 85.47 | 0.2322 | | 0.977 | 2.219 | 6.50 |

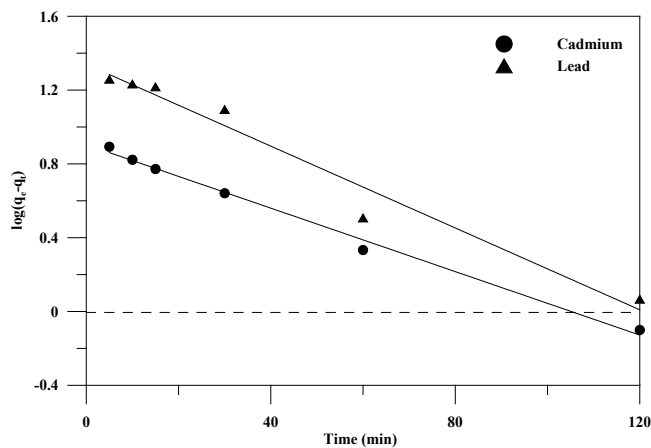


Fig. 8. Pseudo-first-order kinetic model of Cd²⁺ and Pb²⁺ in competitive adsorption.

factor of Freundlich isotherm (K_f) as Cd²⁺ concentration was increased. Similar findings were reported by Li et al. [30] and Depci et al. [18], who investigated the adsorption of Pb²⁺ from competitive solution onto *Phanerochaete chrysosporium* and AC produced from van apple pulp, respectively. It was also observed that, similar to Cd²⁺, the values of R_L are between 0 and 1, which indicate favorable adsorption.

3.2.6. Adsorption kinetic models for Cd²⁺ and Pb²⁺ in competitive adsorption

Pseudo-first-order and pseudo-second-order models were fitted to the experimental data of Cd²⁺ adsorption in competitive solution using Eqs. (6) and (7), respectively:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} \times t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (7)$$

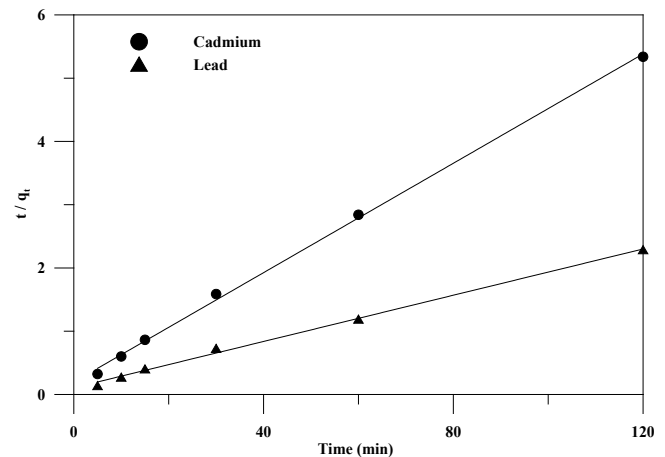


Fig. 9. Pseudo-second-order kinetic model of Cd²⁺ and Pb²⁺ in competitive adsorption.

where q_e is the equilibrium adsorption capacity (mg/g); q_t (mg/g) is the adsorption capacity at time t (min); K_1 (1/min) is the pseudo-first-order constant rate and K_2 (g/mg min) is the pseudo-second-order constant rate. Pseudo-first-order and pseudo-second-order models for both metal ions are shown in Figs. 8 and 9, respectively. The parameters of each model were computed from the slope and intercept of the graph, which are presented in Table 4. The results indicated that, although the adsorption of Cd²⁺ was fitted to the first-order kinetic model with $R^2 = 0.993$, however, theoretical q_e (8.02 mg/g) was not in good agreement with the experimental value (23.2 mg/g). This could be attributed to the fact that the pseudo-first-order model is suitable for describing data measured close to equilibrium only [37]. On the other hand, the pseudo-second-order model was found to be better fitted with higher correlation coefficient $R^2 = 0.998$. Moreover, the theoretical q_e of this model (23.74 mg/g) is in perfect agreement with the experimental q_e value as shown in Table 4. Therefore, the adsorption of Cd²⁺ from competitive solution follows pseudo-second-order model, which suggests chemical adsorption

Table 4
Parameters of both models for Cd²⁺ and Pb²⁺

| Metal ions | Pseudo-first-order | | | Pseudo-second-order | | | q_e (experiment) |
|------------------|--------------------|--------|---------------|---------------------|---------|---------------|-----------------------|
| | R^2 | K_1 | q_e (model) | R^2 | K_2 | q_e (model) | |
| Cd ²⁺ | 0.9932 | 0.0198 | 8.02 | 0.9987 | 0.00758 | 23.74 | 23.2 |
| Pb ²⁺ | 0.9662 | 0.0255 | 21.868 | 0.997 | 0.0025 | 55.98 | 53.6 |

including electrons exchange between the produced AC and Cd²⁺ ions. Taty-Costodes et al. [26] and Mohan et al. [19], who investigated the removal of Cd²⁺ from competitive solutions onto sawdust and Kraft lignin, respectively, reported results that are similar those obtained from the current investigation. Similarly, the experimental data of Pb²⁺ adsorption in competitive solution was also fitted to the pseudo-first-order and pseudo-second-order models, and the parameters of both models are presented in Table 4. The results revealed that, similar to Cd²⁺, the pseudo-second-order model was having better fit ($R^2 = 0.997$) when compared with pseudo-first-order ($R^2 = 0.966$). In addition, the theoretical adsorption capacity of this model is in perfect agreement with the experimental value as shown in Table 4. Therefore, the adsorption of Pb²⁺ from competitive solution follows pseudo-second-order model. Bohli et al. [29] and Depci et al. [18], who investigated the adsorption of Pb²⁺ from competitive solution using AC produced from olive stone and van apple pulp, respectively, reported similar results of the current study.

4. Conclusions

MOSW, which was collected randomly, was utilized in the production of AC that was used in the adsorption of heavy metals from synthetic wastewater. Competitive adsorption of cadmium (Cd²⁺) and lead (Pb²⁺) from binary metal solutions was employed, where the effect of operational parameters such as pH, contact time, initial metal concentration and adsorbent dosage on the performance of the adsorption process was studied. The results clearly indicated that when pH values were increased, the removal efficiency of both metals was also increased. This could be attributed to the strong competition between hydrogen and metal ions for active sites present on the surface of the produced AC. Moreover, the results showed that the increase in the initial concentration of metals resulted in an increase in the adsorption capacity and decrease in the removal efficiency of both metal ions, which was attributed to the limited number of active adsorption sites. Furthermore, competition between metal ions for active adsorption sites was clearly depicted, which was attributed to properties of metal ions such as electronegativity, ionic radius, and hydrated ionic radius. Increasing the adsorbent dosage was found to result in increasing the surface area as well as adsorption sites that resulted in enhancing the removal efficiency of the metal ions. The experimental results were fitted to non-linear Langmuir and Freundlich adsorption isotherms models, and models parameters were determined. The results clearly indicated that non-linear Freundlich isotherm model produced better fit than Langmuir model, while the decrease in the factor of Langmuir isotherm (a_1) with the increase in concentration of metal ions was a clear evidence of

competition between Cd²⁺ and Pb²⁺ ions for active adsorption sites. Moreover, pseudo-first-order and pseudo-second-order models were fitted to the experimental data of Cd²⁺ and Pb²⁺ adsorption in binary solutions. For both metal ions, the results showed that the pseudo-second-order model was found to be better fitted with higher correlation coefficient and the theoretical q_e values of this model were in perfect agreement with the experimental q_e values.

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