



Removal of Cadmium (II) and Lead (II) Ions from Aqueous Solution by Zeolite A4 Supported on Natural Carbon

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ABSTRACT

The performance of the successfully prepared zeolite A4 grown over carbonized palm fronds in the removal of cadmium (II) and lead (II) ions from liquid solution was studied. Different parameters which strongly affect the removal process were investigated such as dose of media, ion initial concentration, pH and temperature of solution. Where the uptake of ion obviously increases with increasing the dose and temperature, however pH is directly affect the structure of media and consequently the ion uptake.

Key words: Zeolite A4; Palm Fronds Carbon; Cadmium (II); Lead (II)

1. INTRODUCTION

Over past few decades, heavy metal uses have been greatly increased, because of their vital presence in many important industries, such as mining, batteries, tanning, pigments, fertilizer and other main industries. Thus, large quantities of waste water contaminated with heavy metals have been discharged directly to the aquatic environment without a sufficient treatment and causes a worldwide environmental problem (Namasivayam and Ranganathan, 1995, and Ajmal, et al., 2003). Therefore, removal of the hazardous heavy metals from the effluents polluted with them has become a great issue and studied widely in the recent years (Taty-Costodes, et al., 2003). The presence of those metals such as Cu, Zn, Ni, Cd, Sb, Cr, Pb, Mn, Hg, etc in the aquatic life is a special issue because they are non-degradable, persistent, toxic and may lead to various and severe diseases (Han, et al., 2004).

Cadmium and lead have different applications in many industries even they are unnecessary metal for human consumption. High concentrations of both cadmium and lead are carcinogenic and highly toxic metals which can lead to numerous diseases and disorders such as, destruction of testicular tissue and red blood cells, kidney damage, high blood pressure, anaemia, reproductive system damage, nervous disorders and sickness even death (Namasivayam and Ranganathan, 1995, Tunali, et al., 2006, and Gupta, et al., 2001). Discharging cadmium and lead to the water body would be dangerous to the aquatic environment and causes many harmful effects when their concentrations exceed the acceptable limit (Singh, et al., 1998, Ahmed, 1998, and Tunali et al., 2006).

Over the years, many methods have been developed to remove cadmium and the other heavy metals from wastewater such as, chemical precipitation, electro floatation, ion-exchange, adsorption, and reverse osmosis (Ajmal, et al., 2003, and Taty-Costodes, et al., 2003). Ion-exchange is efficient even in very low concentration of contaminants and not cost effective when low cost and abundant ion-exchangers are used for removal issue. In case of using of zeolites as an ion-exchanger, it can be

used as adsorbent in the same time due to its outstanding properties.

Zeolites are an inorganic crystalline micro porous minerals (pore diameter < 2 nm) having widespread application such as heterogeneous catalysis, ion-exchange, adsorption and separation process in the refinery, petrochemical, electrochemistry, food industries and pharmaceutical and medical engineering (El-Naggar et al., 2008, and Shams and Mirmohammadi, 2007). Zeolites as eco-friendly solids have been used either purely or embedded of composites because of their properties of abundance of easy-exchange cations present in their three dimensional porous structure, acidity, unique topology, high structure stability, large surface area, and uniform pore size (Melo, et al., 2012 and Tan, et al., 2007). However, zeolite's small pore size has been the main drawback on the zeolite application in the packed bed application such as treatment of organic waste and refining of the crude oil. Since, this drawback comes from mass transfer and diffusion problems of the bulky molecules between the bulk solution and zeolite's pores through a narrow channel system of zeolite, consequently, that all leads to dead zones and useless active sites and high pressure drop throughout the column or reactor system (Tan, et al., 2007, and Xue et al., 2012).

Many attempts have been put to improve the diffusivity of large molecules within micro porous zeolite, such as, using of binders and formulating in different forms of pellet. Although this tactic obviously minimize the pressure drop problem, but in the same time it adds another drawbacks; which are blocking of active sites during blending, aggregation and pelletizing, and dilution of the active sites in considering that most of binding materials used are no active materials (Saini, et al., 2011). Other ways to cope with the pressure drop problem and improve the accessibility of the zeolites pore system have been adopted, including, reducing zeolite crystal size, enlarge zeolites pores, carbon-templated synthesis, desilication and dealumination (Groen, et al., 2006, Tao, et al., 2004, and Jacobsen, et al., 2000). The reduction of the zeolite particles size enhances the zeolite performance because of the short reaction path which accelerates the reaction rate and prolongs catalyst life (Xue et al., 2012, and Ok, et al., 2007).

Nevertheless, it is not easy to produce nanosized crystals of zeolite in addition to the difficulties which obstruct the filtration process during the preparation (Tao, et al., 2004, and Tao, et al., 2003). Developing a mesoporous structured zeolite has been synthesized and adopted by many researchers (Tao, et al., 2004, Jacobsen, et al., 2000, Tao, et al., 2003, Zhou, et al., 2011, Shetti, et al., 2008, and Srivastava, et al., 2006), however no longer dependent because of the low mechanical strength of the pore's wall resulted in the mesoporous structured zeolite. Another well promising approach is incorporating one or two additional porosity levels (meso or/and macroporosity) to the original microporous zeolite structure. While the micropores in zeolite provide active sites and the selectivity, meso/macropores provide easy accessibility to the micropores. In the same time, this approach provides a complete usage of all zeolite present in a specific amount of composite especially if it is applied on a suitable meso/macroporous substrate (Mintova and Valtchev, 1996). Natural wastes and organic residuals of industries are the best examples of such cheap and abundant supports; however, the porosity is the most important property they should have.

In the present study, the conditions which influence the removal of Cd (II) and Pb (II) ions were investigated and modelled using Langmuir and Freundlich models. Moreover, this work revealed a new method for preparing a new kind of composite made of an effective zeolite and palm fronds which is a cheap natural waste in Iraq.

2. EXPERIMENTAL WORK

2.1. Materials

Cadmium nitrate (99% purchased from Sigma-Aldrich) and lead nitrate (99% purchased from Sigma-Aldrich) were used to prepare cadmium and lead solutions respectively. Sodium hydroxide (98% purchased from Sigma-Aldrich) and sulphuric acid (98% purchased from Sigma-Aldrich) were used to adjust the cadmium solutions pH to ~ 4 and ~ 8.3 respectively. While for the preparation of composite zeolite A4 supported on carbonized palm fronds, sodium aluminate (purchased from Sigma-Aldrich) was used as an alumina source and sodium metasilicate (purchased from Fisher) was used as a silica source. Palm fronds were provided from a local field in Baghdad. They are of very low cost, harmless and abundant wastes in Iraq. The use of this high carbon content source results in a high porous support material. The yield of the produced carbon from the palm fronds was about 18%.

2.2. Preparation of the zeolite and composite

Zeolite A4 with a gel composition $3.8\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 1.95\text{SiO}_2 : 200\text{H}_2\text{O}$ was prepared under a hydrothermal treatment conducted at ~ 95°C for 5 h in a stainless steel autoclave. Where, 0.64 g of NaOH were added to 40 g of deionized water and mixed till completely dissolved. Then, 3.31 g of sodium aluminate were added to NaOH solution with continuous mixing to obtain a clear solution. After that, 9.4 g of sodium metasilicate were added to the produced composition till a creamy colour gel was obtained. These over mentioned procedures were used to prepare both pure zeolite A4 and the gel composition required to prepare the composite. The

preparation of carbon support required for composite zeolite started with washing and drying of palm fronds. After that the dried fronds were carbonized in a tubular furnace in the presence of nitrogen gas at 800°C for 2 h and crushed manually to particle sizes ranging from 50 to 250 μm to obtain a carbon substrate. Then the carbon was impregnated with 2% wt zeolite A4 suspension in deionized water under vacuum pressure and dried at 100°C to be used for preparation of composite. Finally, a weight of carbon was added to the final gel composition in the weight ratio 1:1 i.e. the weight of carbon used here was equal to the weight of pure zeolite produced from this batch. The produced zeolite and composite were washed with deionized water to $\text{pH} \geq 8$ and dried for using in the adsorption process.

2.3. Experimental procedure for the removal of cadmium and lead ions

Adsorption process was conducted in a volumetric flasks furnished with a shaker for mixing at room temperature ~ 20 °C. 100 ml of both Cd and Pb solution was mixed with 0.2, 0.4 and 0.6 g of composite zeolite A4 on carbon to study the effect of media weight on the removal of ions, and 0.2 g of the composite was mixed with 100 ml of 100, 300, 500 ppm to study the effect of ion concentration on the ion uptake. The effect of pH solution was studied for $\text{pH} \sim 4$ and ~ 8.3 for 0.2 g media and 100 ml of 200 ppm solution. The samples of solution were taken at time intervals 1, 2, 3 and 4 h. The samples were filtrated before dilution with deionized water and then analysed by atomic absorption (AA320N Atomic Absorption Spectrophotometer-Angstrom Advanced Incorporation).

One more experiment to study the competitive adsorption of Cd and Pb ions was carried out by using 0.2 g of composite for 100 ml of 100 ppm of each metal. Moreover, two experiments to compare the removal performance of the composite zeolite A4 with a pure zeolite A4 were carried out using 0.2 g of pure zeolite A4 for 100 ml of 100 ppm Cd (II) and 100 ml of 100 ppm Pb (II).

2.4. Analysis

The crystallinity of the zeolite was found by X-ray diffraction (XRD) analyses using Shimadzu 6000 x-ray Diffractometer. Zeolite pattern in XRD was found at a scanning rate 1.5 (2 θ /min), 0.03 step, 30 kV and 15 A. The composite was found by scanning electron microscopy (SEM) imaging using VEGA3 SBU – EasyProbe Scanning Electron Microscope.

3. ADSORPTION ISOTHERM STUDY

The equilibrium data for the adsorption of Cd^{2+} ions and Pb^{2+} ions at different initial ions concentration were fitted in both the nonlinear Langmuir isotherm represented in equation 1 and Freundlich isotherm represented in the equation 2.

$$q_e = \frac{b \cdot k_l C_e}{1 + b C_e} \quad (1)$$

Where: q_e is amount of ions adsorbed at equilibrium, b , k_1 are Langmuir constants and C_e is equilibrium concentration of ions.

$$q_e = a. (C_e)^{1/n} \quad (2)$$

Where, a and n are Freundlich constants.

In the present study, Langmuir and Freundlich constants were calculated using solver program present in the Microsoft Excel.

4. RESULTS AND DISCUSSION

In this study, a cheap composite zeolite A4/palm fronds carbon was successfully prepared by a hydrothermal treatment. XRD analyses shown in

Figure 1 confirmed that only pure zeolite A4 grew over the carbon surface with high crystallinity degree as represented by the cubic crystals shown in the SEM images shown in **Error! Reference source not found.** **Error! Reference source not found.** showed the elements composition of the produced zeolite as obtained from atomic absorption for the digestive sample by a concentrated HNO_3 .

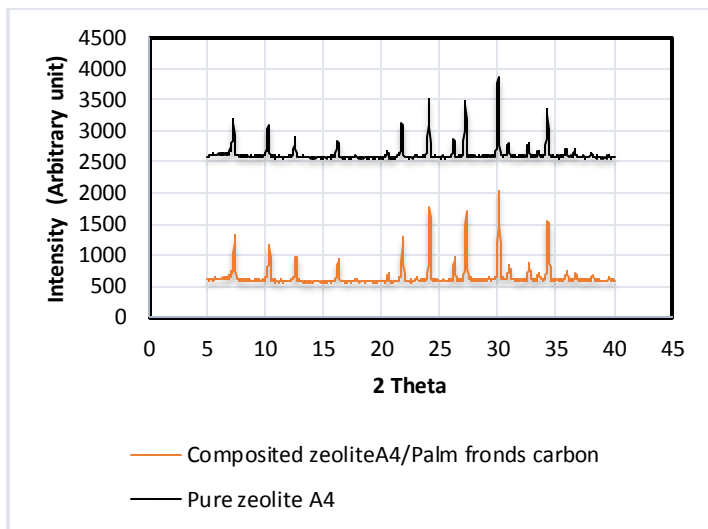


Figure 1: X-Ray Diffraction of Pure And Composite Zeolite A4.

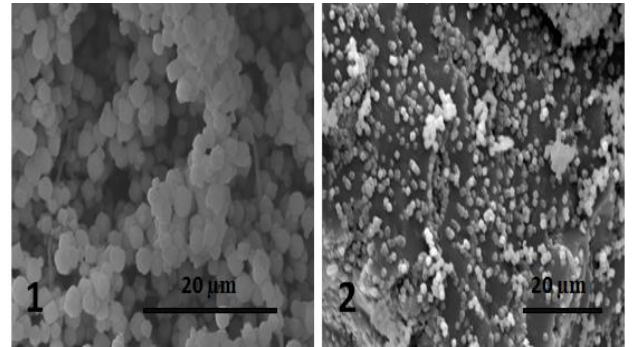


Figure 2: SEM Images, (1) Pure Zeolite A4 and (2) Composite Zeolite A4/Carbon

Table 1: The elements composition of the composite zeolite A4/carbon

Elements	Weight%
Al	12.984
Si	13.565
Na	07.846
O	38.638
C	26.967

All adsorption isotherm results were displayed by plotting of the concentration of metal ions remaining in solution (ppm) and the weight of adsorbed metal ions per a weight of the adsorbent q (mg metal ions/g adsorbent) versus time (h).

$$q = (C_0 - C_t) * \frac{v}{w_t} \quad (3)$$

Where, C_0 is the initial concentration of metal ions, C_t is the concentration of the remaining metal ions in the solution at time equal t , v is the volume of batch and w is the weight of media used.

As it can be seen in the adsorption results that all adsorption experiments reached the equilibrium after 2 h, since there were no obvious change can be observed after that interval. The results in **Error! Reference source not found.** and **Error! Reference source not found.** showed the zeolite A4/carbon composite efficiency in the removal of Cd (II) and Pb (II) ions at different composite doses. Since, the uptake of those two heavy metals increased significantly by increasing the composite dose. However, there is no significant difference in the behaviour of the two ions.

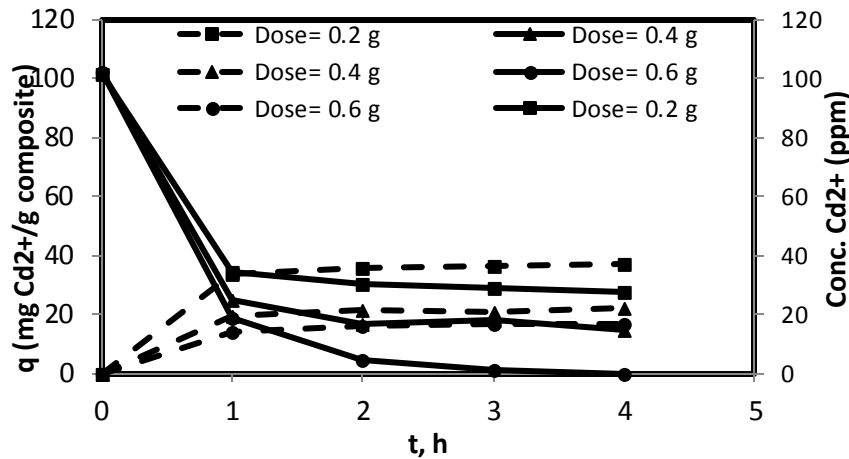


Figure 3: Effect of composite zeolite A4/ carbon dose on the uptake of Cd²⁺ ions (Cd²⁺ concentration = 100 ppm)

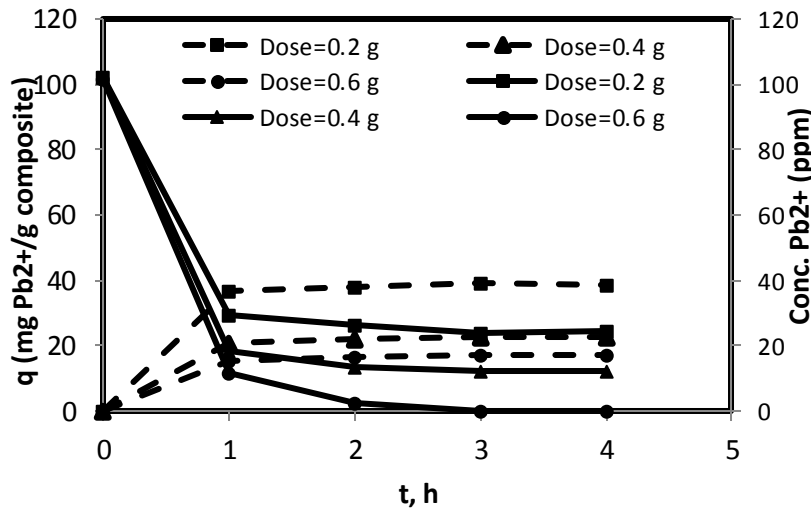


Figure 4: Effect of composite zeolite A4/ carbon dose on the uptake of Pb²⁺ ions (Pb²⁺ concentration = 100 ppm)

The results of the effect of ions concentration were shown in **Error! Reference source not found.** and **Error! Reference source not found.** Where, the general trend for the Cd (II) and Pb (II) ions, according to the results obtained in this study, was

that the concentration of ions adsorbed by the composite decreased by increasing the initial concentration of those metals indicating increasing the competition of ions on the relatively same number of active sites.

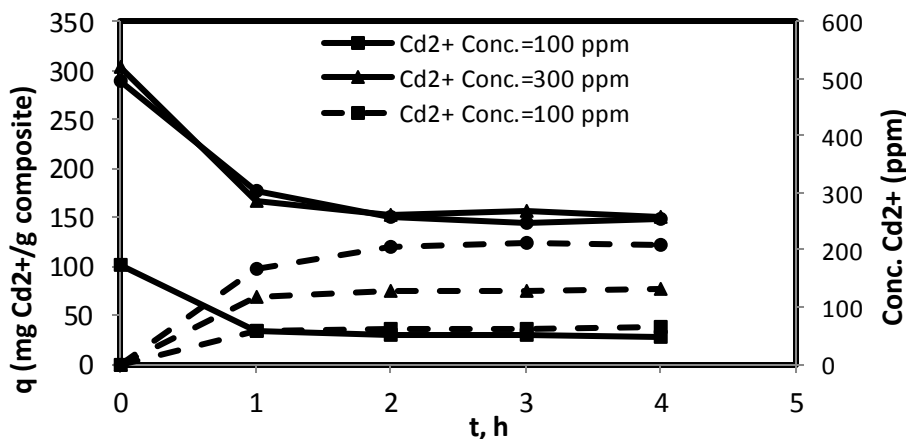


Figure 5: Effect of initial concentration on the uptake of Cd²⁺ ions (composite dose =0.2g).

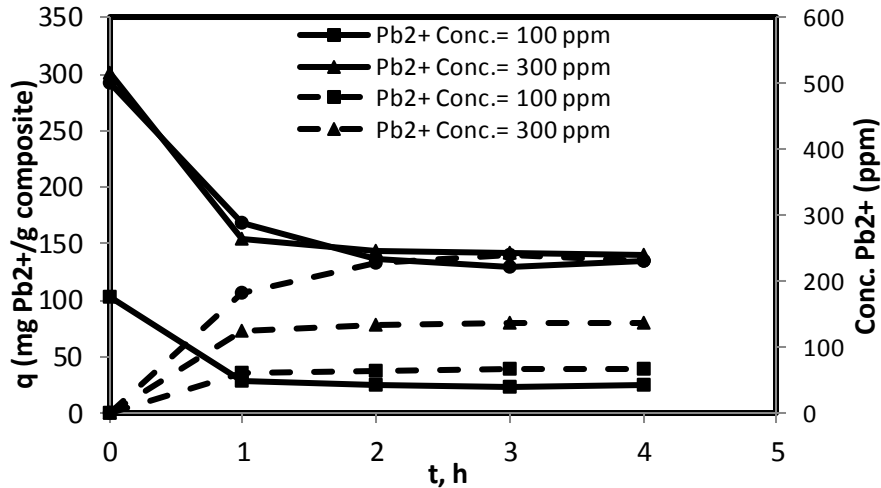


Figure 6: Effect of initial concentration on the uptake of Pb²⁺ ions (composite dose =0.2g)

However, the results showed that the uptake of Pb (II) ions was higher than that of Cd (II) ions, and that was also confirmed by the results obtained from the competitive adsorption experiments (see **Error! Reference source not found.**); indicating that the performance of the composite zeolite for Pb (II) ions is higher than that for Cd (II) ions. Therefore, Pb (II) is the most selectively removed relative to Cd (II). On the other hand, the results present in **Error! Reference source not**

found. and **Error! Reference source not found.** showed high uptake of both Cd (II) and Pb (II) at pH ~ 8.3, while it decreased when the solution pH ~ 4. That because of the hydrolysis of zeolite A4 structure which have Si/Al ~ 1 (low Si/Al ratio) at low pH; however, the low concentration of H⁺ at high pH solutions give chance for more heavy metal ions being adsorbed and removed from solution.

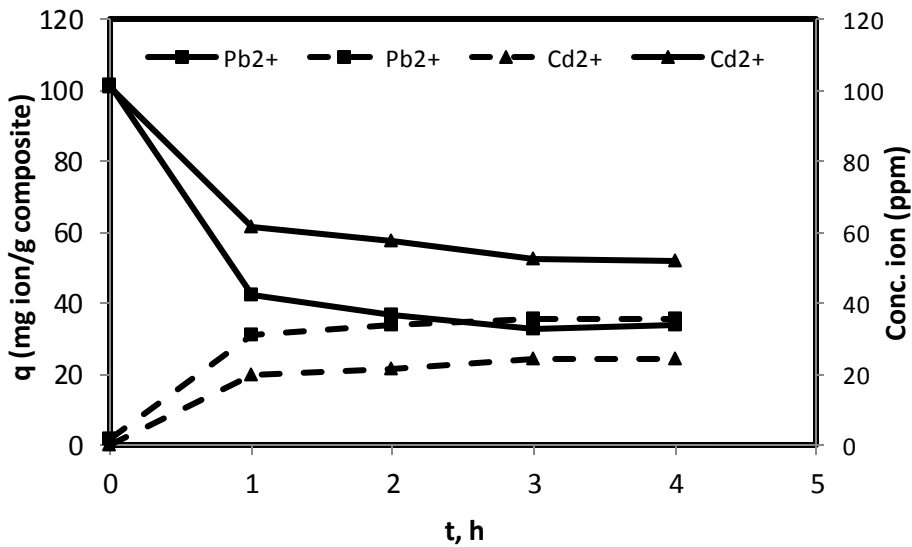


Figure 7: A Competitive Adsorption For A Mixture Of Cd²⁺ And Pb²⁺.

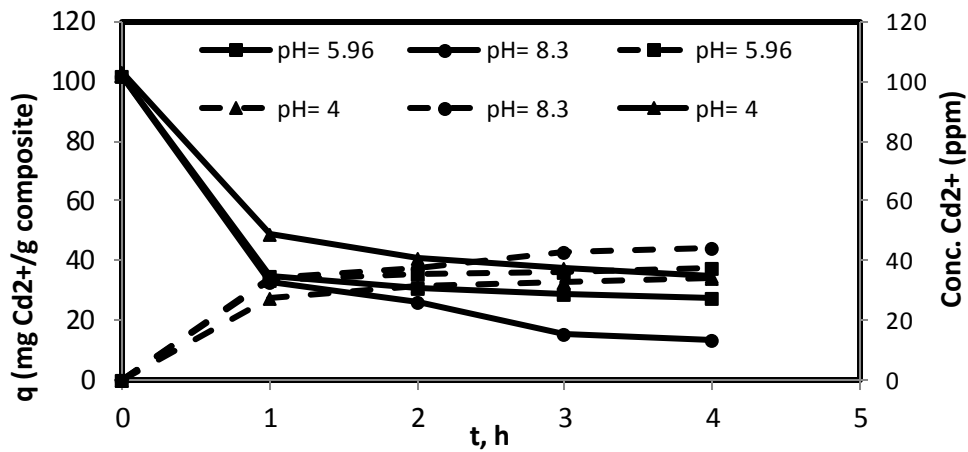


Figure 8: Effect Of Ph Solution On The Uptake Of Cd^{2+} Ions.

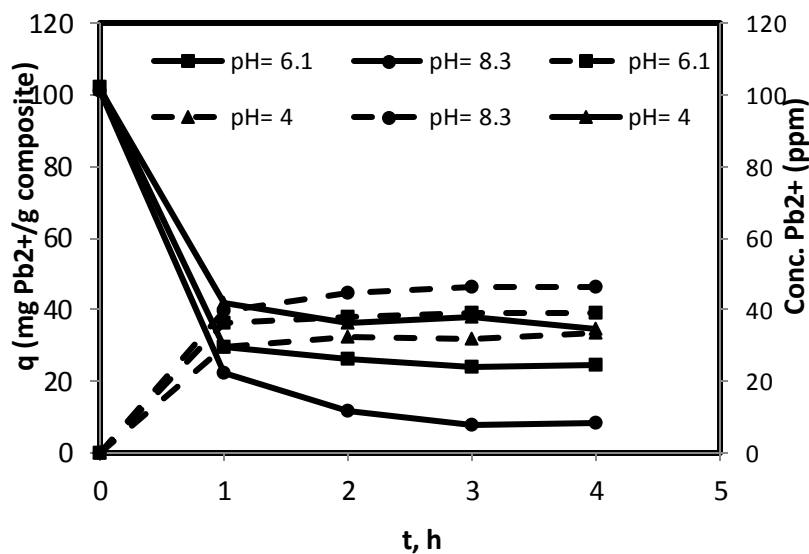


Figure 9: Effect of pH solution on the uptake of Pb^{2+} ions.

A comparison between the removal efficiency of pure zeolite A4 and the composite zeolite A4 was carried out depending on the results shown in the **Error! Reference source not found.** and **Error! Reference source not found.**, since the adsorption

on the composite zeolite A4 significantly closed to that on the pure zeolite A4 although the ratio of zeolite A4: carbon in the composite was 1:1. That indicates a smaller amount of zeolite can be exploited by spreading it over a cheap and available macroporous material to obtain higher performance and reduce waste size in the environment.

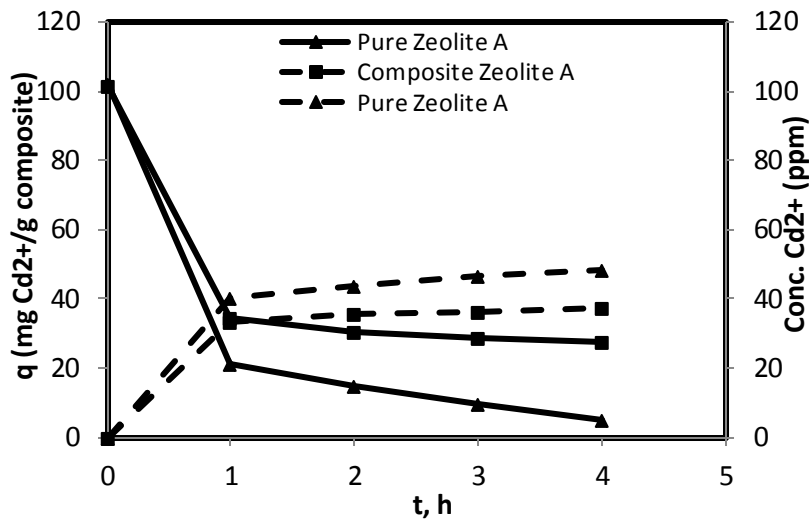


Figure 10: A Comparison Between The Adsorption Of Cd²⁺ On A Pure ZeoliteA4 And Composite Zeolite A4.

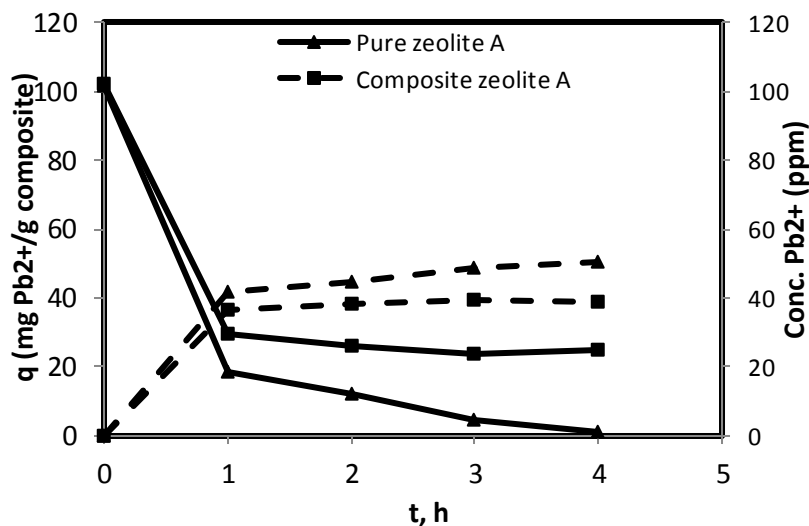


Figure 11: A comparison between the adsorption of Pb²⁺ on a pure zeoliteA4 and composite zeolite A4.

Langmuir and Freundlich constants values are shown in the **Error! Reference source not found.** While both the experimental and theoretical equilibrium isotherms for Cd²⁺ ions and Pb²⁺ ions were shown in the **Error! Reference source not found.** and **Error! Reference source not found.**

respectively. As shown in the figures, the experimental isotherm of the adsorption of both Cd²⁺ and Pb²⁺ fit to the Freundlich isotherm much better than Langmuir isotherm.

Table 2: Langmuir and Freundlich constants for adsorption of Cd²⁺ and Pb²⁺ ions at conditions: composite dose 0.2 g, vol. solution 100 ml, ions concentrations 100, 300 and 500 ppm pH 5.96 and 6.1 respectively.

Ions	b	k ₁	a	n
Cd ²⁺	0.003782	232.942	3.598856	1.600639
Pb ²⁺	0.002302	364.683	4.535139	1.645059

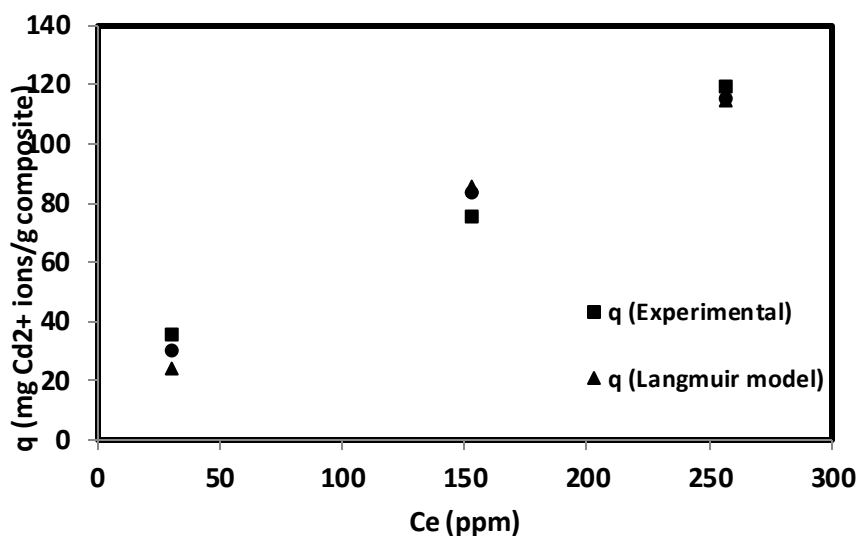


Figure 12: Adsorption isotherm of Cd²⁺ described by Langmuir and Freundlich models.

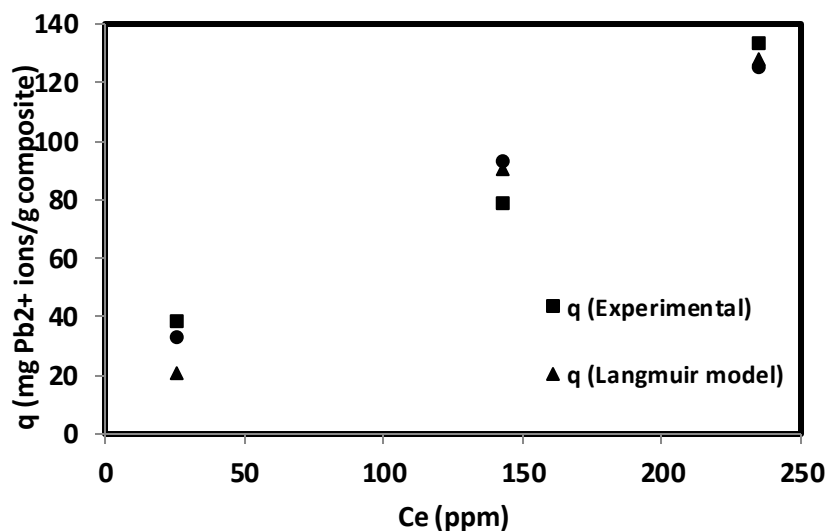


Figure 13: Adsorption Isotherm Of Pb²⁺ Described By Langmuir And Freundlich Models.

5. CONCLUSIONS

In conclusion, an efficient uptake of Cd (II) and Pb (II) ions can be conducted using a new and simple prepared composite made of zeolite A4 over palm fronds carbon. Increasing the dose of the composite zeolite material and pH of ions solution significantly leads to increasing the uptake of Cd (II) and Pb (II), however, increasing the initial concentration of the ions gave a reverse results. In general, Pb (II) ions were more preferable by the pure and composite zeolite than Cd (II).

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