



## Research Article

# Heavy Metals Adsorption on Cyanex-272 Modified Activated Carbon: Efficacy and Selectivity

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**Abstract:** This study investigated the potential use of activated carbon functionalized with Cyanex272 (AC-Cyanex 272), in the removal of lead, copper and zinc cations from aqueous solutions. The modified adsorbent was characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Zeta potential and particle size distribution. Batch adsorption experiments were performed as a function of pH, contact time, and initial metal ion concentration. Adsorption was found dependent on these parameters. The adsorption capacities were very high (126.36, 175.5 and 157.16 mg·g<sup>-1</sup> for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> respectively). Langmuir and Freundlich isotherms were used as models for the equilibrium adsorption data and adsorption kinetic data are best described by the second order model.

**Keywords:** heavy metals; activated carbon; adsorption; Cyanex 272

## 1. Introduction

There is no doubt that water plays an essential role in supporting the development of any country. Thus, the availability of clean water resources is crucial, but unfortunately, many of these resources, are increasingly polluted. Nowadays, industrial activities being hydrometallurgical, electronics or chemical industries are the main contribute to pollution through the direct discharge of heavy metals, such as lead, copper, zinc and nickel ions, in the aquatic environment [1]. The accumulation of heavy metals pollution leads to serious health problems [2]. In order to solve this issue, researchers focused on reducing heavy metals concentration in water.

Various water treatment techniques are used for heavy metals removal, such as adsorption, chemical precipitation, ion exchange and filtration [3–6]. Among these methods, adsorption is considered as one of the most efficient methods since it is simple, rapid, versatile and economic [7]. Moreover, several adsorbents are available such as zeolite [8], biomass [9], activated carbon [10] and polymeric hydrogels [11].

Carbon-based adsorbents are the most important, due to their large surface areas and organized porous structures [12]. Activated carbon, mesoporous carbon and carbon nanotubes are the main carbon adsorbents. Activated carbon is very interesting as an adsorbent due to its unique properties such as its low price, its broad spectrum of effectiveness and its large specific surface [13]. Although activated carbon can act as adsorbents for a wide range of contaminants, research on modifying activated carbon is gaining interest [14]. Several types of modifications are applied, including the carbon functionalization with chelating agents [15]. The latter increases the adsorption capacity of activated carbon. In

previous studies, activated carbon was modified by different functional groups such as amine [16] and thiol [17] in order to enhance their adsorption capacity. On the other hand, Cyanex is an effective chelating agent and activated carbon was not modified by this agent before that's why it was chosen herein to perform adsorption study and test the efficiency of such modified activated carbon in heavy metal ions removal.

In this study, commercial activated carbon was modified by Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid]. This modification method is simple and inexpensive which favors its applicability. Then the adsorption capacities for Pb (II), Cu (II) and Zn (II) were studied in details. The effects of different parameters on the adsorption process were performed, such as contact time, solution pH and metal ions concentration. Pseudo-first and pseudo-second-order kinetic models were used to analyze the adsorption data. The experimental equilibrium results were fitted by Langmuir isotherm. Moreover, the selectivity of the prepared adsorbent was investigated as well.

## 2. Materials and methods

### 2.1 Chemicals

Bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH) and toluene were all purchased from Sigma Aldrich. Lead Nitrate (Pb (NO<sub>3</sub>)<sub>2</sub>; 99.9%) was purchased from UNICHEM, copper nitrate (Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) from Alpha Chemika, and Zinc chloride (ZnCl<sub>2</sub>) from AnlytiCals. All analytical products were used as received, without any purification. Ultrapure water was produced in the laboratory.

### 2.2 Activated carbon modification

Commercially available oak activated carbon (AC) was used. Prior to usage, the carbon was grinded, washed with boiled distilled water and oven-dried at 120 °C for 24 h. Then, 2 g of activated carbon was added to a mixture of 10 ml bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and 10 ml toluene. Then, this mixture was refluxed at 70 °C for 24 hours. After Buchner filtration, the modified activated carbon (AC-Cyx 272) was washed 3 times with 10 ml of toluene, then dried at 100 °C for 2 hours (Figure 1).

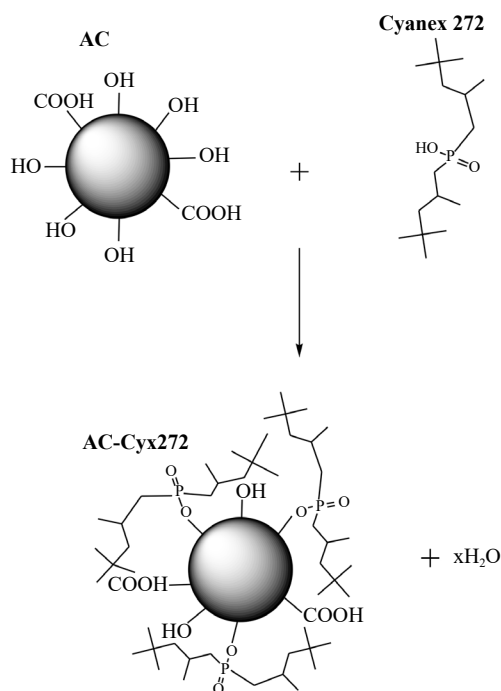


Figure 1. Modification route of the activated carbon by Cyanex 272

### 2.3 Characterization of the activated carbon

The size distribution of AC was determined by granulometry before and after modification using Partica LA-950V2 Horiba. After modification, the functional groups were identified by Fourier Transform Infrared (FTIR) Spectroscopy in the range between 400–4000  $\text{cm}^{-1}$  using FT-IR – 6300 JASCO. Powder X-ray diffraction (XRD) patterns were recorded on an Empyrean X-ray diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation from  $10^\circ$  to  $60^\circ 2\theta$ . The zeta potential of AC-Cyx 272 was measured using a Zeta-Meter System 4.0 unit. The pH was adjusted by using hydrochloric acid (HCl) or sodium hydroxide (NaOH) solution.

### 2.4 Batch adsorption tests

Copper (II), lead (II) and zinc (II) stock solutions (1000  $\text{mg/L}$ ) were prepared, then the solutions of different concentrations were prepared by dilution. In batch adsorption experiments, 50 mg of the modified activated carbon AC-Cyx272 was placed in a beaker containing 20 mL of metal solutions with the desired concentration. The beaker was continuously stirred at room temperature RT at 250 rpm for 120 min. For the kinetic study, the contact time was different for each experiment. All the experiments were carried out by adjusting the pH to 6, using solutions of 0.1 M NaOH and 0.1 M HCl. For obtaining the adsorption isotherms, the initial metal ions concentrations were varied between 10  $\text{mg}\cdot\text{L}^{-1}$  and 500  $\text{mg}\cdot\text{L}^{-1}$ . The electrolyte effect was studied by adding 50 mg of the adsorbents to 20 ml distilled water, 20 ml of 0.2 M NaCl solution and 20 ml of 0.2M KCl solution then the three beakers was continuously stirred at room temperature RT at 250 rpm for 120 min. concerning the regeneration study, 50 mg of the adsorbents were added to 20 ml aqueous lead ions solution and the beaker was continuously stirred at room temperature RT at 250 rpm for 120 min. then the adsorbents were collected on a filter paper, dried and treated with 10 ml of 0.1 HCl solution in order to be used once again for lead adsorption. This step was repeated three times in order to investigate the regeneration possibility of the adsorbent and to determine the efficiency after using it several times. At the end of each experiment (except of regeneration study), the solution was separated from the adsorbent by filtration using a 0.45  $\mu\text{m}$  syringe filter. Once collected, the filtrate was analyzed by atomic absorption spectrophotometer (RAYLEIGH WFX-210), in order to determine the concentration of the metal ions remaining in the solution. The adsorption percentage for each metal ion was calculated using Equation (1):

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$R$  is the adsorption rate (%),  $C_0$  is the initial concentration and  $C_t$  is the concentration at time  $t$ . The adsorption capacity of the adsorbent at equilibrium was calculated by Equation (2):

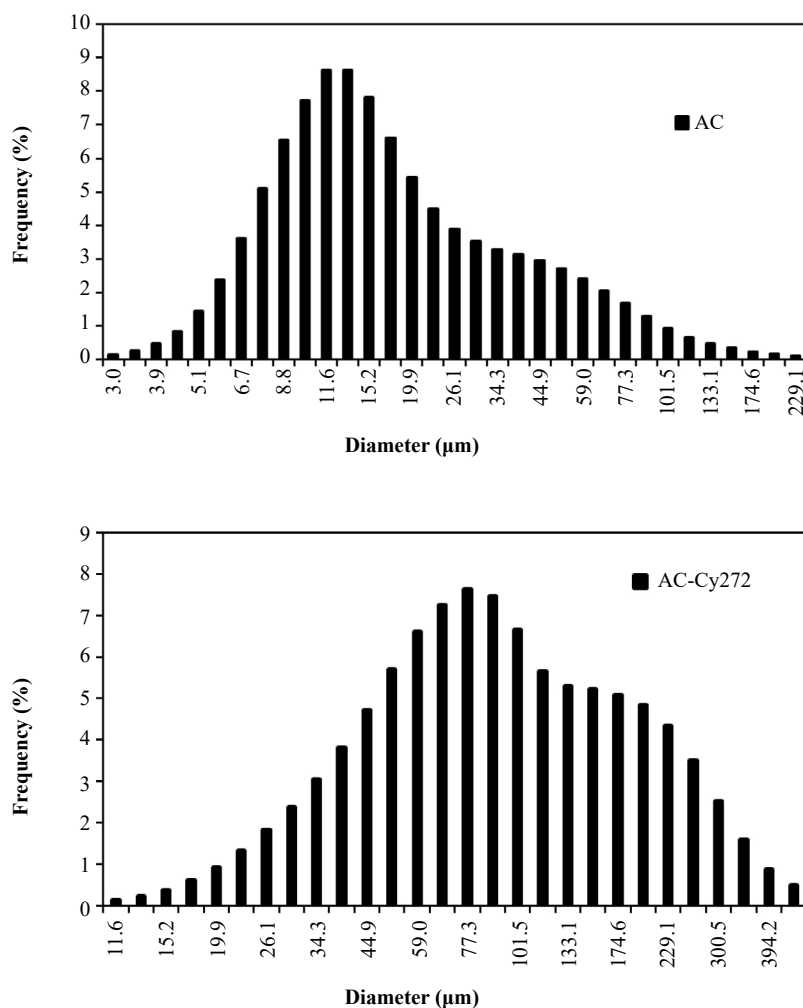
$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

$q_e$  is the adsorption capacity at equilibrium in  $\text{mg}\cdot\text{g}^{-1}$ ,  $C_0$  is the initial concentration and  $C_e$  is the ions concentration at equilibrium,  $V$  is the volume of metal solution in L and  $m$  is the adsorbent mass in g.

## 3. Results

### 3.1 Granulometric analysis

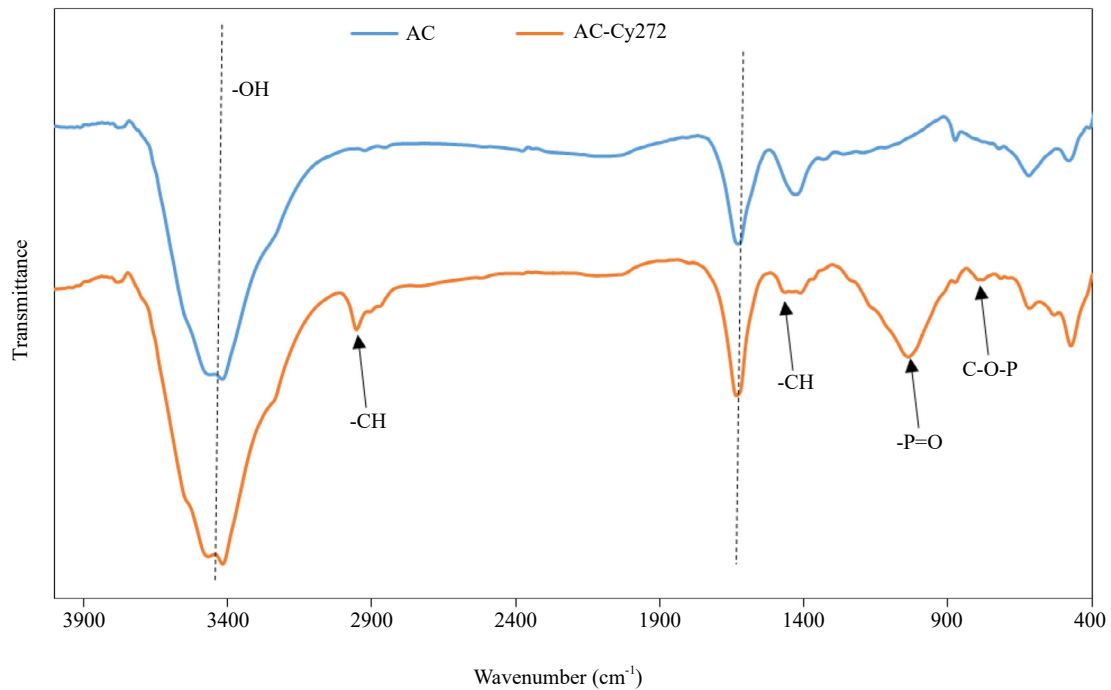
Figure 2 shows the size distribution of the activated carbon samples. The purpose of particle size analysis is to obtain quantitative data on the mean size and particle size distribution. Before modification, the average diameter was 36.7  $\mu\text{m}$ . After modification with Cyanex 272, the average diameter increased to 152.4  $\mu\text{m}$ . These results show the increase of particle size of the activated carbon after modification and this increase is due to the incorporation of Cyanex 272 on the surface of the carbon thus increasing the particle size.



**Figure 2.** The size distribution of the activated carbon samples before (**above**) and after modification (**below**).

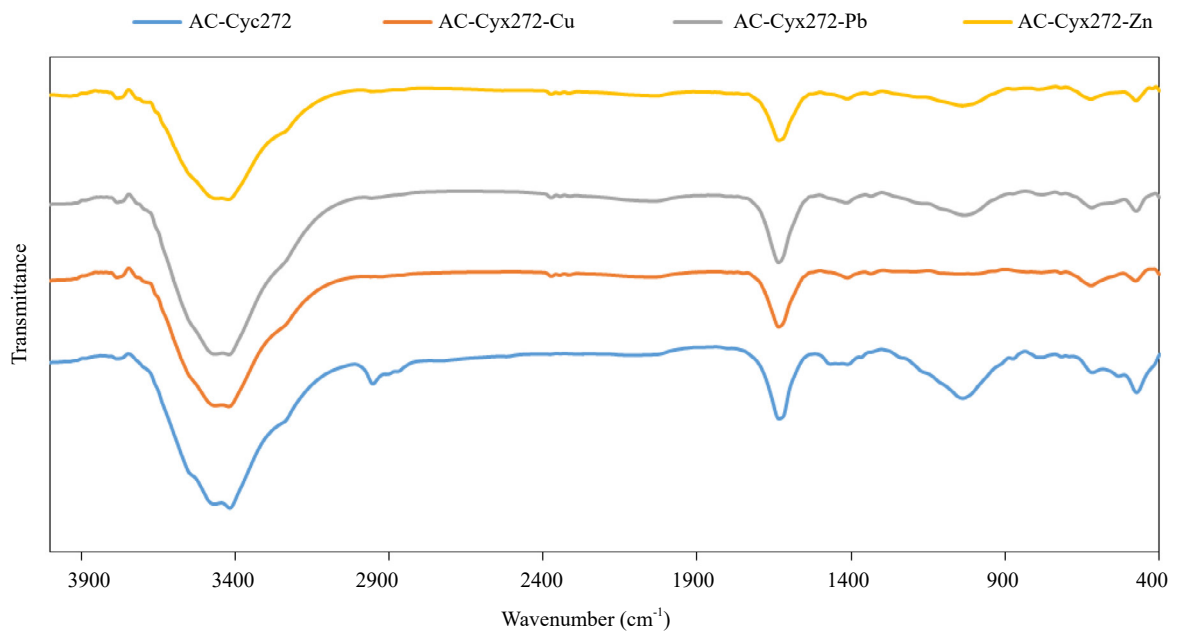
### 3.2 FT-IR spectroscopy

The obtained IR spectra for AC before and after modification are shown in Figure 3. In AC and AC-Cy272 spectra, the broad band in the region  $3300\text{--}3600\text{ cm}^{-1}$  is attributed typically to -OH stretching or adsorbed water molecules and the band at  $1750\text{ cm}^{-1}$  is characteristic to -COOH groups. After modification, the new bands that appeared at  $2954\text{ cm}^{-1}$  can be attributed to -CH stretching of CH<sub>3</sub> contained in the 3-methylamyl group of Cyanex 272, and the two peaks at ( $1477$  and  $1365\text{ cm}^{-1}$ ) are due to the -CH deformation vibration of Cyanex 272. The peak at  $1171\text{ cm}^{-1}$  corresponds to the P=O group of Cyanex 272, the C-O-P stretching bands in AC-Cy272 appeared at ( $960$  and  $818\text{ cm}^{-1}$ ) [15]. This proves that the Cyanex 272 was successfully fixed on AC surface.



**Figure 3.** IR spectra for AC before and after modification with Cyanex 272

After metals adsorption on AC-Cyx272, the peaks at  $1171\text{ cm}^{-1}$  and  $818\text{ cm}^{-1}$  which correspond to P=O group and C-O-P stretching bands of AC-Cyx272 respectively, decreased significantly (Figure 4). Also, the bands at  $2954\text{ cm}^{-1}$ , corresponding to -CH stretching of  $\text{CH}_3$  contained in the 3-methylamyl group of Cyanex 272, disappeared. These findings prove the complexation of metal ions by AC-Cyx 272 through the interaction with phosphinic acid groups.



**Figure 4.** IR spectra of AC-Cyx 272 after heavy metals adsorption

### 3.3 X-Ray Diffraction

The diffractograms of the activated carbon before and after Cyanex 272 modification are shown in Figure 5. The broad band in the range of 20–30° and a narrow peak at  $2\theta = 26^\circ$  were detected due to the amorphous carbon structure, which corresponds to the (111) and (002) planes, respectively. The greatest intensity peak at  $2\theta = 26$  in both diffractograms can be attributed to hexagonal graphite. In addition, it can be seen from the figure 5 that a significant  $\text{SiO}_2$  diffraction peaks also appeared at  $2\theta = 21, 36$  and  $50^\circ$ , corresponding to (100), (110) and (112) planes, respectively. The presence of silicon oxide hydrate and quartz was responsible for the nature source of activated carbon itself which is manufactured from agricultural wastes. After modification all the peaks existed but with decreased intensity which means that activated carbon was successfully modified with Cyanex 272 without affecting the carbon structure since it has stable structural properties.

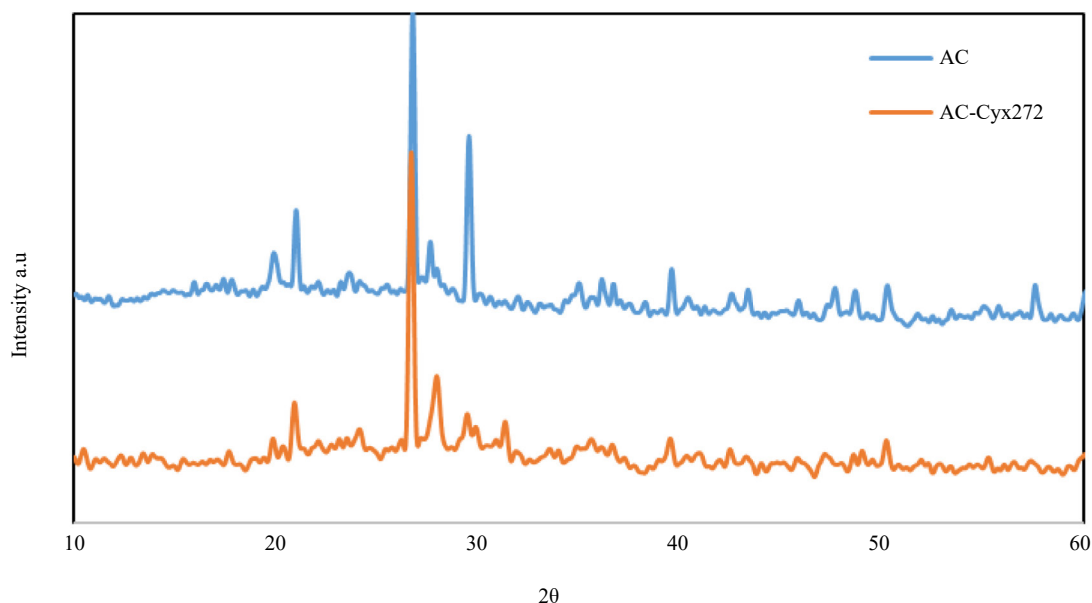
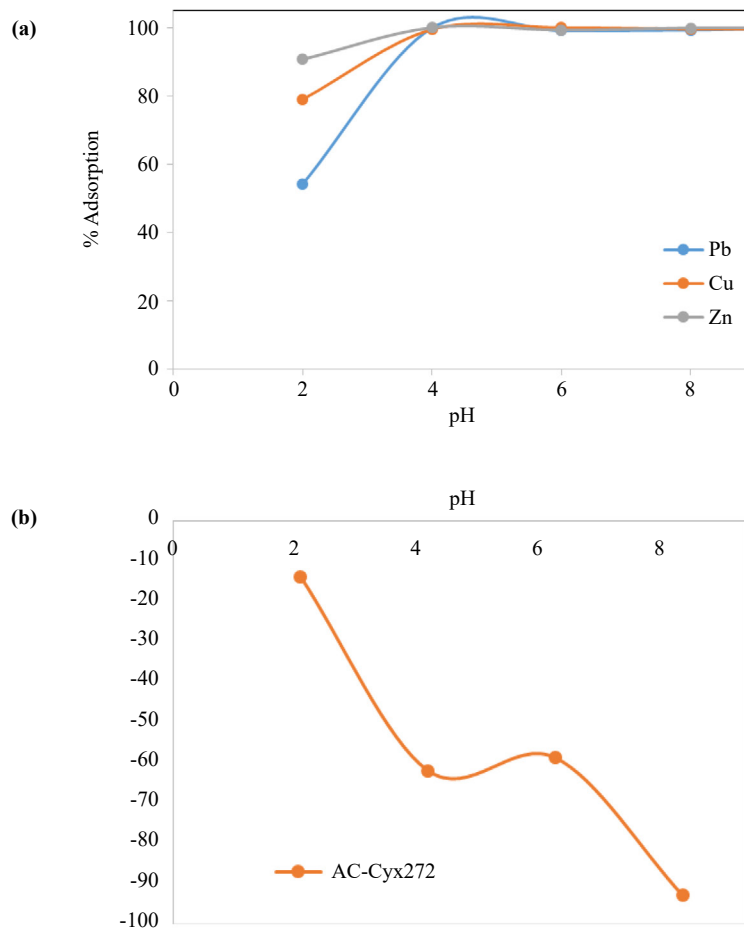


Figure 5. The diffractograms of the activated carbon before and after Cyanex 272 modification

### 3.4 Effect of pH on metal ions adsorption

As pH increased from 2 to 4 the adsorption of all metal ions on AC-Cyx272 increased to reach its maximum between pH 4 and 6 (Figure 6a). These results can be explained by both the speciation of metal ions as a function of pH and the surface charge of the modified carbon. At higher pH values, precipitation occurred, precipitation of lead and zinc, as  $\text{Pb}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$ , respectively, starts at pH 8, while that of copper above pH 6. Based on these facts, all the adsorption experiments were performed at pH = 6 to ensure that the metal ions are present as positively charged cations in the aqueous solution so adsorption on AC-Cyx272 can occur. Moreover, as figure 6a shows, adsorption remained high as pH increased and this can be explained by release of protons from the Cyanex 272 upon adsorption of metal ions which will cause a decrease in the pH thus preventing the precipitation of metals. The other factor that must be taken into consideration is the surface charge of the modified carbon. At pH = 2 the zeta potential of AC-Cyx272 is  $-13.89$  mV which increased to  $-62$  mV and  $-59$  mV (more electronegative) as pH increased to 4 and 6 respectively (Figure 6b). This explains the increase in metal adsorption at these pH values.



**Figure 6.** Effect of pH on metal ions adsorption on AC-Cyx272 (a) and on zeta potential of modified carbon (b)

### 3.5 Adsorption Kinetic models

The two kinetic models pseudo first-order and pseudo-second order are expressed in Equations (3) and (4) respectively [18]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $q_t$  and  $q_e$  are the quantity of metal ions adsorbed ( $\text{mg} \cdot \text{g}^{-1}$ ) at time  $t$  (min) and at equilibrium respectively.  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) are the pseudo-first and second order rate constants.

The effect of contact time on heavy metals ions adsorption on AC-Cyx272 was studied between 5 min and 120 min, at pH = 6 and metal ions concentrations 10 and 30 ppm (Figure 7). The adsorption process of metal ions on AC-Cyx272 was fast, since equilibrium was reached within the first 15 min for the two initial concentrations (10 and 30 ppm). This indicates the large affinity of the adsorbent towards each of the metal ions [19]. The kinetic parameters, the correlation coefficients ( $R^2$ ) and the experimental equilibrium capacities are reported in Table 1. Several models can be used to express the mechanism of sorption onto an adsorbent sorbent such as pseudo-first-order kinetic model and pseudo-second-order kinetic model. The theoretical  $q_e$  values calculated from the pseudo-second-order kinetic were very close to the experimental values. The obtained results show that metal ions adsorption on AC-Cyx272 followed the

pseudo-second order kinetic model (Figure 7). A pseudo-second order rate expression is based on sorption equilibrium capacity and it assumes that the sorption capacity is proportional to the number of active sites occupied on the sorbent [20]. This suggests that the adsorption rate mainly depends on the active adsorption site content on the adsorbent surface and the rate-limiting step is chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and metal ions [21]. The chemical interaction between Cyx272 found on the surface of AC and metal ions is correlated and in accordance with the kinetic results obtained.

**Table 1.** kinetic parameters for metal ions adsorption on AC-Cyx 272

Metal	Ci (ppm)	qe exp (mg·g <sup>-1</sup> )	pseudo-first-order			pseudo-second-order		
			qe theo (mg·g <sup>-1</sup> )	k <sub>1</sub>	R <sup>2</sup>	qe theo (mg·g <sup>-1</sup> )	k <sub>2</sub>	R <sup>2</sup>
Pb (II)	10	3.98	8.07	0.03	0.620	3.96	3.11	0.999
	30	11.97	5.72	0.22	0.995	12.03	0.22	0.999
Cu (II)	10	3.87	3.16	0.08	0.737	3.88	2.07	0.999
	30	11.84	2.36	0.08	0.763	11.83	1.02	0.999
Zn (II)	10	3.97	3.73	0.09	0.395	3.98	1.51	0.999
	30	11.94	1.85	0.07	0.914	12	0.14	0.999



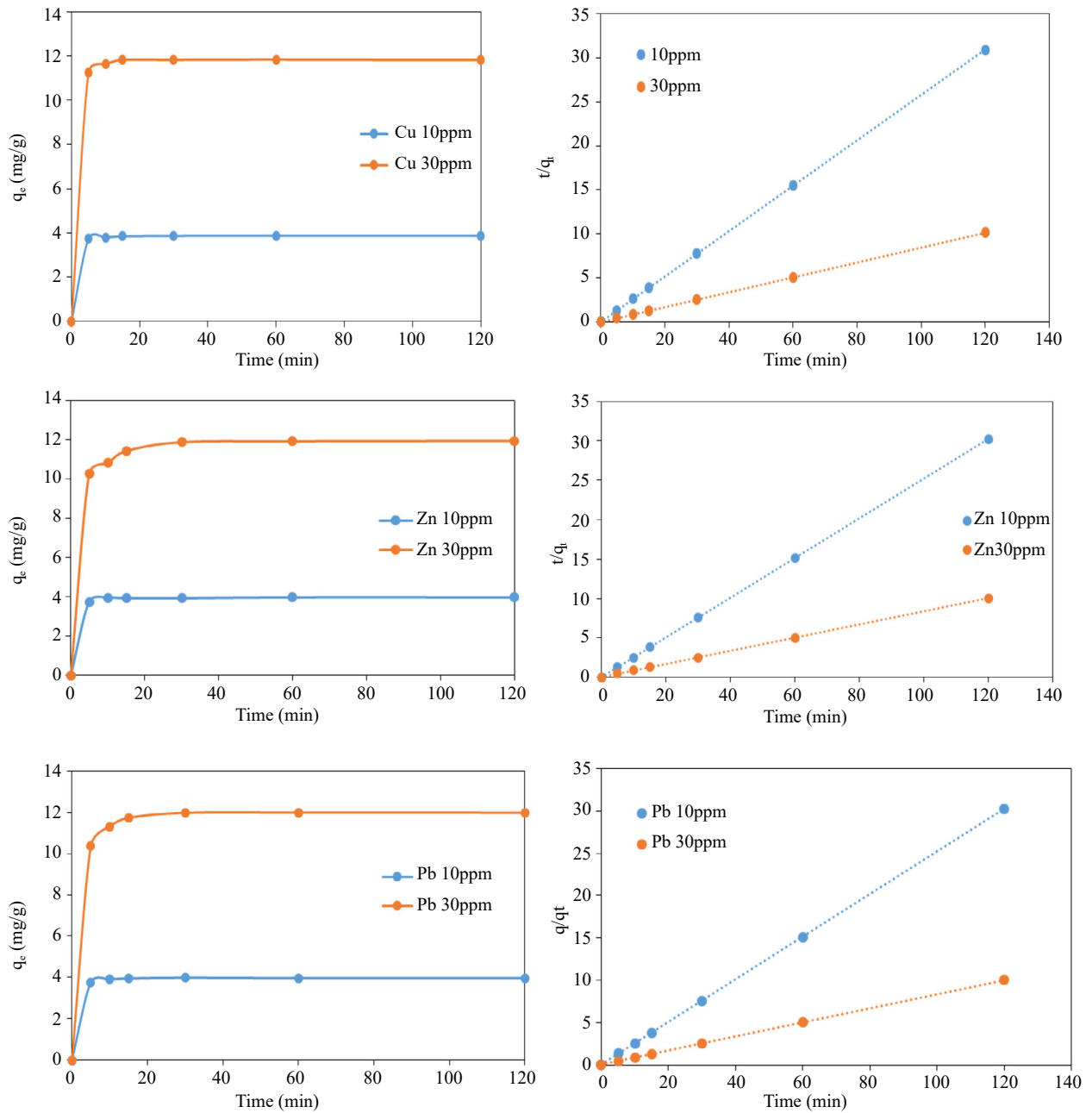


Figure 7. The effect of contact time on heavy metals adsorption on AC-Cyx272 and Pseudo second order kinetic model fit

### 3.6 Adsorption Isotherms

The adsorption isotherm behavior was analyzed using the Langmuir and Freundlich, models that are among the isotherms can be used to model the amount of solute adsorbed per unit of adsorbent,  $q_e$ , as a function of equilibrium concentration in the bulk solution,  $C_e$ , at constant temperature. Langmuir and Freundlich, models, are expressed in Equations (5) and (6) respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (5)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

where  $C_e$  and  $q_{max}$  denote the metal concentration ( $\text{mg}\cdot\text{L}^{-1}$ ) at the equilibrium state and the adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ ), respectively. The value of  $n$  is the inverse of the heterogeneity factor of the adsorption process. Meanwhile,  $K_L$  and  $K_f$  are the Langmuir ( $\text{L}\cdot\text{mg}^{-1}$ ) and Freundlich ( $\text{mg}\cdot\text{g}^{-1}$ ) constants related to the mean free energy of adsorption, respectively [22, 23].

The adsorption isotherms of the experimental data are shown in Figure 8 and the parameters of these two models are shown in Table 2. From the linear regression correlation coefficient  $R^2$ , it can be deduced that the equilibrium data could be well described by the Freundlich isotherm so the adsorption is reversible in a heterogeneous system that is not limited to the formation of monolayers [24]. The values of  $n$  were all between 1 and 10 indicating that the adsorption performance of all metal ions on AC-Cyx 272 adsorbent was favorable under the studied conditions [25], so AC-Cyx 272 is a good adsorbent for heavy metal ions. Moreover, the Freundlich expression is an exponential equation and therefore, assumes that as the metal ions concentration increases, their concentration on the adsorbent surface also increases and indicating a non-ideal adsorption, not limited to monolayer formation.

**Table 2.** Langmuir and Freundlich models for  $\text{Me}^{2+}$  adsorption on AC-Cyx 272

$\text{Me}^{2+}$	Langmuir Model			Freundlich Model		
	$q_{max}^{exp}$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$K_L$ ( $\text{L}\cdot\text{mg}^{-1}$ )	$R^2$	$n$	$K_f$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$
$\text{Pb}^{2+}$	184.1	0.1	0.964	3.32	25.12	0.974
$\text{Zn}^{2+}$	107	0.03	0.682	1.28	4	0.985
$\text{Cu}^{2+}$	175.5	0.114	0.907	2.37	27.2	0.993

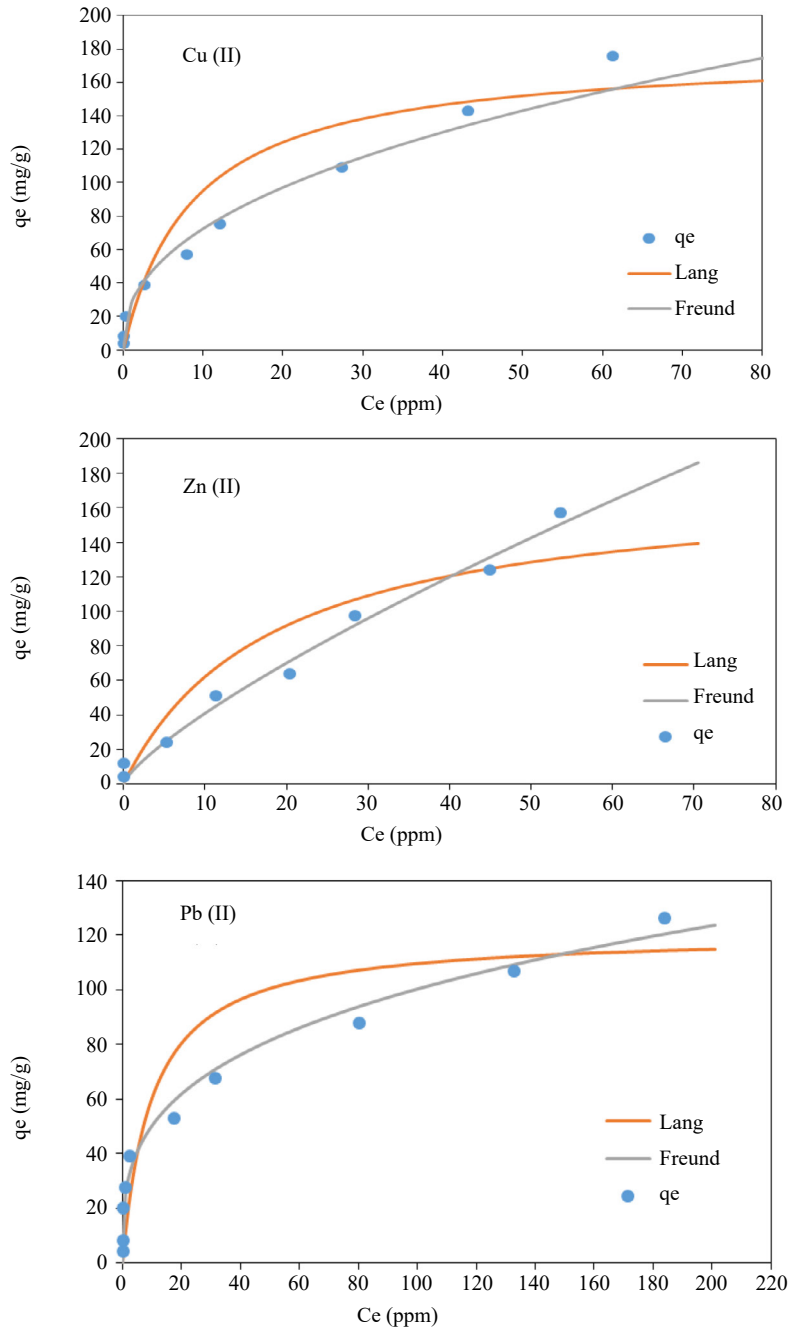


Figure 8. Langmuir and Freundlich isotherms fit for the experimental results

### 3.7 Effect of changing the matrix electrolyte type

In the presence of NaCl, only  $Pb^{2+}$  ions adsorption on AC-Cyx272 decreased by 1.8%. On the other hand, the presence of KCl affected the adsorption rate by 3.8% for  $Pb^{2+}$  while the removal of  $Zn^{2+}$  and  $Cu^{2+}$  has not been affected at all (Figure 9). This decrease is due to competition between sodium and potassium ions with the heavy metal ions for the available specific sites on the surface of the modified AC. By adding NaCl or KCl,  $Na^+$  and  $K^+$  will be present in the aqueous solution besides metal ions. AC-Cyx272 will adsorb some of these two ions as well as metal ions so there will be more cations to adsorb which will consequently decrease slightly the removal of metal ions.

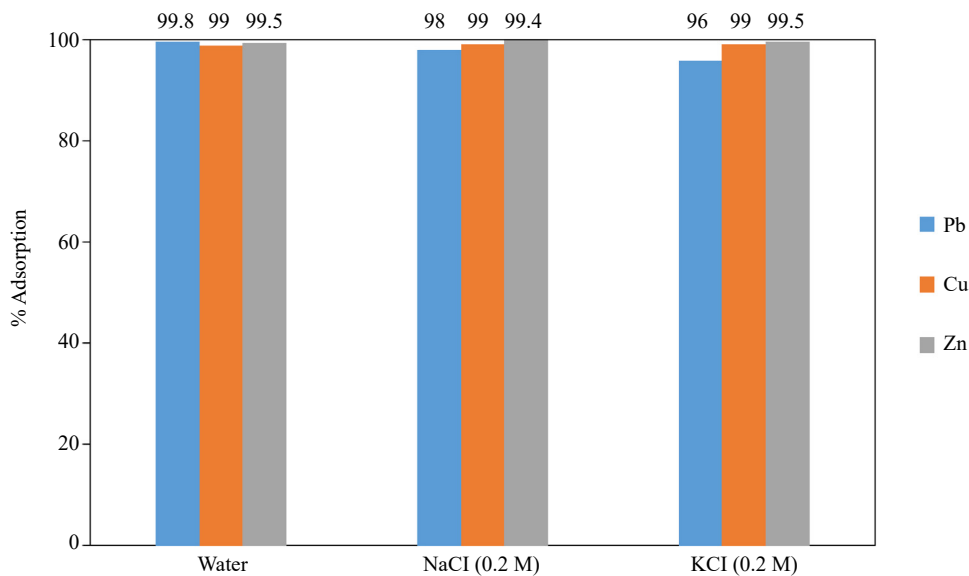


Figure 9. Effect of changing the matrix electrolyte type on metal ions adsorption

### 3.8 Ion competitive adsorption study

In case of mixed metal ions solution, the binding sites are competitively divided among the various metal ions. It was observed that  $Zn^{2+}$  has the highest adsorption capacity over  $Pb^{2+}$  and  $Cu^{2+}$  with respective amounts of 86.3%, 83% and 77.7%. The adsorption capacity of AC-Cyx272 in removing heavy metals from aqueous solution could be arranged in the following order:  $Zn^{2+} > Pb^{2+} > Cu^{2+}$  indicating that the adsorbent has more affinity for zinc.

According to the technical brochure of Cyanex 272, it is more selective for  $Zn^{2+}$  over  $Pb^{2+}$  and  $Cu^{2+}$  (CYTEC, Cyanex-272, 2008. Technical Brochure. CYTEC Industries) which is in consistent with the results obtained in our study (Figure 10). Concerning  $Pb^{2+}$  and  $Cu^{2+}$ , AC-Cyx272 was more selective for lead since it is more electronegative than Cu so it is preferentially adsorbed. The electronegativity of  $Pb^{2+}$  and  $Cu^{2+}$  are 2.33 and 1.9 respectively.

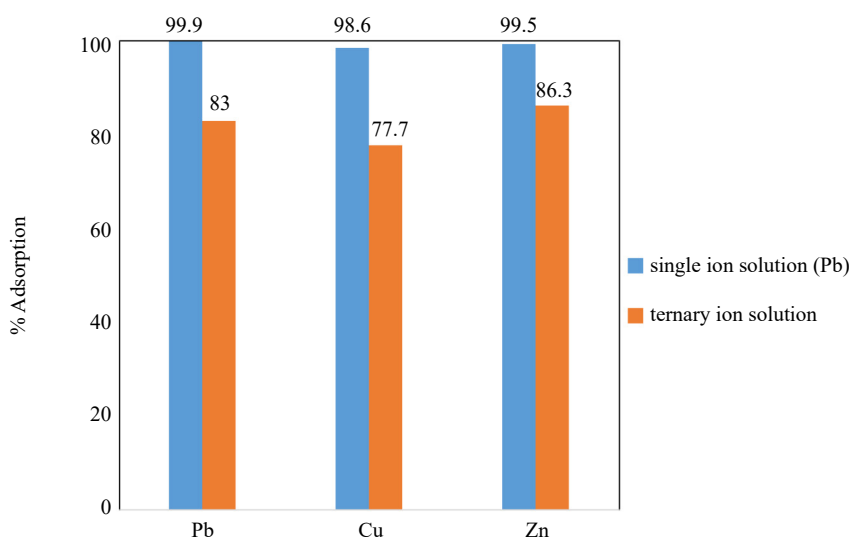


Figure 10. Ion competitive study of AC-Cyx 272 in a ternary ion solution

### 3.9 Regeneration

The efficiency of an adsorbent after regeneration was investigated because good regeneration capacity decrease pretreatment costs and makes the adsorbent more practical to apply on a wide range. Herein, desorption or regeneration experiments were done using 0.1 M HCl. The adsorption capacity of the recycled AC-Cyx 272 was investigated over three cycles (Figure 11). After three cycles, the adsorption rate of Pb (II) decreased from 99.89 % to 95.81 % which proves that the prepared adsorbent is still effective after regeneration.

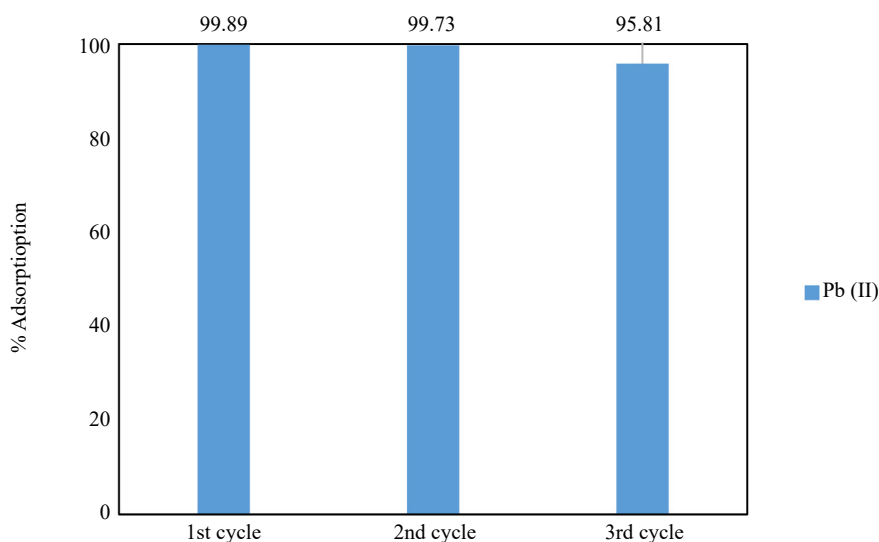


Figure 11. The adsorption capacity of the recycled AC-Cyx 272 after three consecutive adsorption-desorption cycles

### 3.10 Comparison with other adsorbents

The adsorption capacity of AC-Cyx 272 prepared herein was found to be higher than others prepared elsewhere in literature. Table 3 summarizes the results obtained with other adsorbents compared to AC-Cyx 272 for the same metal ions.

Table 3. Comparison with other adsorbents in literature

Adsorbent	Metal Removed	Adsorption Capacity (mg·g <sup>-1</sup> )	Ref.
Chitosan nanocomposite beads	Cu <sup>2+</sup>	114.6	[26]
Magnetic sodium alginate/carboxymethyl cellulose	Cu <sup>2+</sup> and Pb <sup>2+</sup>	105.93 and 89.49	[27]
Oxidized cellulose nanofibers	Cu <sup>2+</sup> and Zn <sup>2+</sup>	102.9 and 73.9	[28]
Guanyl-modified cellulose	Cu <sup>2+</sup>	115	[29]
Activated carbon from Sea-buckthorn stones	Pb <sup>2+</sup>	51.81	[30]
Musa paradisiaca peels	Pb <sup>2+</sup>	10	[31]
Roundnut (Arachis hypogaea) shell	Pb <sup>2+</sup> and Zn <sup>2+</sup>	94.07 and 86.13	[32]
AC-Cyx 272	Pb <sup>2+</sup> , Cu <sup>2+</sup> and Zn <sup>2+</sup>	126.36, 175.5 and 157.16	This study

## 4. Conclusions

In this study, activated carbon was modified by the bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), fully characterized then the efficiency of heavy metal ions (Pb, Cu and Zn) adsorption was investigated. XRD results proved the structural stability of the adsorbent after modification. The obtained batch adsorption results showed that the adsorption process depends on pH and the optimum pH for adsorption was 6. Effect of contact time and initial ions concentration were investigated as well. The adsorption capacities for Pb(II), Cu(II) and Zn(II) were 126.36, 175.5 and 157.16 mg·g<sup>-1</sup> respectively. Freundlich isotherm showed a better fit for all the studied metal ions indicating adsorption in a heterogeneous system. The adsorption of the three metals followed the pseudo-second-order kinetic pattern suggesting chemisorption. The addition of electrolytes didn't significantly affect the adsorption capacity. The adsorbent had higher affinity for Zn(II) in a mixed ions solution. The adsorption capacity remained high after regeneration which makes this adsorbent promising for future application on large scale.

## Acknowledgments

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## Conflict of interest

The authors have no competing interests to declare that are relevant to the content of this article.

## References

- [1] Bankole, M.T.; Abdulkareem, A.S.; Mohammed, I.; Ochigbo, S.S.; Tijani, J.O.; Abubakre, O.K.; Roos, W.D. Selected Heavy Metals Removal from Electroplating Wastewater by Purified and Polyhydroxybutyrate Functionalized Carbon Nanotubes Adsorbents. *Sci. Rep.* **2019**, *9*, 1–19, <https://doi.org/10.1038/s41598-018-37899-4>.
- [2] Qu, X.; Alvarez, P.J.; Li, Q. Applications of nanotechnology in water and wastewater treatment. *Water Res.* **2013**, *47*, 3931–3946, <https://doi.org/10.1016/j.watres.2012.09.058>.
- [3] Jumina; Siswanta, D.; Nofiaty, K.; Imawan, A.C.; Priastomo, Y.; Ohto, K. Synthesis of C-4-Hydroxy-3-methoxyphenylcalix[4]resorcinarene and Its Application as Adsorbent for Lead(II), Copper(II) and Chromium(III). *Bull. Chem. Soc. Jpn.* **2019**, *92*, 825–831, <https://doi.org/10.1246/bcsj.20180323>.
- [4] Castro, L.; Blázquez, M.L.; González, F.; Muñoz, J.A.; Ballester, A. Heavy metal adsorption using biogenic iron compounds. *Hydrometallurgy* **2018**, *179*, 44–51, <https://doi.org/10.1016/j.hydromet.2018.05.029>.
- [5] Wu, H.; Wang, W.; Huang, Y.; Han, G.; Yang, S.; Su, S.; Sana, H.; Peng, W.; Cao, Y.; Liu, J. Comprehensive evaluation on a prospective precipitation-flotation process for metal-ions removal from wastewater simulants. *J. Hazard. Mater.* **2019**, *371*, 592–602, <https://doi.org/10.1016/j.jhazmat.2019.03.048>.
- [6] Tavakoli, O.; Goodarzi, V.; Saeb, M.R.; Mahmoodi, N.M.; Borja, R. Competitive removal of heavy metal ions from squid oil under isothermal condition by CR11 chelate ion exchanger. *J. Hazard. Mater.* **2017**, *334*, 256–266, <https://doi.org/10.1016/j.jhazmat.2017.04.023>.
- [7] Luo, X.; Lei, X.; Cai, N.; Xie, X.; Xue, Y.; Yu, F. Removal of heavy metal ions from water by magnetic cellulose-based beads with embedded chemically modified magnetite nanoparticles and activated carbon. *ACS Sustain. Chem. Eng.* **2016**, *4*, 3960–3969, <https://doi.org/10.1021/acssuschemeng.6b00790>.
- [8] Taamneh, Y.; Sharadqah, S. The removal of heavy metals from aqueous solution using natural Jordanian zeolite. *Appl. Water Sci.* **2016**, *7*, 2021–2028, <https://doi.org/10.1007/s13201-016-0382-7>.
- [9] He, K.; Chen, Y.; Tang, Z.; Hu, Y. Removal of heavy metal ions from aqueous solution by zeolite synthesized from fly ash. *Environ. Sci. Pollut. Res.* **2015**, *23*, 2778–2788, <https://doi.org/10.1007/s11356-015-5422-6>.
- [10] Khan, A.M.; Ahmad, C.S.; Farooq, U.; Mahmood, K.; Sarfraz, M.; Balkhair, K.S.; Ashraf, M.A. Removal of metallic elements from industrial waste water through biomass and clay. *Front. Life Sci.* **2015**, *8*, 223–230, <https://doi.org/10.1080/21553769.2015.1041187>.

- [11] Zhang, M.; Song, L.; Jiang, H.; Li, S.; Shao, Y.; Yang, J.; Li, J. Biomass based hydrogel as an adsorbent for the fast removal of heavy metal ions from aqueous solutions. *J. Mater. Chem. A* **2017**, *5*, 3434–3446, <https://doi.org/10.1039/c6ta10513k>.
- [12] Kadirvelu, K.; Faur-Brasquet, C.; Le Cloirec, P. Removal of Cu(II), Pb(II), and Ni(II) by Adsorption onto Activated Carbon Cloths. *Langmuir* **2000**, *16*, 8404–8409, <https://doi.org/10.1021/la0004810>.
- [13] Rao, M.M.; Ramesh, A.; Rao, G.P.C.; Seshaiiah, K. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. *J. Hazard. Mater.* **2006**, *129*, 123–129, <https://doi.org/10.1016/j.jhazmat.2005.08.018>.
- [14] Hamad, H.; Ezzeddine, Z.; Kanaan, S.; Lakis, F.; Hijazi, A.; Moussawi, M.-A. A novel modification and selective route for the adsorption of Pb<sup>2+</sup> by oak charcoal functionalized with glutaraldehyde. *Adv. Powder Technol.* **2016**, *27*, 631–637, <https://doi.org/10.1016/j.apt.2016.02.019>.
- [15] Bari, F.; Begum, N.; Jamaludin, S.B.; Hussin, K. Synthesis of sol-gel silica chemically bonded with cyanex 272 for the removal of Cu(II), Ni(II), and Zn(II). *J. Mater. Sci.* **2009**, *44*, 2628–2636, <https://doi.org/10.1007/s10853-009-3343-9>.
- [16] Ismail, M.S.; Yahya, M.D.; Auta, M.; Obayomi, K.S. Facile preparation of amine -functionalized corn husk derived activated carbon for effective removal of selected heavy metals from battery recycling wastewater. *Heliyon* **2022**, *8*, <https://doi.org/10.1016/j.heliyon.2022.e09516>.
- [17] Li, J.; Xing, X.; Li, J.; Shi, M.; Lin, A.; Xu, C.; Zheng, J.; Li, R. Preparation of thiol-functionalized activated carbon from sewage sludge with coal blending for heavy metal removal from contaminated water. *Environ. Pollut.* **2018**, *234*, 677–683, <https://doi.org/10.1016/j.envpol.2017.11.102>.
- [18] Febrianto, J.; Kosasih, A.N.; Sunarso, J.; Ju, Y.-H.; Indraswati, N.; Ismadji, S. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *J. Hazard. Mater.* **2009**, *162*, 616–645, <https://doi.org/10.1016/j.jhazmat.2008.06.042>.
- [19] El-Ashtoukhy, E.-S.; Amin, N.; Abdelwahab, O. Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination* **2008**, *223*, 162–173, <https://doi.org/10.1016/j.desal.2007.01.206>.
- [20] Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465, [doi:10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5).
- [21] Jing, X.; Liu, F.; Yang, X.; Ling, P.; Li, L.; Long, C.; Li, A. Adsorption performances and mechanisms of the newly synthesized N,N'-di (carboxymethyl) dithiocarbamate chelating resin toward divalent heavy metal ions from aqueous media. *J. Hazard. Mater.* **2009**, *167*, 589–596, <https://doi.org/10.1016/j.jhazmat.2009.01.020>.
- [22] Freundlich, H.M.F. Über die Adsorption in Lösungen. *Zeitschrift Phys. Chemie* **1907**, *57U*, 385–470, <https://doi.org/10.1515/zpch-1907-5723>.
- [23] Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403, [doi:10.1021/ja02242a004](https://doi.org/10.1021/ja02242a004).
- [24] Vimonses, V.; Lei, S.; Jin, B.; Chow, C.; Saint, C. Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. *Chem. Eng. J.* **2009**, *148*, 354–364, <https://doi.org/10.1016/j.cej.2008.09.009>.
- [25] Hameed, B. Equilibrium and kinetic studies of methyl violet sorption by agricultural waste. *J. Hazard. Mater.* **2008**, *154*, 204–212, <https://doi.org/10.1016/j.jhazmat.2007.10.010>.
- [26] Xu, K.; Li, L.; Huang, Z.; Tian, Z.; Li, H. Efficient adsorption of heavy metals from wastewater on nanocomposite beads prepared by chitosan and paper sludge. *Sci. Total Environ.* **2022**, *846*, <https://doi.org/10.1016/j.scitotenv.2022.157399>.
- [27] Wu, S.; Guo, J.; Wang, Y.; Huang, C.; Hu, Y. Facile preparation of magnetic sodium alginate/carboxymethyl cellulose composite hydrogel for removal of heavy metal ions from aqueous solution. *J. Mater. Sci.* **2021**, *56*, 13096–13107, <https://doi.org/10.1007/s10853-021-06044-4>.
- [28] Li, M.; Messele, S.A.; Boluk, Y.; El-Din, M.G. Isolated cellulose nanofibers for Cu (II) and Zn (II) removal: performance and mechanisms. *Carbohydr. Polym.* **2019**, *221*, 231–241, <https://doi.org/10.1016/j.carbpol.2019.05.078>.
- [29] Kenawy, I.; Ismail, M.; Hafez, M.; Hashem, M. Synthesis and characterization of novel ion-imprinted guanlyl-modified cellulose for selective extraction of copper ions from geological and municipality sample. *Int. J. Biol. Macromol.* **2018**, *115*, 625–634, <https://doi.org/10.1016/j.ijbiomac.2018.04.100>.
- [30] Mohammadi, S.Z.; Karimi, M.A.; Afzali, D.; Mansouri, F. Removal of Pb(II) from aqueous solutions using activated carbon from Sea-buckthorn stones by chemical activation. *Desalination* **2010**, *262*, 86–93, <https://doi.org/10.1016/j.desal.2010.05.048>.

- [31] Ibis, N.E. ; Asoluka, C.A. Use of agro-waste (*Musa paradisiaca* peels) as a sustainable biosorbent for toxic metal ions removal from contaminated water. *Chem. Int.* **2018**, 4, 52–59, <https://doi.org/10.5281/zenodo.1475334>.
- [32] Babarinde, A.; Onyiaocha, G.O. Equilibrium sorption of divalent metal ions onto groundnut (*Arachis hypogaea*) shell: kinetics, isotherm and thermodynamics. *Chem. Int.* **2016**, 2, 37–46.