Egypt. J. Chem. **Vol. 67**, No. 11, pp. 433 - 442 (2024)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Simultaneous effective removal of Zn^{2+} and Cu^{2+} from aqueous solution using alginate functionalized biochar

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Abstract

The contamination with metal is a serious issue towards environmental and human health consequences because of its poisonous nature and to accumulation affinity via the chain of food. Sugarcane bagasse-biochar was functionalized with alginate to obtain cost-effective bio-adsorbent for removing Zn^{2+} and Cu^{2+} ions from aqueous solution. SEM XRD patterns, FTIR spectra and surface area analyses were investigated. Kinetics and isothermal adsorption trials were carried out to assess the capacitive adsorption of the engineered biochar. The functionalized biochar showed comparable removal of aqueous Cu^{2+} and Zn^{2+} with maximal sorption capacities of 69 and 71 mg/g, respectively, assuming monolayer sorption onto the identical homogeneous sites of biochar. Sorption kinetics showed a good agreement with the *Pseudo-second order* model. Moreover, Langmuir, Dubinin–Kaganer–Radushkevich (DKR) and Temkin isothermal models were applicable for the description of Zn^{2+} and Cu^{2+} binding onto the carbonaceous lattice of the engineered biochar. To recapitulate, alginate-biochar composites could be considered as a promising potent biosorbent for the effective removal of metal from water.

Keywords*:* Sugarcane bagasse; biochar; copper; zinc; adsorption; simultaneous

Introduction

The exponential increase of aqueous pollutants in water bodies worldwide within the last few decades has triggered an urgent need to contextualize evergreen and cost-effective techniques for effective decontamination of metal ions from waters. The extensive use of pesticides and fertilizers is associated with the high potentiality of contamination with heavy metals that basically are discharged into the agricultural drainage water. Additionally, in some areas, the industrial wastewater is discharged into the agricultural drainage channels leading to increase heavy metals and other pollutants load in water resources. For instance, higher levels of Cr, Cu, Fe, Mn and Pb were detected in different fishes from the Kitchener Drainage, Egypt (the longest drain in Egypt) **[1]**. Zinc and copper are two of the hazardous heavy metals that are discharged *via* a variety of industrial processes, including the production of explosives, batteries, paper, textiles, photographic materials, painting, and galvanizing **[2].** However, in the context of higher energy and severe enduring environmental pollution, the discovery of appropriate materials to remove organic and inorganic pollutants is priority duty for scientists. The environmental contamination with numerous harmful heavy metals is presently one of the most trustworthy complications provoking both the scientific and public society. Therefore, the decontamination of water from metals has emergent disquiet for protecting public health and environment. The physical/chemical management method for wastewater; nanofiltration, reverse osmosis (RO), oxidation/reduction, or activated carbon, are facing vast challenges by require for

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Received 15 April 2024; Received in revised form 6 June. 2024; Accepted 11 Jun. 2024
DOI: 10.21608/ejchem.2024.282913.9595

enormously energy and expensive particularly in application at large scale treatment plants **[3]**. Recently, there are global concerns for reuse the derived by-products from agricultural wastes to the remediating the environmental contamination. Modified biochar is a good eco-friendly material that could be employed for removing heavy metals from industrial effluents. Globally, it is estimated that 54 million tons of sugarcane bagasse waste is generated annually **[4]**. According to **Abdel-Mageed [5]**, about 16 million tons of sugarcane is annually cultivated in Egypt, which makes Egypt the largest producer of sugarcane among the Arab nation followed by Sudan **[6]**. Several by-products are produced during the extracting process of sugar from sugarcane, namely, bagasse, filter mud/cake, and furnace ash. Thirty percent of these by-products are bagasse, which remains after crushing sugarcane to extract their juice **[7]**. Consequently, it was estimated that 4.7 million tons of sugarcane bagasse waste were annually produced in Egypt **[8-9]**. Sugarcane bagasse boasts exceptional mechanical properties such as flawless finish, high strength, low thermal conductivity and easy manufacturing **[4]**. Due to these unique physical properties, sugarcane bagasse residue is considered as a good substrate to be converted into a value-added biochar with high functionality in agro-environmental applications. There are different methods of the surface modification for biochar products. Among them, chemical modification using sodium alginate received a recent high interest due to their huge surface area, high textural porosity, and functional groups, which increase the adsorption capacity of the functionalized biochar **[10-12]**. The scientific community paid a wide attention into the utilization of biochar and its derivatives toward wastewater recycling owing to their intrinsic porous structure toward binding of aqueous metal ions. The adsorption of trace metals in single metal solutions has been thoroughly investigated **[13-15]**. While the simultaneous adsorption of metal ions from waters has received less attention in the literature. The simultaneous adsorption considered the competition between pollutants with the adsorbent material, and their binding capacity varied according to their affinity to the active sorption sites of the sorbent material. Therefore, the primary goal of this study was to produce an environmentally acceptable adsorbent material from sugarcane bagasse, an agricultural by-product, and use it to simultaneously adsorb zinc and copper ions from aqueous solutions under various circumstances. To clarify the observed outcomes, the produced biochar's physico-chemical properties were investigated.

Experimental

Biochar preparation from sugarcane bagasse

The biomass sample of sugarcane (*Saccharum officinarum*) bagasse was ground, sieved and dried overnight at 70 °C prior to pyrolysis. After being dried, the biomasses were transferred into crucibles, covered with lids and placed in the muffle furnace. The furnace was heated to 450 °C (with a heating ramp of 20 ^{o}C/min) under a constant flow of nitrogen gas and maintained for 2 h. Then, the furnace was switched off and the crucibles were allowed to cool to room temperature.

Chemical modification of biochar

The original biochar (OBC) was ground manually in a ceramic mortar and sieved to obtain the sized fraction of 0.425 - 1.0 mm. Chemically modified biochar was prepared as previously described [16]. Briefly, the modified biochar was prepared by adding the original form of biochar into 1 % sodium alginate solution (1:100 w/v) and shaken at 40 rpm. The biochar suspension was added to 0.1 M $CaCl_2$. biochar beads were dried at 70 °C.

Characterization of the produced sugarcane biochar

Biochar produced is characterized by different techniques which are completely described in supplementary material.

Batch adsorption experiment.
Effect of pH

To exclude the metals (Cu, Zn) removal via precipitation, pH control experiments was conducted in absence of adsorbent for 120 min at STP and 120. To define the optimal pH for the metal adsorption using biochar, fifty mL of the metal mixture solution with concentration of 50 mg/L for each metal was shaken with biochar (0.05 g) at different pH. The pH was adjusted by 0.01 M NaOH or HCl solutions using Thermo Scientific/Orion VERSASTAR advanced electrochemistry meter.

Effect of Contact time

To scrutinize the contact time influence on the metal adsorption capacity using biochar, a set of 50 mL of metals solutions with concentration levels of 50 mg/L were incubated with 0.05 g of biochar. The mixture was shaken for 120 min at 120 rpm using thermostatic shaker at ambient temperature. The samples were filtered using Whatman filter prior metal analysis by ICP-OES.

Effect of sorbent dose

The effect of biochar dose was conducted using 50 ml of metal ions (Cu^{2+}, Zn^{2+}) mixture solution with initial level of 100 mg/l for each metal. The solutions were incubated with various biochar doses and agitated at 120 rpm using a thermostatic shaker at ambient temperature at equilibrium time. The capability and leading adsorption capacity for biochar were scrutinized using different metal concentrations (50-300 mg/L).

The metal removal effectiveness (R %) was estimated using Eq. (1) as follows:

$$R = \frac{C_o - C_e}{C_o} \times 100\ \% \qquad (1)$$

Where

C_o: original metal (Cu & Zn) concentration (mg/L),
C_e: equilibrium or final metal (Cu & Zn) concentration in the solution.

The adsorption capacity q_e (mg Cu-Zn/g biochar) i.e., amount of metal adsorbed by unit mass of biochar was determined by following equation (2):

$$q_e = (C_o - C_e) \times \frac{V}{m} \qquad (2)$$

Where,

q_e: Equilibrium metal capacity (mg/g),
m: biochar amount (g),
V: treated volume (L).

The distributing coefficient (K_d) of metals ions between the aqueous phase and the solid phase was estimated from the following equation (3):

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \qquad (3)$$

Kinetic and isotherm models

Different kinetic and isotherm models for metal adsorption are investigated, the detailed description is supplied in supplementary material.

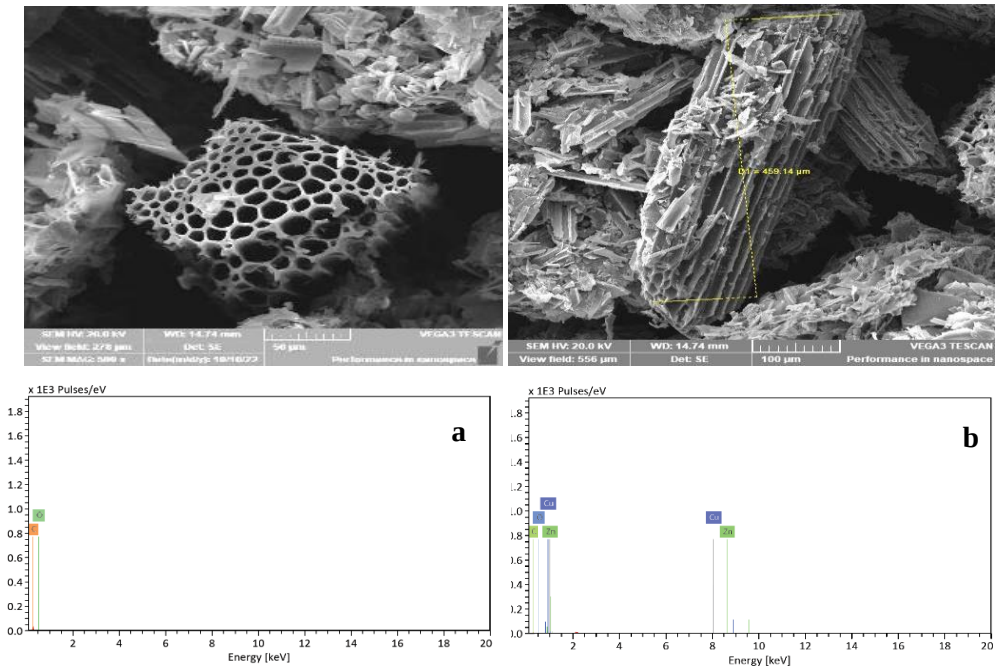
Analytical method

The concentration of Cu^{2+} and Zn^{2+} level in water was analyzed using ICP-OES according to **APHA [17]**. ICP-OES analysis is conducted using Agilent ICP-OES 5100, Australia. Synchronous Vertical Dual View (SVDV) after calibration with a series of calibration solutions. Linearity is guaranteed for a calibration range of 0.1- 100 mg/L.

Results and Discussion

Modified biochar Characterization

Fig. 1 shows SEM of BC and metal loaded BC. According to SEM images the surface morphology of biochar was rough with an irregular fragment The carbonaceous lattice of the engineered biochar exhibited pours channels and a large number of macro and meso-pores given the hollow structure of sugarcane bagasse that facilitates sorption of Zn^{2+} and Cu^{2+} ions through increasing the surface area and providing more binding sites. In addition to some of micro-pores that began to appear and it's expected that these micro-pores improve the previous characteristics. The pore size of biochar was about 459 μm. The elemental composition of biochar was determined by EDX analysis that associated with SEM. EDX micrographs indicated that both biochar (pre- and post-sorption samples) are dominated with C and O peaks as their mass normalized percentages were 84.1 and 73.4 % for C for raw biochar and after adsorption of metal ions, respectively. Both of them had similar percentages of O (15.9 % and 15.4 %, respectively). The mass normalized percentage for Cu^{2+} and Zn^{2+} ions were 11 % and 0.22 %, respectively. On the other hand, the atomic percent (At. %) provides the proportion of one type of atom to all other atoms, which have the same trends for C and O for both (Fig. 1).



Adsorbent material (Before treatment)			Adsorbent material (After treatment)			
Element	C	O	C	O	Cu	Zn
Mass Norm. %	84.12	15.88	73.42	15.36	11	0.22
AT. %	87.58	12.42	84.32	13.25	2.39	0.05

Fig.1. SEM micrographs of (a) MBC, (b) metal loaded-MBC with EDX of MBC before and after adsorption

XRD analysis was conducted to investigate the crystalline minerals in modified biochar and data are shown in Fig. 2. XRD images detected a broad diffraction peaks at ~ 22.6 ^{o} and 41^{o} were observed, which indicates the amorphous structure of the obtained MBC. This result is inconsistence with previous study related to previous publication by **Mosa et al. [18]**.

Thermogravimetric analysis (TGA) showed about 1% reduction in the initial thermal decomposition stage (up to 154 °C) due to the evaporation of bound moisture. The second thermal decomposition rate (up to 309 °C) was approximately 6.4% given the decay of volatile organic compounds, carbohydrates and polysaccharides. The third decomposition rate was about 10.45% at temperature of about 385 °C due to the decomposition of lignin. Finally, the fourth decomposition rate was 18.4% following the decomposition of calcite ($CaCO_3$). These results in agreement with those previously reported by **Li et al. [19]** and **Mosa et al. [20]**.

As it shown in Table 1, The specific surface area (SSA) was relatively high (i.e.137 m^2/g) due to the multiplicity of pours channels and the large number of micro and meso-pores, which provide more reactive sorption site for Cu^{2+} and Zn^{2+} ions.

Also, the results of total pore volume and pore diameter are 0.122 cm^3/g and 1.94 nm respectively. Zeta Potential (ZP) determination was performed to investigate the electrostatic potential of biochar. The result of ZP (ζ) – 38.44 mV showed higher electronegativity, which act a great role in electrostatic reaction between sorbent and sorbate and it also promoting high stability of sorbent material. This high electronegativity potential suggests the active contribution of electrostatic attraction in sorption process. FTIR spectra of pre and post sorption biochar samples showed the presence of O-H (OH stretching group) at region between (4000-3500 cm^{-1}), also C-H (aliphatic stretching group) appeared at region (3000-2850 cm^{-1}), other peaks were appeared at wavenumber ranges between

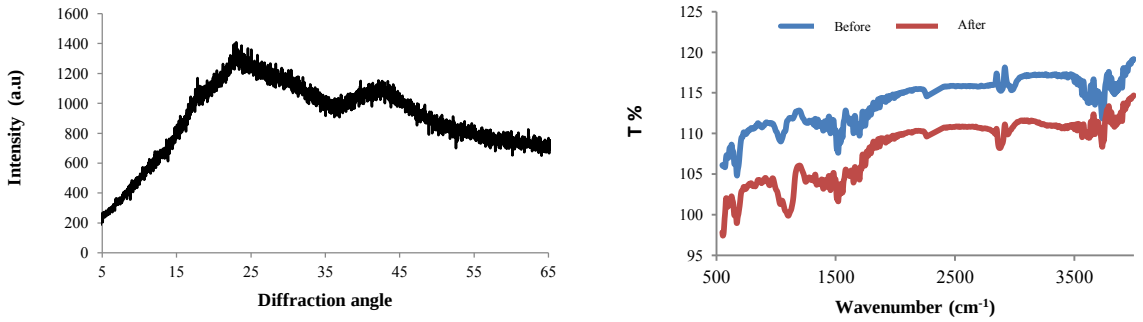


Fig.2. XRD pattern of modified biochar (MBC), FTIR for MBC before and after adsorption.

(1747-1650 cm^{-1}) and (1550-1510 cm^{-1}), which accredited to ketone group C=O and nitro group N-O, respectively. Furthermore, sulfate group S=O and sulfoxide group S=O was existed only in prior sorption biochar samples at region (1410-1330 cm^{-1}) and (1039 cm^{-1}) respectively. However, a slight shifting was found in the FTIR pattern of post-sorption samples confirming limited contribution of complexation onto active functional groups of modified biochar sample.

Batch Sorption

Effect of the solution pH and biochar dosage on Cu^{2+} and Zn^{2+} ions removal

The solution pH is one of the major factors that influence the metal ions form on the biochar surface [21]. Fig. 3 shows removal rates of Cu^{2+} and Zn^{2+} ions by the modified biochar. The maximum sorption capacities of metal ions were recorded at pH of 5.5 with higher removal efficiency of Cu^{2+} and Zn^{2+} (91 and 85.2%, respectively). However, a, the lowest removal capacity (53.3 % for Cu^{2+} and 49.8 % for Zn^{2+}) were observed at pH 2.5. The higher pH value provided more negative charges on biochar surface, which favoured the active contribution of electrostatic attraction force for Cu^{2+} and Zn^{2+} binding onto the carbonaceous lattice of biochar. However, the lower pH values lead the competing between positive hydrogen ion and metal ions for adsorptive positions of biochar that decreased the sorption capacity due to occupying the sorption sites. The PZC of MBC is estimated to be pH 6.05, indicating that the negatively charged surface of MBC existed at pH lower than 6. The effects of biochar dosage are shown in fig.4 with adsorption time of 30 min and concentration initial concentration of 100 ppm. The adsorption of Cu^{2+} and Zn^{2+} ions increased with increasing the biochar dosage, as it showed the highest removal value of metal ions (59 and 52 % for Cu^{2+} and Zn^{2+}, respectively) was at 0.05g of biochar. The percentage of removal increases as the BC dose is increased up to 1.0 g/L and then no detectable improvement, and there was no significance in increase for the adsorptive rate. However, the adsorptive capacity declined with increasing the adsorbent dose above 1.0 g. This could be attributed to the potential sedimentation and reducing the diffusion of sorbates into pores of the biochar matrix. During the same concentration of metal solution, there will be several sorption sites for Cu^{2+} and Zn^{2+} ions in the case of the adsorbed is overloaded [22].

Table 1. Physiochemical properties of modified biochar (MBC)

Samples	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Pore volume (nm)	Zeta Potential (ζ) (mV)
MBC	137	0.122	1.94	-38.4

Effect of initial concentration of metal

The metal concentrations change effect on the adsorbing efficiency and capacity of metal adsorption is shown in Figure 4. It shows that the elimination rate decreased with raising the concentration of Cu^{2+} and Zn^{2+} due to the limited availability of active surface sites of MBC for adsorption and the adsorptive capacity increased with increasing metal concentrations.

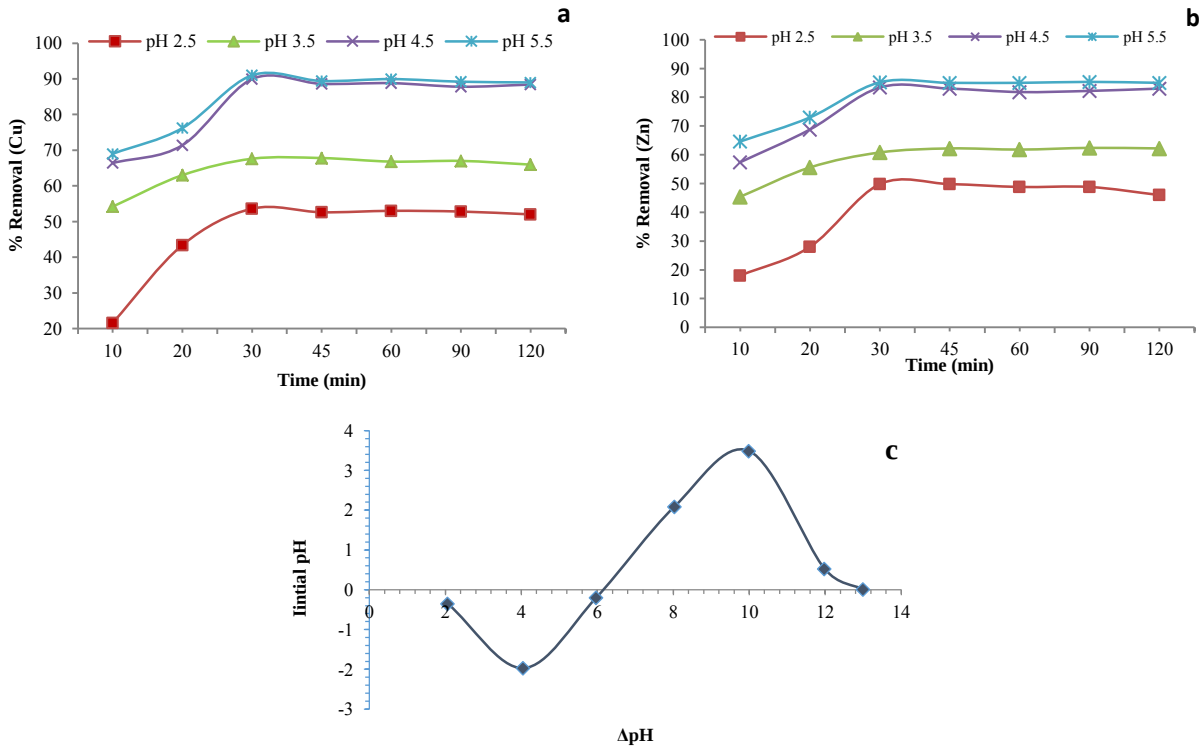


Fig. 3. Effect of pH and contact time on the removal efficiency of Cu^{2+} & Zn^{2+} ions adsorption onto biochar (C_0: 50 mg/L, w: 1 g/L, t: 25 ºC, rpm: 120, time: 10-120 min.), Point of Zero Charge (c)

Sorption kinetics

Adsorption kinetic was scrutinized and experimental adsorption is well fitted with pseudo-second order model; where the correlation coefficient values of Cu^{2+} and Zn^{2+} ions were higher (R^2 = 0.999, 0.999) than those of pseudo-first order (R^2 = 0.362, 0.439), respectively. The result of linear model showed a rapid ascending in Cu^{2+} and Zn^{2+} sorption onto sorption sites of modified biochar within the initial 30 min until reaching a removal efficiency 91% for Cu^{2+} and 85.2% for Zn^{2+} at pH (5.5). Sorptivity of metal ions onto biochar surfaces declined rapidly until reaching equilibrium at 120 min. This ascending is predominately related to physisorption mechanisms followed by chemisorption interaction, which participated in this process through different mechanisms, ion exchange with other ions or *via* complexes formation with functional group on biochar surface, or precipitation on biochar surface sorption sites. Likewise, the great biochar surface area supported with micro and meso-pours, and zeta potential provided more sorption sites leading to increasing in sorption capacity of Zn^{2+} and Cu^{2+} ions.

Sorption isotherm

Sorption isotherm of Cu^{2+} and Zn^{2+} onto biochar showed a rapid sorption at initial concentration of 50 ppm with a Cu removal efficiency of 61%. Sorption of Zn^{2+}, however, showed ascending until the concentration of 100 ppm with high removal value of 55%, followed by descending in sorption curve with further high concentration for metals in water. Adsorption isotherm was fitted well using Temkin model with R^2 values of 0.98 and 0.97 for Zn^{2+} and Cu^{2+}, respectively.

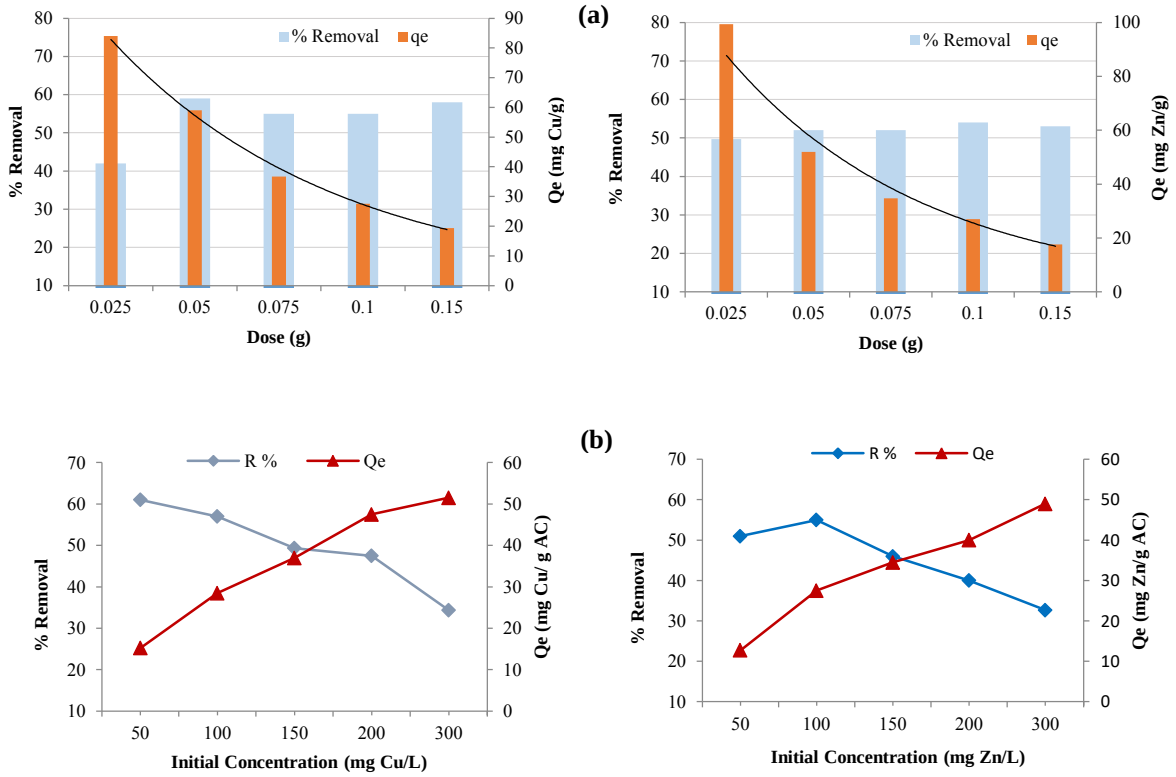


Fig. 4. (a) Effect of adsorbent dosage on the removal efficiency and adsorption capacity of Cu^{2+} & Zn^{2+} ions onto modified biochar (pH: 5.5, v: 50 mL, C_o: 100 mg/L, time: 30 min, T: 25 ºC, rpm: 120)**, (b)** Effects of initial Cu^{2+} & Zn^{2+} ions concentration on removal efficiency and adsorption capacity (pH: 5.5, v: 50 ml, time: 30 min, w: 0.05 g biochar, T: 25 ºC, rpm: 120).

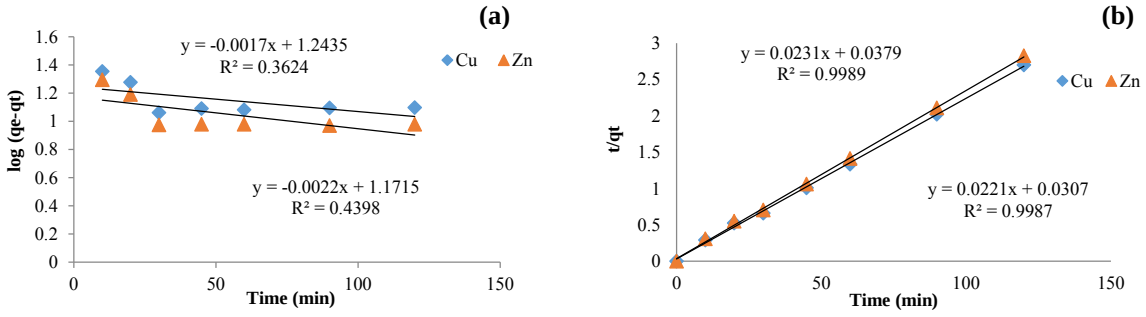


Fig. 5. (a) *Pseudo-first order* kinetics, **(b)** *Pseudo-second order* kinetics of Cu^{+2} and Zn^{+2} ions adsorption onto MBC

Langmuir model also shows well-fitting with experimental ones and recorded high correlation values (R^2= 0.98 for Cu^{2+} and 0.90 for Zn^{2+}). The Temkin constant (B) expresses the sorption capacity of Zn^{2+} and Cu^{2+} onto biochar as (B_T) constant value is 16.429 for Cu^{2+} and 16.437 for Zn^{2+}. The values of (q_{max}) of Langmuir model emphasized the sorption of Zn^{2+} and Cu^{2+} onto biochar surface (69.44 mg/g for Cu^{2+} and 72.46 mg/g for Zn^{2+}). Also, the sorption process was estimated with Dubinin-Kaganer-Radushkevich (DKR) and Freundlich model. Both Kinetic and isotherm emphasized the participation of chemical and physical sorption force into the internal and external of biochar surface.

Table 2: Kinetics and Isotherm models

Adsorbate	Model equation	Parameter 1	Parameter 2	R^2
Kinetic sorption				
	First-order			
Cu^{2+}	$\log (q_e - q_t) = \log q_e - k_1 t$	q_e = 3.468 mg/g	k_1 = - 0.0039	0.362
Zn^{2+}		q_e = 3.227 mg/kg	k_1 = - 0.0051	0.439
	Second-order			
Cu^{2+}	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left[\frac{1}{q_e}\right]$	q_e = 45.25 mg/g	k_2=0.015909	0.999
Zn^{2+}		q_e = 43.29 mg/kg	k_2=0.014079	0.999
Isotherm				
	Langmuir			
Cu^{2+}	$C_e/q_e = 1/b.q_{max} + C_e/q_{max}$	q_{max} = 69.44 mg/g	k = 0.0158	0.98
Zn^{2+}		q_{max} = 72.47 mg/g	k = 0.0106	0.95
	Freundlich			
Cu^{2+}	$\log q_e = \log k_f + 1/n \log C_e$	n = 1.85	k_f = 3.41	0.94
Zn^{2+}		n = 1.67	k_f = 2.26	0.90
	Dubinin-Kaganer-Radushkevich			
Cu^{2+}	$\ln q_e = \ln X_m - \beta\varepsilon^2$	β = -6.398E^{-09} mol^2/J^2	x_m= 0.0034 mol/g	0.96
Zn^{2+}		β = -7.232E^{-09} mol^2/J^2	x_m= 0.004 mol/g	0.92
	Temkin			
Cu^{2+}	$q_e = B\ ln\ K_T + B\ ln\ C_e$	K_T = 0.134 L/mg	B_T = 16.429 J/mol	0.97
Zn^{2+}		K_T = 0.0996 L/mg	B_T = 16.437 J/mol	0.98

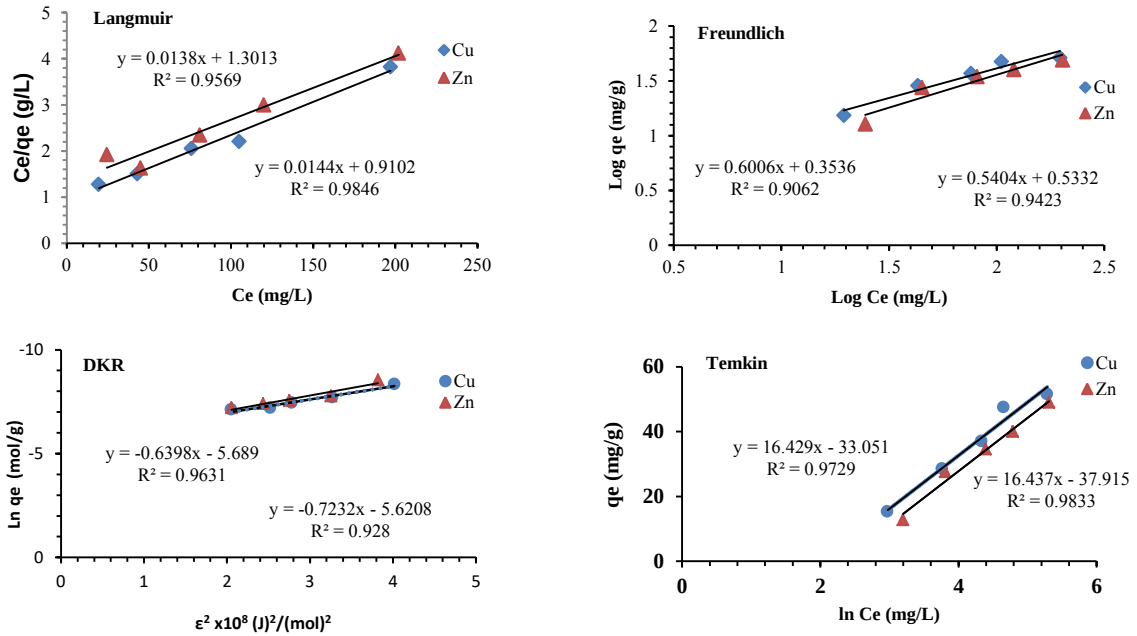


Fig. 6: Adsorption Isotherm of Cu^{+2} and Zn^{+2} ions onto MBC

Conclusion

Adsorbent of modified biochar with alginate was employed for removing copper and zinc ions from waters. The material is characterized with high surface area and negative zeta-potential that liable for metals removal. Modified biochar shows monolayer adsorption with maximal adsorptive capacity (q_{max}) of 69 and 71 mg/g for Cu^{2+} and Zn^{2+}, respectively. As well kinetic studies reveal the fitting of the experimental results with pseudo-second order kinetic model data confirming heterogeneous chemical adsorption. DKR and Temkin models' data are fitted with experimental data. Conclusively, modified biochar with alginate could be applied as a cost-efficient adsorbent for the treatment of metal-containing water. Further investigations should be undertaken to evaluate the applicability of alginate-modified biochar for potentially toxic anions decontamination.

Conflicts of interest

The authors declare that there are no conflicts of interest between them.

Formatting of funding sources

The present investigation was conducted as a part of the research project no. 41584, which was funded by the Science, Technology & Innovation Funding Authority (STDF), 101 Kasr Al-Ainy St., Cairo, Egypt. Project title: Eco-friendly applications for mitigating the toxicity of organic and inorganic contaminants in aquaculture farming systems. Project PI: Prof. Mohamed Bedair M. Ahmed.

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