

Short communication

# Comparison for adsorption modelling of copper and zinc from aqueous solution by *Ulva fasciata* sp.

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## Abstract

The removal of copper and zinc from aqueous solution by adsorption on *Ulva fasciata* sp. was studied, as a function of contact time and pH of the solution. Adsorption of copper and zinc on *U. fasciata* sp. was compared. It was shown that *U. fasciata* sp. has high metal removal efficiency. The maximum adsorption capacity of *U. fasciata* sp. for copper and zinc was 26.88 and 13.5 mg/g, respectively. The adsorption of copper and zinc on *U. fasciata* sp. was increased with increase in pH from 2 to 5 and decreased with increase in pH from 5 to 10. The Freundlich and Langmuir model can describe the adsorption equilibrium of copper and zinc on *U. fasciata* sp. The Freundlich and Langmuir constants for adsorption of copper and zinc on *U. fasciata* sp. were determined.

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**Keywords:** *Ulva fasciata* sp.; Heavy metal removal; Copper and Zinc; Adsorption

## 1. Introduction

Heavy metals, such as lead, copper, zinc, cadmium, and nickel, are among the most toxic pollutants present in marine, ground, and industrial wastewaters. In addition to their toxicity effects even at low concentrations, heavy metals can accumulate throughout the food chain, which leads to serious ecological and health hazards as a result of their solubility and mobility. Copper for example, which is essential to human life and health, has adverse effects on environment and human health. In humans, copper can cause serious problems such as stomach intestinal distress, kidney damage and anemia [1,2]. The main sources of copper in industrial wastewaters include electroplating, metal cleaning plating baths, mining, fertilizers, pulp and paper, and petroleum industries. A concentration of copper ions in these wastewaters can reach values of 1000 mg/L [3]. In addition, copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate [4].

In order to minimize the adverse effects of these heavy metals, authorities and environmental agencies all over the

world enforced stringent standards for the maximum allowable limits of heavy metals discharge into open landscapes and water bodies. These strict regulations and standards encouraged researchers to search for new technologies, which are environmentally friendly and can reduce heavy metals concentrations in the discharged wastewaters to be within the maximum allowable limits. The conventional methods used to treat wastewaters containing heavy metals include chemical precipitation, coagulation, ion exchange, solvent extraction, membrane processes, reverse osmosis, and adsorption. However, most of these methods have several disadvantages, such as: the high cost of treatment, the need for continuous input of chemicals, the production of toxic sludge, or the concentration of heavy metals in the treated wastewater may not be below the maximum allowable limit [5].

Biosorption, which involves the use of biomass or natural substances as sorbents, presents an attractive alternative to the traditional physicochemical means for removing toxic heavy metal from ground and wastewaters [6–11]. The cell wall of most of these biosorbents consists of lipids, polysaccharides and proteins. These biopolymers provide different functional groups, such as imidazole, thioether, carboxyl, hydroxyl, carbonyl, phosphate, phenolic, etc., groups that can form coordination complexes with metals [8,12]. *Ulva fasciata* sp. algal cell walls are

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porous and allow the free passage of molecules and ions in aqueous solutions. The constituents of the cell wall provide an array of ligands with different functional groups capable of binding various heavy metals. These cells can be used live or dead. However, in practical applications, the use of nonliving biomass is more convenient and practical because living biomass cells often require the addition of fermentation media, which increases the biological oxygen demand (BOD) or chemical oxygen demand (COD) in the effluent [7]. In addition, non-living biomass is not affected by the toxicity of the metal ions, they can be subjected to different chemical and physical treatment techniques to enhance their performance, and adsorbed metals can be easily recovered from the biomass by many chemical and physical methods, leading to repeated use of the biomass and better process economy [8,13].

The objective of the present study was to explore the feasibility of using the *U. fasciata* sp. for the removal of toxic heavy metals from aqueous solutions. Batch experiments were carried out to investigate metal adsorption properties of *U. fasciata* sp. The effects of pH on the biosorption were studied.

## 2. Materials and methods

### 2.1. Adsorbent preparation

The green colored marine algae *U. fasciata* sp. used in the present study was collected from the coastal belt of Visakhapatnam, Andhra Pradesh, INDIA. The collected algae was washed with deionized water several times to remove impurities. The washing process was continued till the wash water contains no dirt. The washed algae was then completely dried in sunlight for 10 days. The resulting product was directly used as adsorbent. The dried algae was then cut into small pieces and was powdered using domestic mixer. In the present study the powdered material range of 75  $\mu\text{m}$  particle size was then directly used as adsorbent without any pretreatment.

### 2.2. Preparation of metal ion solution

The stock solution of copper and zinc were prepared by dissolving their sulphate salts in distilled water separately. The test solutions containing single copper or zinc ions were prepared by diluting of 1 g/L stock metal ion solution. The initial metal ion concentration ranged from 20 to 100 mg/L. The pH of each solution was adjusted to the required value with HCl or NaOH before mixing the adsorbent.

### 2.3. Adsorption studies

Adsorption experiments were carried in an Erlenmeyer flask by taking 0.1 g of *U. fasciata* sp. in a 30 mL of metal solution at the desired temperature ( $30 \pm 1^\circ\text{C}$ ) and pH. The flasks were agitated on shaker for 24 h, which is more than ample time for adsorption equilibrium. The amount of metal adsorbed was determined by difference between the initial metal ion concentration and the final one after equilibrium was reached.

### 2.4. Analysis of metal ion

The total metal concentration in solution was determined with atomic absorption spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wave length of 327.4 nm, slit width 0.2 nm, lamp current 3 mA for copper and at a wave length of 213.9 nm, slit width 0.2 nm and lamp current 5.0 mA for zinc.

The results are given as a unit of adsorbed and unadsorbed metal concentrations per gram of adsorbent in solution at equilibrium and calculated by

$$q_e = \frac{(C_o - C_{eq})V}{X}$$

where  $X$  is the weight of adsorbent (g),  $q_e$  the adsorbed metal ion quantity per gram of adsorbent at equilibrium (mg/g),  $C_o$  the initial metal concentration (mg/L),  $C_{eq}$  the metal concentration at equilibrium (mg/L) and  $V$  is the working solution volume (L).

### 2.5. Adsorption isotherms

To test the fit of data, the Langmuir [14] and Freundlich [15] isotherm models were applied to this study. The Langmuir isotherm model is valid for monolayer sorption onto surface and finite number of identical sites and is given by Eq. (1)

$$q_{eq} = \frac{Q_{max}bC_{eq}}{1 + bC_{eq}} \quad (1)$$

where  $Q_{max}$  (mg/g) is the maximum amount of the metal ion per unit weight of cell to form a complete monolayer on the surface bound at high  $C_{eq}$  (mg/g) and  $b$  (L/mg) the constant related to the affinity of the binding sites,  $Q_{max}$  represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments.  $Q_{max}$  and  $b$  can be determined from the linear plot of  $C_{eq}/q_{eq}$  versus  $C_{eq}$ .

The empirical Freundlich isotherm model based on a heterogeneous surface is given below by Eq. (2)

$$q_{eq} = K_f C_{eq}^n \quad (2)$$

Where  $K_f$  (mg/g) and  $n$  are Freundlich constants characteristic of the system.  $K_f$  and  $n$  are indicators of adsorption capacity and intensity, respectively. The values of  $K_f$  and  $n$  were evaluated from the intercept and the slope, respectively, of the linear plot of  $\ln q_{eq}$  versus  $\ln C_{eq}$  based on experimental data. The Freundlich isotherm is also more widely used but provides an information on the monolayer adsorption capacity, in contrast to the Langmuir model.

## 3. Results and discussion

### 3.1. Effect of contact time

Preliminary experiments were carried out to determine the time of equilibrium for adsorption. Fig. 1 typically shows the time profiles of dimensionless metal ion concentration ( $C/C_o$ ) for adsorption of two kinds of metal ions i.e. copper and zinc

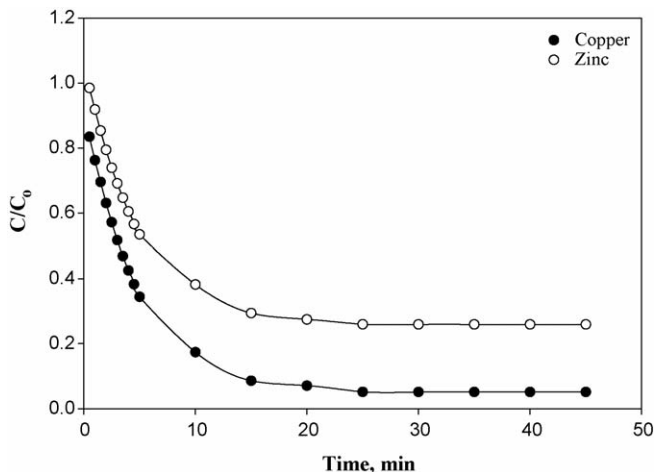


Fig. 1. Adsorption rate of metal ions by *U. fasciata* sp. (pH=5, concentration=20 mg/L).

by *U. fasciata* sp. Fig. 1 shows that more than 75% of metal ion adsorption was completed within 10 min and equilibrium was reached after 20 min and the adsorption did not change significantly with further increase in contact time.

Microbial metal uptake by nonliving cells, which is metabolism-independent passive binding process to cell walls (adsorption), and to other external surfaces, and is generally considered as a rapid process, taking place within a few minutes [16]. The rapid metal sorption is also highly desirable for successful deployment of the biosorbents for practical applications [17].

### 3.2. Effect of pH

Earlier studies on heavy metal adsorption have shown that pH was the single most important parameter affecting the adsorption process. In all cases, metal adsorption by the cells increases with increasing pH reaching to a maximum and then showed a rapid decline in adsorption. The effects of pH for copper and zinc removal is shown in Figs. 2 and 3.

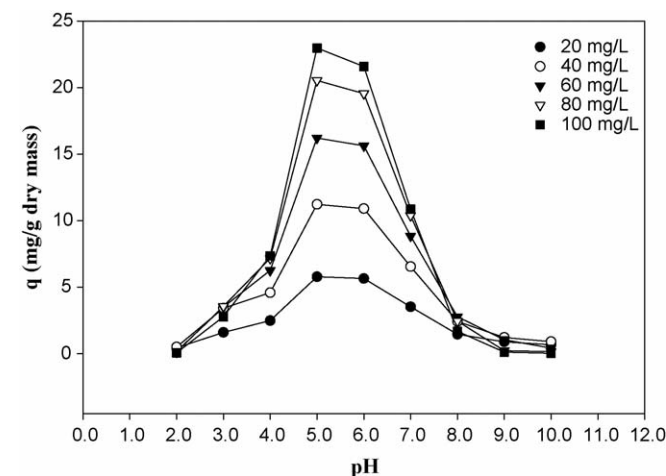


Fig. 2. Effect of pH on copper adsorption by *U. fasciata* sp.

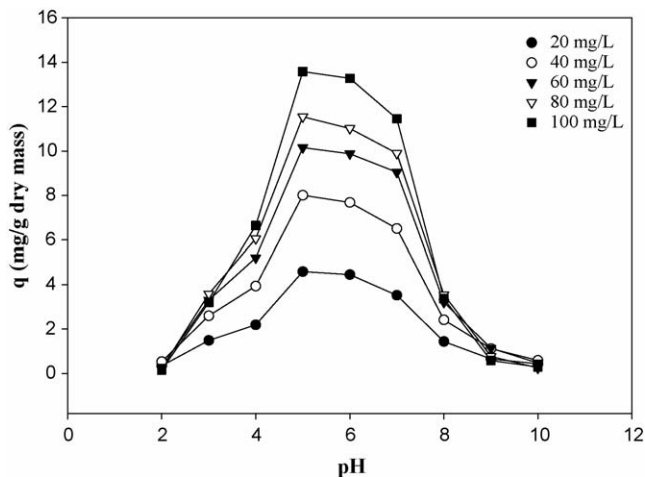


Fig. 3. Effect of pH on zinc adsorption by *U. fasciata* sp.

The pH dependence of metal uptake could be related to the functional groups of the biomass and also to solution chemistry. At pH values less than 5, metals are in their free ionic form and as such the sharp increase in metal uptake. This leads to the hypothesis that the cell wall functional groups and their associated ionic state are responsible for the extent of adsorption.

Biosorbent materials primarily contain weak acidic and basic functional groups. It follows from the theory of acid–base equilibria that, in the pH range 2–5, the binding of heavy metal cations is determined primarily by the state of dissociation of the weak acidic groups. Carboxyl groups (–COOH) are the important groups for metal uptake by biological materials [18,19]. At pH 5, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater copper and zinc sorption. But for pH values from 6 to 10 lower adsorption capacity was observed for copper and zinc, this might be due to the precipitation and lower polarity of copper and zinc ions at higher pH values. In this study, these copper and zinc cation at around 5 would be expected to interact

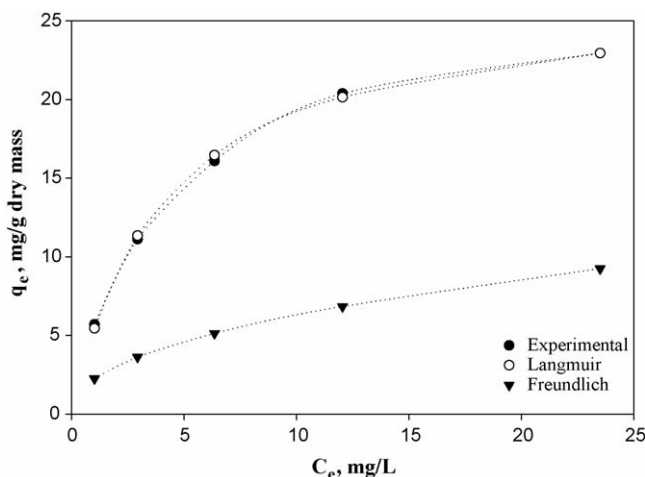


Fig. 4. Equilibrium curves for copper adsorption onto *U. fasciata* sp.

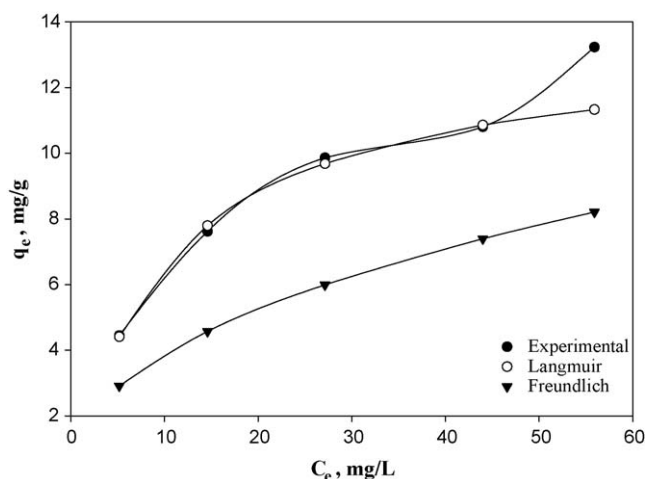


Fig. 5. Equilibrium curves for zinc adsorption onto *U. fasciata* sp.

Table 1  
Freundlich and Langmuir model parameters for adsorption of metal ions by *U. fasciata* sp.

Metal ion	Freundlich isotherm			Langmuir isotherm		
	$K_f$ (mg/g)	$n$	$R^2$	$b$ (L/mg)	$Q_{\max}$ (mg/g)	$R^2$
Copper	2.2230	0.4512	0.9606	0.2483	26.88	0.9995
Zinc	1.4209	0.4359	0.9828	0.0936	13.5	0.9989

more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for copper and zinc adsorption was found as 5. The effect of pH on the adsorption of copper and zinc has been investigated by various investigators using a variety of different adsorbent types [20–22], and the optimum adsorption capacity of copper and zinc at pH 5 has been reported.

Table 2  
Maximum adsorption capacities for copper adsorption of different adsorbents

Adsorbent	Operation conditions				$q_{\max}$ (mg/g)	Reference
	pH	$T$ ( $^{\circ}\text{C}$ )	$C_0$ (mg/L)	$X$ (g/L)		
<i>Chlorella vulgaris</i>	4.5	25	100	1	40.0	[26]
<i>Scenedesmus obliquus</i>	4.5	25	100	1	20.0	[26]
<i>Synechocystis</i> sp.	4.5	25	100	1	23.4	[26]
<i>Chlorella fusca</i>	6	20	6.3	n.a. <sup>a</sup>	3.2	[27]
<i>Chlorella vulgaris</i>	4	25	100	0.75	37.6	[28]
<i>Chlorella vulgaris</i>	6	25	20	1	7.5	[29]
<i>Spirulina platensis</i>	6	25	20	1	10.0	[29]
<i>Chlorella vulgaris</i>	5	25	5	1	1.8	[30]
<i>Scenedesmus quadricauda</i>	4	25	5	1	2.8	[30]
<i>Saccharomyces cerevisiae</i>	5	25	100	0.1	1.25	[31]
<i>O. Limnetica</i>	4–5	25	1000	1	23.96	[32]
<i>A. Spiroides</i>	4–5	25	1000	1	0.2	[32]
<i>E. Elegans</i>	4–5	25	1000	1	1.08	[32]
<i>C. Vulgaris</i>	4–5	25	1000	1	9.47	[32]
<i>Ulva reticulata</i>	5.5		2000	0.2	74.63	[33]
<i>Manihot esculenta</i> Cranz	5	30	500	2.5	71.3	[34]
<i>Thuja orientalis</i>	7.7	16	50	4	19.23	[35]
<i>Ulva fasciata</i> sp.	5	$30 \pm 1$ $^{\circ}\text{C}$	100	0.1	26.88	Present study

<sup>a</sup> n.a.: not available.

### 3.3. Langmuir and Freundlich adsorption isotherms

The isotherm represents the equilibrium relationship between the metal uptake by the adsorbent and the final metal concentration in the aqueous phase, showing the adsorption capacity of the adsorbent. The pH value of 5.0 was chosen as the experimental condition for the determination of adsorption isotherms.

The curves in Figs. 4 and 5 were generated from Freundlich and Langmuir model equations, respectively. As seen from Figs. 4 and 5, the Langmuir model fitted to the experimental data well. The values of Freundlich and Langmuir constants resulting from equilibrium adsorption studies of copper and zinc by *U. fasciata* sp. are determined and listed in Table 1.

The best-fit equilibrium model was determined based on the linear regression correlation coefficient  $R^2$ . From the table it was observed that the adsorption data were very well represented by Langmuir isotherm with an average higher correlation coefficient of 0.9995. The higher  $R^2$  value for Langmuir isotherm confirms the approximation of equilibrium data to Henry's law at lower initial concentration. From the table, the Langmuir adsorption capacity  $Q_{\max}$  (mg/g) for copper and zinc is 26.88 and 13.5, respectively and the equilibrium constant  $b$  (L/mg) for copper and zinc is 0.2483 and 0.0936, respectively. The Freundlich constant  $K_f$  indicates the sorption capacity of the sorbent and the value of  $K_f$  (mg/g) is 2.223 and 1.4209 for copper and zinc. Furthermore, the value of ' $n$ ' at equilibrium is 0.4512 and 0.4359 for copper and zinc. It is noted that the value of ' $n$ ' is smaller than 1, reflecting the unfavorable adsorption.

Tables 2 and 3 shows a comparison between the results of this work and others found in the literature. The values of copper and zinc specific uptake found in this work were significantly higher than reported elsewhere. The comparison of sorption capacities of algae used in this study with those obtained in the literature shows that all the microorganisms are more effective for this

Table 3  
Maximum adsorption capacities for zinc adsorption of different adsorbents

Adsorbent material	Operating conditions					Reference
	Adsorption capacity (mg/g)	pH	T (°C)	Initial concentration range (mg/L)	Biomass (g/L)	
Activated carbon	31.11	4.5	25	1–1000	4.0	[36]
<i>Streptovorticillium cinnamomeum</i>	21.3	5.5	28	50–1000	2.0	[37]
<i>Fontinalis antipyretica</i>	12 ± 1 <sup>a</sup>	5.0	5	100	2.0	[38]
<i>Aspergillus niger</i> 405	4.70	5.0	25	10	10.0	[39]
<i>Mucor rouxii</i> (live)	4.89	5.0	n.a.	10	n.a.	[40]
<i>Mucor rouxii</i> (NaOH pretreated)	5.63	5.0	n.a.	10	n.a.	[40]
<i>Mucor rouxii</i> (Na <sub>2</sub> CO <sub>3</sub> pretreated)	3.26	5.0	n.a.	10	n.a.	[40]
<i>Mucor rouxii</i> (NaHCO <sub>3</sub> pretreated)	6.28	5.0	n.a.	10	n.a.	[40]
<i>Phanerochaete chrysosporium</i> <sup>b</sup>	39.0	7.0	25	30–600	n.a.	[41]
<i>Sargassum</i> sp.	24.35	4.5	30	98	4.0	[42]
Animal bones	11.55	5.0	20	15–79	4.0	[43]
<i>Ulva fasciata</i> sp.	13.5	5.0	30 ± 1 °C	20	0.1	Present study

<sup>a</sup> Standard deviation of the mean.

<sup>b</sup> Ca-alginate immobilized.

purpose. As a result of this investigation, the order of the sorption capacity was: Cu > Zn.

The effect of isotherm shape can be used to predict whether a sorption system is 'favourable' or 'unfavourable' both in fixed-bed systems [23] as well as in batch processes [24]. According to Hall et al. [25], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $K_R$ , which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0}$$

where  $K_R$  is a dimensionless separation factor,  $C_0$  the initial concentration (mg/L) and  $K_a$  the Langmuir constant (L/mg). The parameter  $K_R$  indicates the shape of the isotherm accordingly:

Values of $K_R$	Type of isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

The values of  $K_R$  for copper and zinc at different concentrations are shown in Fig. 6 and the values are tabulated in Table 4. The  $K_R$  values indicated that adsorption was more favourable for the higher initial concentrations of copper and zinc than the lower ones. However, the *U. fasciata* sp. would be an effective adsorbent for removing copper and zinc from solution.

Table 4  
 $K_R$  values relating to the initial copper and zinc ion concentrations at pH = 5

Concentration (mg/L)	$K_R$	
	Copper	Zinc
20	0.2014	0.3482
40	0.0915	0.2108
60	0.0629	0.1511
80	0.0479	0.1178
100	0.0387	0.0965

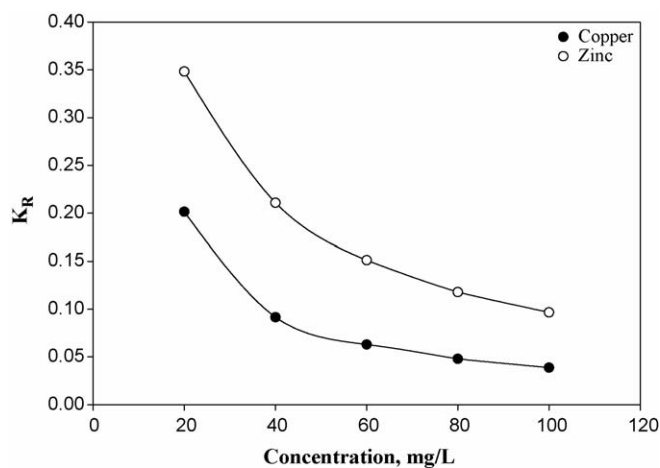


Fig. 6. Values of the separation factor,  $K_R$  for the adsorption of copper and zinc using *U. fasciata* sp.

#### 4. Conclusion

*U. fasciata* sp. used in this study was determined to be a perfect adsorbent for the removal of copper and zinc ions from aqueous solution. The removal of copper and zinc ions by *U. fasciata* sp. was about 94 and 74%, respectively. Percent adsorption of copper and zinc ions from aqueous solution by the *U. fasciata* sp. was found to be higher at lower concentrations. The pH was effective on the adsorption of copper and zinc from aqueous solution on the *U. fasciata* sp. remarkably. Two equilibrium models Freundlich and Langmuir were used to explain the adsorption isotherms data and the adsorption follows the Langmuir isotherm.

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