Comparative Studies on Removal of Chromium (VI) from Monocotyledon (*Allium cepa*) Tunic and Dicotyledon Plant (*Tabebuia aurea*)

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Abstract

In the present study, the influence of various important parameters such as pH, adsorbent dosage, shaking velocity, and concentration of Cr(VI) on the adsorbent *Allium cepa* tunic and *Tabebuia aurea* capacity were investigated. Isotherms such as Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich and kinetic studies were done. The maximum removal efficiencies were obtained at 75 rpm for both monocot and dicot plant species. At pH 3, the adsorbent *T. aurea* gives 87% *A. cepa*, and at pH 5 gives 96.4% removal of Cr(VI) from aqueous solution containing the concentration of 50 mg/L with the adsorbent dosage of 10 g/l. From this study *T. aurea* maximum percentage removal were noticed at pH 5, adsorbent: 10 mg/L, shaking period: 75 rpm, initial concentration: 150 mg/L were as maximum percentage removal for *A. cepa* were obtained at pH 3, adsorbent: 10 mg/L, shaking period: 75 rpm, initial concentration: 150 mg/L. At the end of the experiment both Monocotyledon (*Allium cepa*) tunic and Dicotyledon plant (*Tabebuia aurea*) gave a better removal percentage at high concentrations.

Introduction

One of the major reasons for pollution of water and soil is the rapid growth of industries. Effluents from industries are the main sources of water contamination. Discharged concentrations of many criteria metals in the aquatic environment have been reduced over the last few decades, through the implementation of stringent Environmental Quality Standards. But heavy metals are highly toxic even at low concentrations and can accumulate in living organisms, causing several disorders and diseases [1, 2]. In India, many industrial tannery units are spread mostly across

Tamil Nadu, especially at Chennai – a major trading center for hides and skins. Heavy metals are non-biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders [3]. There are numerous methods for the removal of these heavy metal ions from wastewater streams, including chemical precipitation [4, 5], reverse osmosis [6], filtration methods [7], and electro coagulation [8, 9].

Biosorption is generally defined as the accumulation of metals by biological materials without active uptake, and can be considered a collective term for a number of passive accumulation processes that may include ion exchange, coordination, complexation, chelation, adsorption, and micro precipitation [10, 11]. Conventional methods of removing toxic

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heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology, and evaporation recovery. However, these processes have considerable disadvantages such as incomplete metal removal, expensive equipment and monitoring systems, high reagent or energy requirements, generation of toxic sludge, and other waste products that require disposal [12]. Based on the literature, we have chosen both Monocotyledon (*Allium cepa*) tunic and Dicotyledon plant (*Tabebuia aurea*), which they have not used in their experiments.

Materials and Methods

Selection of the Plant

Tabebuia aurea (dicotyledon) leaves were collected at the Coimbatore Institute of Technology, and the tunic of *Allium cepa* (Monocotyledon) was collected from the local market at Hosur, Krishnagiri district, Tamilnadu. These monocotyledon tunic and dicotyledon plants were selected as biosorbents for the removal of chromium (VI) ion in this study.

Preparation of Adsorbents

Tabebuia aurea leaves and tunic of *Allium cepa* were washed thoroughly in running water to remove impurities and any adhering particles. The leaves were dried at room temperature for 20 days until they became crisp. The dried leaves were crushed and blended to powder and sieved. 1.676 mm mesh size particle were collected and it was stored in an airtight container for further use to avoid contact with moisture in the atmosphere.

Preparation of Cr(VI) and Metal Analysis

Stock solution of chromium (VI) was prepared by dissolving 2.82 g of potassium dichromate in 1 L of distilled water. The working solution was prepared by diluting the stock solution. Chromium was analyzed using the UV Spectrophotometric method with 1, 5-diphenycarbazide at 540 nm.

Batch Experiments

Effect of Shaking Velocity

1 g of each leaf powder (*T. aurea* and *A. cepa*) was added to the concentration of 50 mg/L. Flasks were maintained at different shaking velocities such as 75, 150, and 200 rpm in an orbital shaker. Contact time ranged from 0-5 hours.

Effect of pH

Effects of pH were conducted by using 50 mg/L of chromium (VI) concentration with an adsorbent dosage of 1 g/L and contact time of 5 hours.

Effect of Concentration

1 g of adsorbent to different chromium (VI) concentrations (50, 75, and 150 mg/L), at pH 5 for *T. aurea* and at pH 3 for *A. cepa* respectively, contact time ranged from 0-5 hours.

Effect of Dosage

The effect of adsorbent dosage level on percent removal of chromium (VI) was studied using concentrations of 50 mg/L, pH 5, 3 for *T. aurea* and *A. cepa,* respectively, and the amount of adsorbent used for this study was 5 g, 10 g, and 15 g with contact time ranging from 0-5 hours.

Calculation of Metal Uptake

(i) The amount of metal adsorbed by the adsorbent is calculated by:

$$q = \frac{(C - Ce)V}{M} \qquad (1)$$

...where:
q – amount of metal ion adsorbed in mg/g
C, C_e – initial and final metal ion concentrations in mg/L
V – volume of metal ion solution in l
M – mass of adsorbents in g

(ii) The percentage of removal of metal ions was determined by:

$$\% \text{ Removal} = \frac{C - Ce}{C} \times 100 \qquad (2)$$

Adsorption Isotherms

Isotherm studies at equilibrium constant concentration of metals was investigated using the two most widely used model equations of Freundlich [13], and Langmuir and Temkin isotherms (Figs. 1-3) [14, 15], Dubinin-Radushkevich [16].
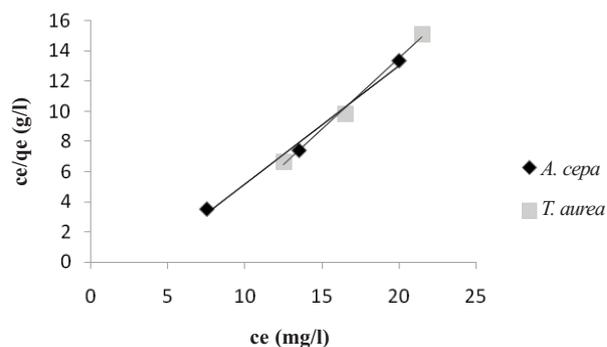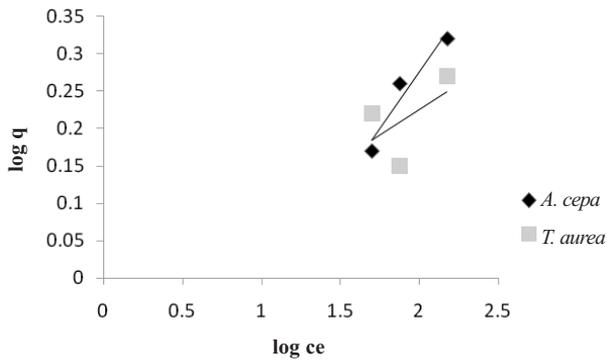

Fig. 1. Langmuir isotherm.
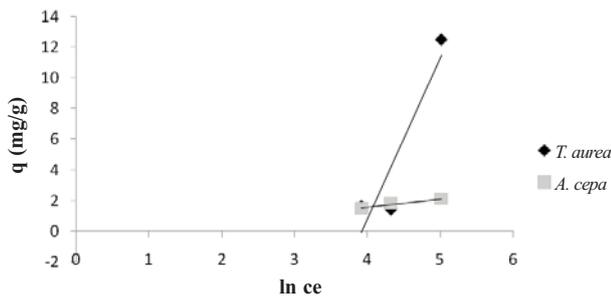
Fig. 2. Freundlich isotherm.

Fig. 3. Temkin isotherm.

Kinetic Studies

Pseudo First-Order Model

The possibility of adsorption data following Lagergren pseudo first-order kinetics (Figs. 4-6) is given by:

$$\frac{dq}{dt} = K_I (q_e - q) \tag{3}$$

Integrating the above equation with respect to integration conditions $q = 0$ to $q = q$ at $t = 0$ to $t = t$, the kinetic rate expression becomes:

$$log(q_e - q) = log\ q_e - \frac{K_1}{2.3} t \tag{4}$$

The pseudo first-order rate constant K_1 can be obtained from the slope of plot between log (q_e-q) *versus* time, t.

Pseudo-Second Order Model

A pseudo second-order model can be used to explain the adsorption kinetics (Figs. 7 and 8). This model is based on the assumption that the adsorption follows second-order chemisorptions. The pseudo second-order model can be expressed as:

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \tag{5}$$

Separating the variables from the above equation:

$$\frac{dq}{(q_e - q)^2} = K_2 dt \tag{6}$$

Integrating Eq. (6) for the boundary conditions $q = 0$ to $q = q$ at $t=0$ to $t = t$, simplifies to:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\ t \tag{7}$$

...where t is the contact time (min), and q_e (mg/g) and q (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t. A plot between t/q_t versus t gives the value of the constant K_2 (g·(mg·min)⁻¹), and also q_e (mg/g) can be calculated.
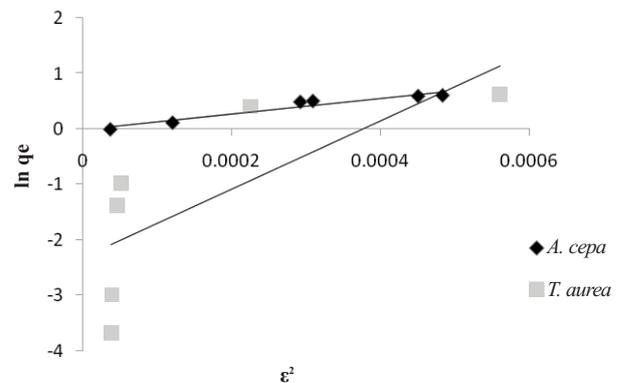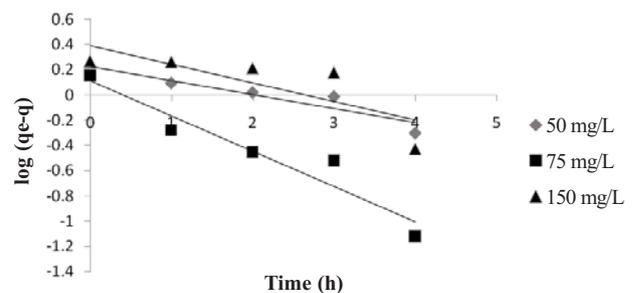

Fig. 4. Dubinin-Radushkevich isotherm.

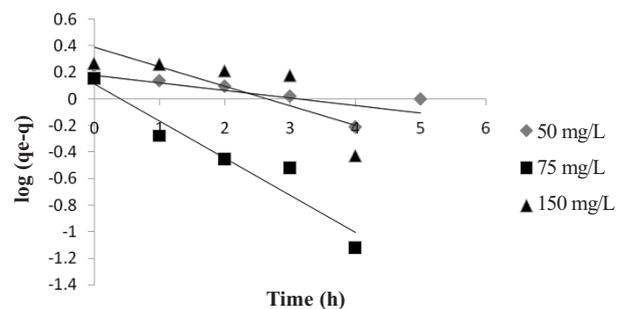Fig. 5. Pseudo first-order kinetics for *T. aurea*.

Fig. 6. Pseudo first-order kinetics for *A. cepa*.

Table 1. Effect of various Shaking periods on removal of Cr(VI) using *T. aurea* and *A. cepa*.

Shaking period	*T. auria* % removal of Cr(VI)	*A. cepa* % removal of Cr(VI)
75	92	93
100	89	90
125	84	83
150	81	80
175	80.2	75
200	79	58

Results and Discussion

Effect of Shaking Period

The maximum removal efficiencies were obtained at 75 rpm for both *T. auria* and *A. cepa*, the maximum adsorption capacities were found to be 92% and 93%, respectively. The adsorptions were lowest at 200 rpm for both *T. auria* and *A. cepa*. Increasing the shaking speed shows a decline in the adsorption capacity (Table 1 and Fig. 9).

This effect can probably be attributed to the decrease in boundary layer thickness around the adsorbent particles, which results from increasing the degree of mixing. When the mixture was shaken, the solid particles moved around rapidly in the solution, and this increased the concentration of heavy metals near the surface of the solid particles, possibly to a level near that of the bulk concentration. Because heavy metal diffusion to the boundary layer between adsorbent particles and the surrounding solution would increase with increased shaking, the external mass transfer speed of the metals would increase and equilibrium would be reached more rapidly. This may occur because the high shaking speed provided sufficient additional energy to break newly formed bonds between the metal ions and the adsorbent surface [17].

Effect of pH

Solution pH plays a major role in the bioadsorption of Cr(VI), and it could be related to the type and ionic state of the functional group present on the bioadsorbent surface [13].

At an initial pH value of 3, adsorbent *A. cepa* gives 87% removal of Cr(VI) from aqueous solution containing the concentration of 50 mg/L. from the speciation graph it was found that *T. aurea* gives maximum 96.4% removal of Cr(VI) from aqueous solution at pH5. *T. aurea* gives maximum percentage of removal when compared with *A. cepa* (Table 2 and Fig. 10). This implies that the dicot plant is more efficient in removal of chromium (VI) than the monocot plant.

More adsorption at acidic pH indicated that the lower pH resulted in an increase in H$^+$ ions on the adsorbent sur-

face, which resulted in insignificantly strong electrostatic attraction between the positively charged adsorbent surface and chromate ions [18, 19].

Effect of Concentration

The adsorption of Cr(VI) was carried out at 50, 75, and 150 mg/L as Initial Cr(VI) ion concentration for a period of 5 hours at pH 5 for *T. aurea* and pH 3 for *A. cepa*). Adsorbent amount used was 10 g/l. *T. aurea* and *A. cepa* shows 75% and 85% removal at 150 mg/L (Table 3 and Fig. 11).

The initial concentration provides an important driving force to overcome all mass transfer resistances of solutes between the aqueous and solid phases. The amount of Cr(VI) adsorbed on the biomass increased with initial concentration of the metal ions [11].
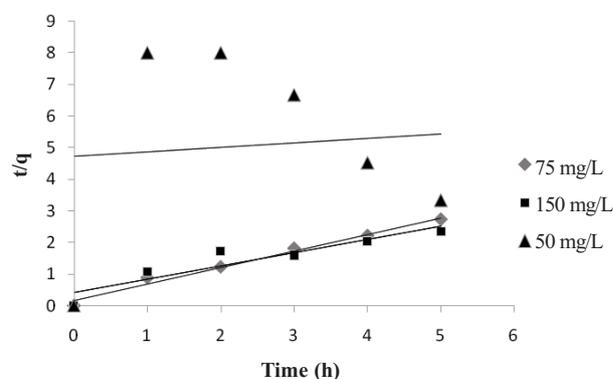

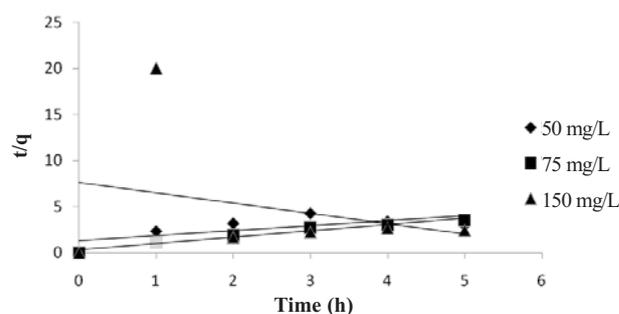Fig. 7. Pseudo second-order kinetics for *A. cepa*.

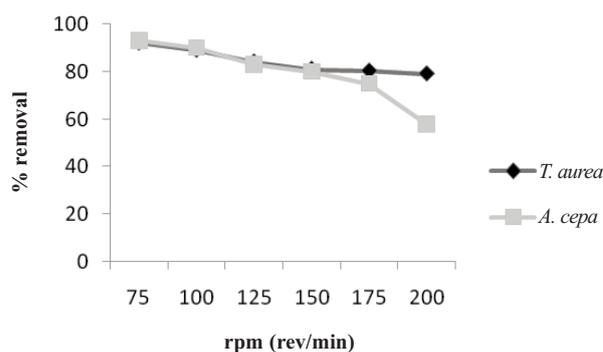Fig. 8. Pseudo second-order kinetics for *T. aurea*.

Fig. 9. Effects of various rpm on *T. aurea* and *A. cepa*.

Table 2. Effect of various pH on removal of Cr(VI) using *T. aurea* and *A. cepa*.

pH	*T. auria* % removal of Cr(VI)	*A. cepa* % removal of Cr(VI)
3	87	87
4	90	82
5	96.45	80
6	86	78
7	76	76

Table 3. Effect of various concentrations on removal of Cr(VI) using *T. aurea* and *A. cepa*.

Concentrations (mg/L)	*T. auria* % removal of Cr(VI)	*A. cepa* % removal of Cr(VI)
50	67	60
75	57	73
150	75	85
50	67	60

Table 4. Effect of various dosages on removal of Cr(VI) using *T. aurea* and *A. cepa*.

Dosage (ml)	*T. auria* % removal of Cr(VI)	*A. cepa* % removal of Cr(VI)
5	80	90
7	86	94
10	92	95
15	92	94

Effect of Dosage

The percentage of Cr(VI) removal was found to be increased with an increase in the adsorbent amount from 5 g·L⁻¹ to 15 g·L⁻¹, respectively. The percentage removal of Cr(VI) with the amount of adsorbent and adsorption percentage was shown in Figs. 11 and 12. The increase in Cr(VI) removal was due to the increase in surface area and adsorption sites available for adsorption [2]. With adsorbent 15 g·L⁻¹ at the concentration of 50 mg·L⁻¹ the % removal was found to be 92 and 94 for *T. aurea* and *A. cepa,* respectively (Table 4 and Fig. 12).

Adsorption Equilibrium

The adsorption equilibrium defines the distribution of a solute phase between the liquid phases and solid phases after the adsorption reaction reached equilibrium condition. In the present study, equilibrium studies were carried out at room temperature. The equilibrium data were analyzed

using the following isotherm equations and the values are shown in Tables 5-7.

The isotherms such as Langmuir, Freundlich, Temkin [15], and kinetic studies were studied for *T. aurea* and *A. cepa* and the R^2 were shown in Table 5 monocot plant *A. cepa* tunic shows better results than dicot plant *T. aurea*.

Dubinin-Radushkevich isotherm showed that the adsorption of chromium (VI) in *T. aurea* and *A. cepa* were physical adsorption. R^2, and E (mean free energy) were shown in Table 5, Fig. 4.

The pseudo first-order rate constant K_1 can be obtained from the slope of plot between log (q_e-q) *versus* time, *t* at the concentration of 50, 75, and 150 mg/L for *T. aurea* and *A. cepa.* The calculated K_1 values and their corresponding linear regression correlation coefficient values are shown in Tables 6 and 7.

A plot between t/q_t versus t gives the value of the constant K_2 (g·(mg·min)⁻¹), and also q_e (mg/g) can be calculated at the concentration of 50, 75, and 150 mg/L for *T. aurea* and *A. cepa.* The pseudo second-order rate constant K_2, the calculated q_e, value and the corresponding lin-
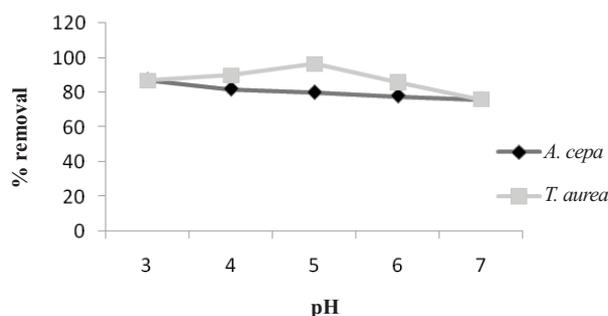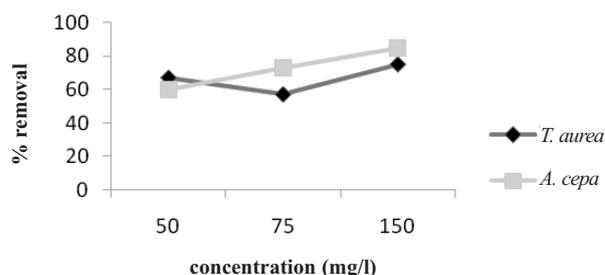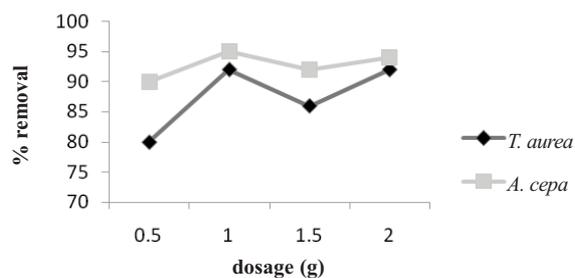

Fig. 10. Effect of various pH on *T. aurea* and *A. cepa.*

Fig. 11. Effect of various concentrations on *T. aurea* and *A. cepa.*

Fig. 12. Effect of various dosage on *T. aurea* and *A. cepa.*

Table 5. Adsorption Equilibrium of Langmuir, Freundlich, Temkin and isotherm.

Adsorbent			
T. aurea	Langmuir Isotherm		
	q_m (mg/g)	b (L/mg)	R^2
	1.006	0.177	0.994
	Freundlich Isotherm		
	K_F (mg/g)	n	R^2
	1.049	7.352	0.298
	Temkin Isotherm		
	A (L/g)	b (J/mol)	R^2
	50.5	10.51	0.853
	Dubinin-Radushkevich Isotherm		
	R^2	K_{DR} (Mol²/KJ²)	E (KJ/mol)
	0.548	6187	0.0089
A. cepa	Langmuir Isotherm		
	1.269	0.294	0.990
	Freundlich Isotherm		
	K_F (mg/g)	n	R^2
	1.388	3.311	0.931
	Temkin Isotherm		
	A (L/g)	b (J/mol)	R^2
	3.05	0.55	0.971
	Dubinin-Radushkevich Isotherm		
	R^2	K_{DR} (Mol²/KJ²)	E (KJ/mol)
	0.932	1408	0.0188

ear regression correlation coefficient values R^2 are given in Tables 6 and 7.

Conclusions

From the previous literature we compared the results of Gholami and Mahvi [2, 20], who reported that Dicotyledon plant species such as plataneus *Orientalis* leaves, plant *Ulmus* leaves and Acharya et al. [22] and the Tamarind wood gives maximum removal percentage of 5.01 (mg/g) (pH=7.0, 24ºC, 120 min), 0.9 (mg/g) (pH=6.0, 24ºC, 60 min), 22 to 82% at 50 mg/l initial feed concentration, respectively, whereas as *T. aurea* gives maximum removal of 92%. In Monocotyledon plant species such as Sugarcanebagasse, Maizecob (Sharma, D. C) ricehulls (CiCi, Mechmet) 13.4 (mg/g), 13.8 (mg/g), 99-38%, were as *A. cepa* gives maximum removal of 94%.

From a comparison of the above results we can conclude that the adsorption of Cr(VI) was carried out at 50, 75, and 150 mg/L as Initial Cr(VI) ion concentration for a period of 5 hours at pH 5, 3 (*T. aurea* and *A. cepa*), adsorbent: 10 g/l. *T. aurea* and *A. cepa* shows 75% and 85% removal at 150 mg/L. the adsorbent amount from 5 g·L⁻¹ to 15 g·L⁻¹ with adsorbent 15 g·L⁻¹ at the concentration of 50 mg·L⁻¹ the rercent removal was found to be 92 and 94 for *T. aurea* and *A. cepa* respectively. From the investigation we concluded that *T. aurea* maximum percentage removal was noticed at pH 5, adsorbent: 10 mg/L, shaking period: 75 rpm, initials concentration 150 mg/L were as maximum percentage removal for *A. cepa* were obtained at pH 3, adsorbent: 10 mg/L, shaking period: 75 rpm, initials concentration: 150 mg/L. Finally both Monocotyledon (*Allium cepa*) tunic and Dicotyledon plant (*Tabebuia aurea*) gave the better removal percentage in high concentration.

Table 6. Pseudo first-order rate constant for *T. aurea*.

T. aurea								
C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	First-order model			Second-order model		
			K_1	q_e (mg/g)	R^2	K_2	q_e (mg/g)	R^2
50	16.5	1.675	0.25	1.12	0.879	0.224	1.828	0.488
75	21.5	1.425	0.64	1.12	0.918	1.505	1.464	0.965
150	12.5	1.875	0.33	1.47	0.621	0.398	2.409	0.857

Table 7. Pseudo first-order rate constant for *A. cepa*.

A. cepa								
C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	First-order model			Second-order model		
			K_1	q_e (mg/g)	R^2	K_2	q_e (mg/g)	R^2
50	20	1.5	0.20	2.31	0.838	0.004	7.19	0.007
75	13.5	1.825	0.99	2.57	0.947	1.540	1.915	0.984
150	7.5	2.125	0.56	2.40	0.878	10.86	2.398	0.909

Acknowledgements

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