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Studies on the application of algae biomass as an adsorbent in the treatment of industrial Azadirachtin insecticide wastewater

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ABSTRACT

This study experimented with the sorption ability of the freshwater algae biomass, *Ottelia alismoides*, by removing color and chemical oxygen demand (COD) from industrial Azadirachtin insecticide wastewater. The differing factors affecting the uptake behavior like biomass dosage (0.05–0.25 g), initial pH (2.0–8.0) and temperature (30°C–60°C) were investigated. The samples of varying initial concentrations of bio-insecticide wastewater maximum COD removal efficiency range from 86% to 96% at the end of 330 min. *Ottelia alismoides* biomass showed maximum degradation and color removal efficiency at 30°C, pH of 5 and biomass dosage of 0.15 g. The isotherm models analyzed the equilibrium data. Experimental kinetic data were assessed using the surface and kinetic diffusion models. This study concluded that *Ottelia alismoides* biomass could be employed as an effective biosorbent material for removing pollutants from bio-insecticide wastewater.

Keywords: Bio-insecticide wastewater; Azadirachtin; *Ottelia alismoides*; Adsorption isotherms; Kinetic models

1. Introduction

Between 1900 and 2000, the world's population grew from 1.5 to 6.9 billion people, increasing food demand and putting strain on agricultural industries. Pesticides are used in modern agriculture to boost productivity to commercially viable levels. Industrial, agricultural, mining, and urban wastewaters pollute rivers, resulting in higher quantities of pesticides from agricultural and landscaping sources [1].

In addition to home wastewater, firms that manufacture chemicals and pesticides generate their pesticides-production wastewater. Before being mixed with domestic wastewater, pesticide-production effluent must undergo extensive treatment. As a result of their high concentrations and recalcitrance in water, pesticide treatment from water sources is a critical research domain [2].

Researchers have attempted physical, chemical and biological techniques to treat the pesticide wastewater before disposal. The methodologies include (i) physical – membrane technology, physical adsorption, (ii) chemical-iron enhanced sand filters, chlorination, advanced oxidation, (iii) biological – degradation by immobilized laccases, constructed wetland and treatment using hybrid technologies [3,4].

Owing to the ever-increasing need for water, much attention has been put on wastewater recovery and reuse. There still are four million known chemicals in the chemical environment, including a large proportion of unknown substances. More than 2,000 chemical contaminants have been discovered in wastewater, with roughly 750 of them recognized in drinking water [5,6]. Adsorption, chemical oxidation, complexation, distillation, gas-stripping, ion exchange, precipitation, remediation, reverse osmosis and solvent extraction are all alternatives for eradicating these

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toxic compounds. Biosorption has proven to be an effective way to eliminate hazardous pollutants from the aquatic ecosystem [7–9].

Biosorbents are low-cost filter materials that have a lot of affinity and capacity. The majority of research on the removal of metals, color, and chemical compounds from aqueous solutions has focused on biological separation methods [10,11]. The efficient removal of heavy metals [12], rare earth elements [13], nuclear waste [14], dyes [15], antibiotics, pesticides [16] and carbon dioxide migration [17] have been attempted using biosorption. As biosorbents, microorganisms including algae, bacteria, yeasts, fungi, plant leaves, and other tissues can be employed to detoxify and recover hazardous or precious metals from industrial wastes. Algae [18,19] is one of the most promising biosorbents.

A green alga *Cladophora sericea* was attempted to adsorb the Cu(II), Co(II), and Zn(II) ions [20]. A synthetic metribuzin aqueous solution, a pesticide was treated effectively using biochar, and biochar is identified as an excellent adsorbent in the removal of dye, heavy metals and toxic pollutants [21,22].

Azadirachta indica, a Neem tree, is majorly found in India. Neem products, especially Neem oil, are used to kill some insects, pests on plants. It is also considered a commercial growth regulator [23]. Azadirachtin is an insecticide that is extracted from the Neem seed using chemical solvents, namely ethanol. Approximately a gram of Neem kernel consists of 2–4 mg of Azadirachtin. Though the origin is a bio-component, the extraction methodologies add toxicity to it. So the wastewater that comes from the Azadirachtin insecticide unit is to be treated before disposal [23].

Ottelia alismoides, commonly known as duck lettuce belongs to the family of *Hydrocharitaceae*, is a rooted aquatic herb that is completely submerged, which is used as an adsorbent in this study. The objectives of the current study are (i) to examine the suitability of the selected adsorbent *Ottelia alismoides*, in the treatment of Azadirachtin insecticide wastewater and (ii) to evaluate the optimum experimental conditions to yield the maximum pollutant removal efficiency.

2. Materials and methods

2.1. Chemicals

For every run, only analytical reagent (AR) grade chemicals were used. Chemicals were utilized for the modification of adsorbent, to change the initial pH of wastewater and the analysis of chemical oxygen demand.

2.2. Biosorbent

The freshwater algae, *Ottelia alismoides*, used in this study was collected from a Thillaividangan, Tamil Nadu, India (Fig. 1). The collected sample was washed thoroughly and the leaves alone were used. The leaves were sun-dried for 3 d. The dried-up biomass was ground into powder of 0.5 mm sieve size using a kitchen blender. The powder was dried once more in a 60°C oven for 6 h.

The powder was treated with 2.0 N HCl for 24 h for further study. The treated powder was filtered and rinsed with distilled water after that. The sample was dried again in a 70°C oven for 6 h until wrapped in plastic bags and stored in desiccators.

2.3. Substrate

The effluent was collected at Cuddalore, Tamil Nadu, India, from the bio-insecticide manufacturing industry. Table 1 lists the physicochemical properties of the samples.

2.4. Experimental procedure

Investigations were performed out in batch reactors with 100 mL of bio-insecticide effluent and a known quantity of biomass (dry matter) under continual agitation (200 rpm) in an incubator rotary shaker to ascertain the contact time required for equilibrium sorption investigations. Samples (10 mL) were gathered at specified intervals, filtered (Millipore 0.45 m pore size), and color and chemical

Table 1
The physicochemical characteristics of bio-insecticide wastewater

Parameters	Concentration (mg/L)
pH	5.0–6.0
Colour	Yellowish
Biochemical oxygen demand	4,000
Chemical oxygen demand	14,000
Total dissolved solids	300
Total suspended solids	150
Total solids	2,100

Fig. 1. *Ottelia alismoides* – freshwater algae.

oxygen demand (COD) were assayed using traditional protocols [24].

Batch equilibrium studies were conducted for 330 min at various biomass dosages (0.05–0.25 g), initial substrate concentrations (2,000–10,000 mg COD/L), initial pH of 2.0–8.0, and temperatures ranging from 30–60°C. To modify the initial pH, NaOH and HCl solutions were applied, and this control was repeated every hour.

2.5. Performance analysis

The treated samples were analyzed for color, using a UV-Visible spectrophotometer (λ_{max} 216 nm) and chemical oxygen demand (COD) by the conventional dichromatic reflux method. The experiments were triplicated to confirm the reproducibility and the plots were made for averaged values.

3. Results and discussion

3.1. Effect of contact time

Equilibrium time is influenced by the nature of adsorbent and adsorbate in the biosorption system. By scanning through the literature it was observed that the equilibrium time was ranged between 15 min to 10 d in various biosorption systems [25].

Figs. 2a & b and 3a & b show the effect of contact time on the biosorption of bio-insecticide effluent using freshwater algae, *Ottelia alismoides*. The biosorption increased gradually with contact time irrespective of the initial concentration of effluent (Fig. 2), biomass dosages (Fig. 3) and reached the equilibrium at 330 min. Based on the observations 330 min was marked as an effective contact time for the given conditions. Figs. 2b and 3b revealed that the COD removal effectiveness of *Ottelia alismoides* was rapid at the initial span due to the availability of enough active sites, but after that became slow and stagnant as contact duration increased. The graphic trend shows that sorption can be divided into two stages: a high sorption rate (a fast surface reaction) and a much slower sorption rate (slow diffusion into the cells) [26].

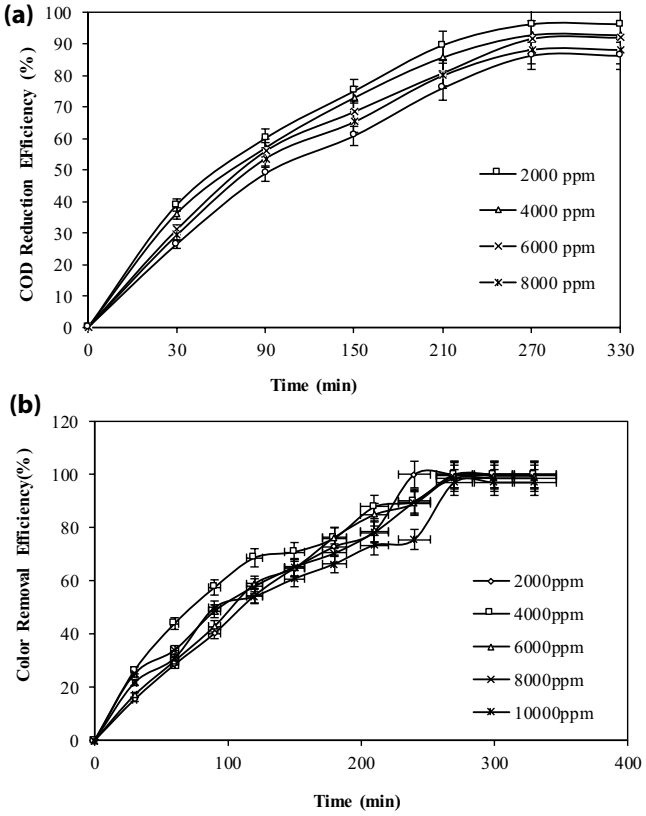

Fig. 2. (a) Effect of time on COD reduction efficiency for different initial concentrations and (b) effect of time on color removal efficiency for different initial concentrations.

3.2. Effect of chemical treatment

The batch adsorption experiments were also carried out using treated (alkali and acid wash) and untreated biomass. For the initial concentration of bio-insecticide effluent with 10,000 mg COD/L, the steady-state value of COD removal efficiency was 22%, using 0.15 g of untreated *Ottelia alismoides* biomass under shaking at the end of 330 min. The steady-state values of COD removal efficiencies were 50% and 86.17%, respectively, for alkali-washed and acid-washed

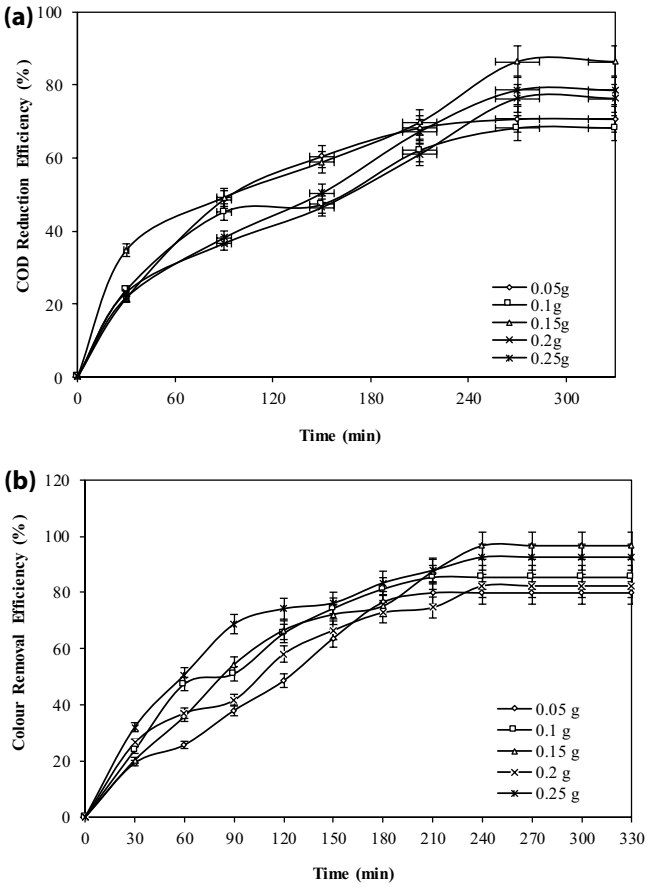

Fig. 3. (a) Effect of time on COD reduction efficiency for different biomass loading (*Ottelia alismoides*) and (b) effect of time on color removal efficiency for different biomass loading (*Ottelia alismoides*).

Ottelia alismoides biomass under shaking at the end of 330 min (Fig. 4). The results revealed that the acid treatment could exhibit the treatability of the biosorbent efficiently. It was supported by the previous studies where the performance of sorbents was evaluated with chemical modification [27].

3.3. Effect of effluent initial concentration

The steady-state values of COD removal efficiency for the five different initial concentrations of bio-insecticide effluent, such as 2,000; 4,000; 6,000; 8,000; 10,000 mg COD/L, were 96.18%, 92.69%, 91.92%, 88.03%, and 86.17%, respectively, using 0.15 g of *Ottelia alismoides* biomass under shaking at the end of 330 min. The steady-state color removal efficiencies were 100%, 100%, 99.52%, 98.59% and 97%, respectively (Fig. 5). With the increase in initial concentration, the equilibrium COD and color removal efficiencies decreased.

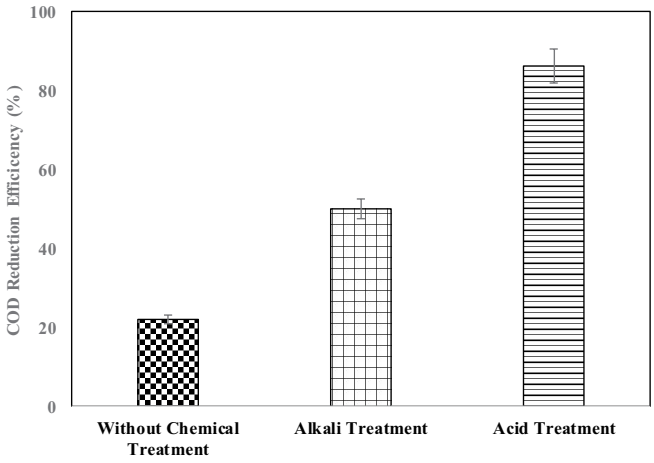

Fig. 4. Effect of chemical treatment on COD reduction efficiency.

The reason behind this trend was, the available number of pollutant molecules are hiked with the initial concentration of the effluent, which could not be treated using the limited quantity of the adsorbent. So at higher concentrations, the removal efficiencies were declined [28].

3.4. Effect of biomass dosage

The experiment was carried out for an initial concentration of 2,000 mg COD/L, for the different biomass dosage values, such as 0.05, 0.1, 0.15, 0.2 and 0.25 g and the corresponding equilibrium COD removal efficiencies were 72.94%, 72.65%, 81.0%, 76.37% and 78.59%, respectively, at the end of 330 min. The corresponding steady-state colour removal efficiencies were 79.84%, 85.37%, 96.65%, 82.23% and 92.58% (Fig. 6a). The color removal efficiency grew as the biomass loading was elevated from 0.05 to 0.15 g due to the availability of more active adsorbing sites for the same constant volume of effluent [29]. The color removal performance dropped as the biomass dosage was upped from 0.15 to 0.25 g either due to the non-existence of pollutants or the block of active sites on adsorbent. The comparison of COD and color removal at the optimum dose is given in Fig. 6b.

3.5. Effect of temperature

The effect of temperature on COD and color removal efficiency are shown in Fig. 7a and b. The steady-state COD and color removal efficiencies were 85.99%, 70.88%, 76.59% and 68.33% and 96.45%, 88.38%, 86.77% and 82.35%, respectively and the corresponding temperatures were 30°C, 40°C, 50°C and 60°C. The experiment was carried out for the initial concentration of 2,000 mg COD/L, ranging from 30°C to 60°C in the increment of 10°C. The maximum COD and color removal efficiencies occurred at 30°C and were 85.99% and 96.45%, respectively and poor degradation at higher temperatures might be due to the mesophilic nature of

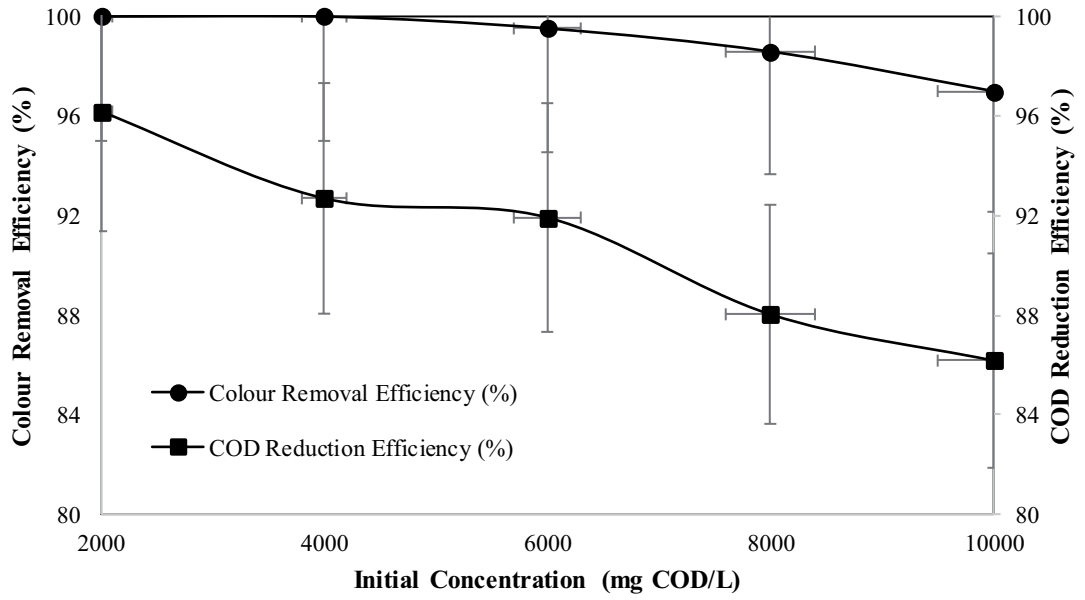

Fig. 5. Effect of initial concentration on removal efficiency.

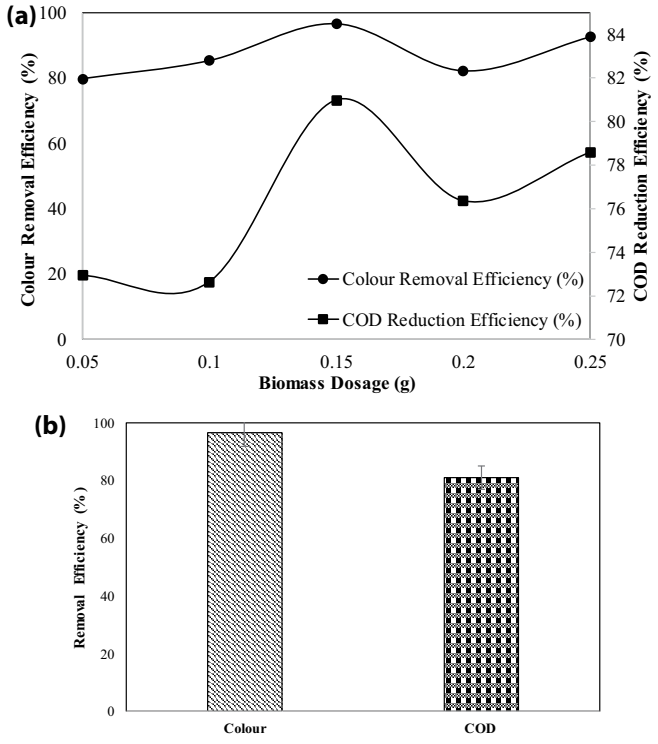

Fig. 6. (a) Effect of biomass dosage (*Ottelia alismoides*) on removal efficiency and (b) performance analysis at optimum biomass dosage.

alga. Fig. 7c shows a comparison of steady-state COD and color removal efficiency at different operating temperatures, where the lower temperature ranges caused higher adsorption. Since the adsorption is decreasing at higher temperatures, it is exothermic [30].

3.6. Effect of initial effluent pH

The effect of initial pH on the adsorption process was studied at acidic and basic pH ranges. The steady-state values of (i) COD removal efficiency were 72.65%, 65.15%, 76.08%, 84.49%, 81.53%, 80.27% and 68.38% and (ii) color removal efficiency were 65.39%, 80.55%, 96.38%, 99.73%, 93.45%, 90.76% and 89.99% respectively (Fig. 8a and b).

The COD and color removal efficiencies were maximum at the initial pH of 5. The uptake of organic matter is less due to H^+ ions suppressing the ionization of organic matter. From Fig. 8c, it was found that a pH of 5.0 is optimum for maximum COD and color removal efficiency. Carboxyl and sulfate groups have been identified in alga. At a pH of 5, these groups generate negatively charged surface and electrostatic interactions between cationic species. This surface could be responsible for better pollutant adsorption.

Similar to the present investigation, the optimal pH range was from 4.5 to 6.5 for *Candida tropicalis* in the treatment of high carbohydrate wastewater [31]; also, biosorbent *Ulva fasciata* sp. works better in the pH range 2.5–5 [32]. In the removal of tetracycline (TC) with the help of zero-valent iron, the effect of initial pH on (i) adsorption, (ii) oxidation and (iii) reduction was also marked [33].

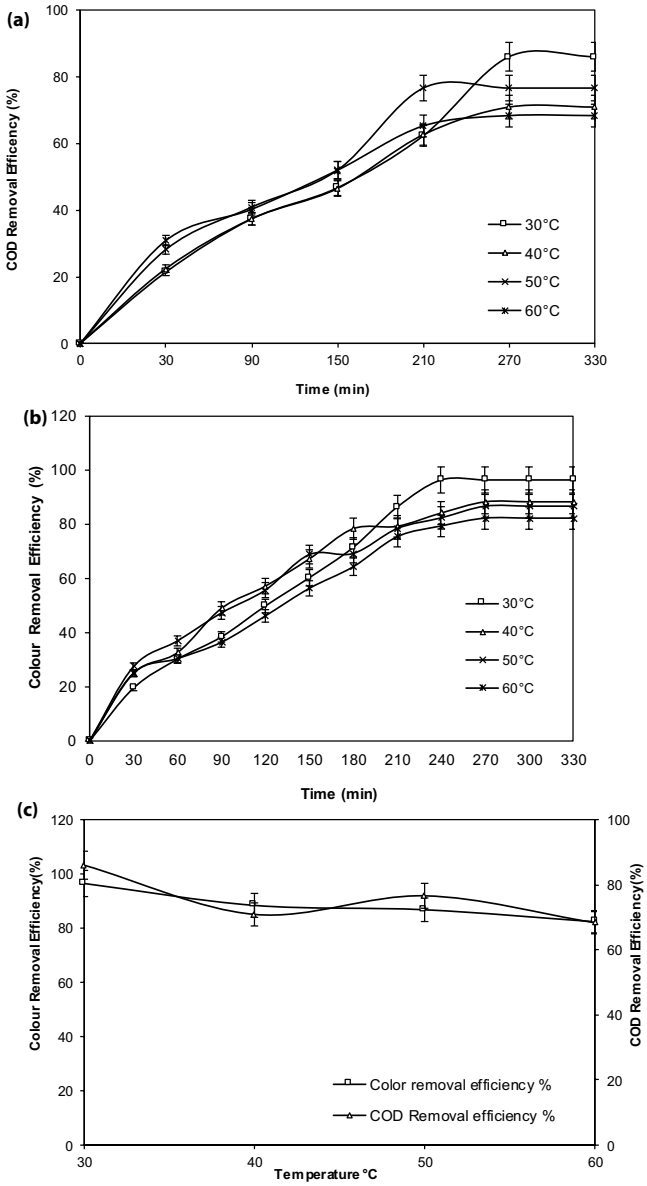

Fig. 7. Effect of temperature on (a) COD reduction efficiency and (b) color removal efficiency. (c) Comparison of the effect of temperature on steady-state removal efficiencies.

3.7. Effect of biosorbent size

The four different biosorbent sizes, such as 14, 18, 22 and 60 mesh, with the corresponding particle diameter (μm) 1307, 1000, 775, 250 were selected for the study. The equilibrium values of COD removal efficiencies were 75.42%, 78.45%, 86.0% and 76.92% (Fig. 9a), and the colour removal efficiencies were 86.44%, 76.33%, 88.37% and 78.58%, respectively (Fig. 9b). The COD and color removal efficiency decreased with an increase in particle size of the biosorbent. The equilibrium removal efficiencies at different biosorbent sizes are compared in Fig. 9c.

The experimental results indicated that the larger the biomass particles, the higher the COD and color removal efficiency. Akin outcomes were found in the high adsorption performance of phosphate using $CaCO_3$ cake [34].

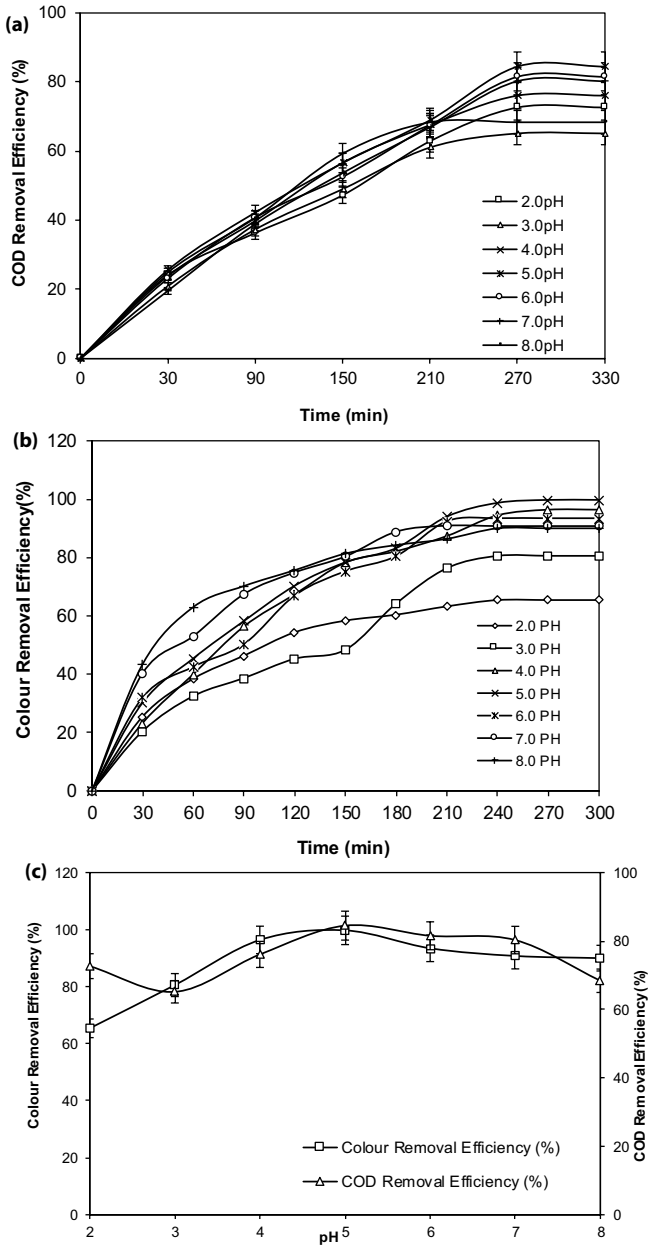

Fig. 8. Effect of initial pH on (a) COD reduction efficiency and (b) color removal efficiency. (c) Comparison of the effect of initial pH on steady-state removal efficiencies.

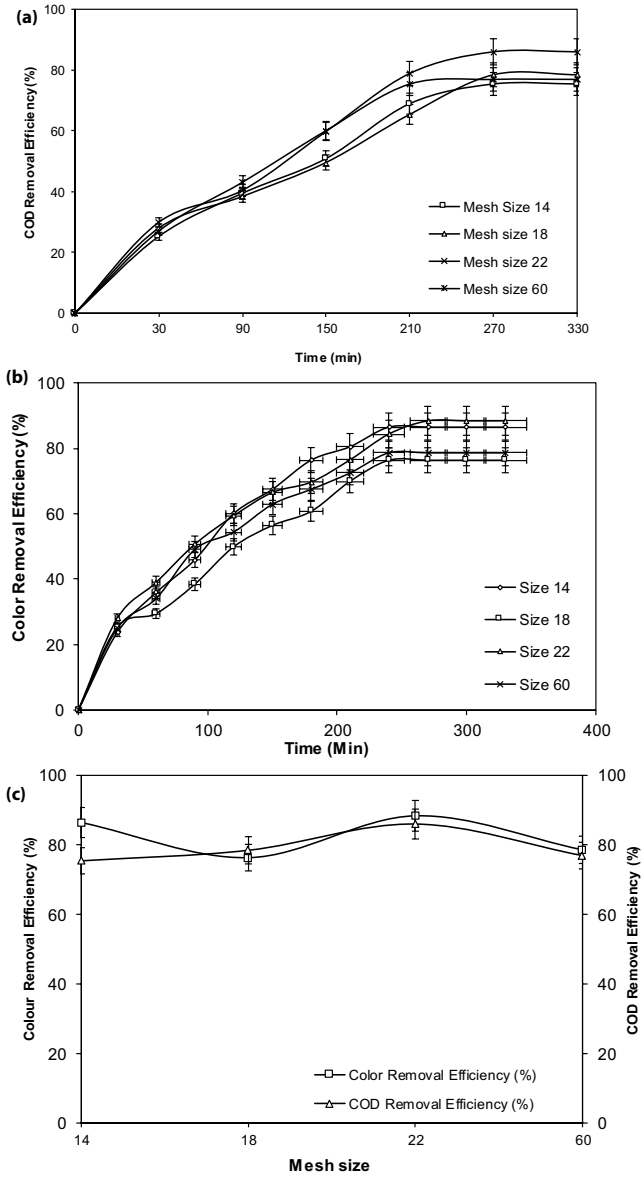

Fig. 9. Effect of *Ottelia alismoides* size on (a) COD reduction efficiency and (b) color removal efficiency. (c) Comparison of the effect of biosorbent size on steady-state removal efficiencies.

3.8. Equilibrium study

Fitting the data points with models, mainly for the description of isotherm adsorption equilibrium, is common in describing the process's equilibrium. The non-linear form of the two-parameter adsorption isotherm models are listed in Table 2a and the model parameters are summarized in Table 2b [35].

Generally, Langmuir adsorption isotherm is used to quantify the adsorptive capacity of an adsorbent for the selected pollutants. In this current study, from the various initial concentration of the solutions, the equilibrium data were fitted into the model equation. From the slope and intercept of the linearized plot, the model parameters were calculated and listed in Table 2b. The noted inference is that the lower (<1) Langmuir adsorption constant k_L values indicated the higher affinity between the adsorbent and the pollutant. The monolayer adsorption capacity was confirmed to be 500 mg/g, which was a very high value. The R_L separation factor, which is between 0 and 1, shows that the adsorption circumstances are favorable. Furthermore, the model's suitability (Fig. S1a) was validated by the greater relation coefficient value (R^2 = 0.9767) [36].

An empirical correlation used for the Freundlich isotherm model (Fig. S1b) is used to explain the monolayer and multilayer coverage of adsorption. The model constants k_F and n_F constants were marked as 143.2 and 1.952, respectively. The values of n greater than 1 indicate a favorable

Table 2a
Two-parameter adsorption isotherm model

	Non-linear form	Linear form	Parameters
Langmuir	$q_e = \frac{q_L k_L C_e}{1 + k_L C_e}; R_L = \frac{1}{1 + k_L C_0}$	$\frac{1}{q_e} = \frac{1}{q_L k_L}\frac{1}{C_e} + \frac{1}{q_L}$	k_L (L/mg) q_L (mg/g) R_L
Freundlich	$q_e = k_F C_e^{1/n_F}$	$\log q_e = \frac{1}{n_F}\log C_e + \log k_F$	n_F (g/L) k_F (L/g)
Temkin	$q_e = \frac{RT}{b_T}\ln\left(k_T C_e\right)$	$q_e = \frac{RT}{b_T}\ln C_e + \frac{RT}{b_T}\ln k_T$	b_T (J/mol) k_T (L/g)
Dubinin–Radushkevich	$q_e = Q_s e^{\left(-\beta\varepsilon^2\right)}; \varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right)$	$\ln q_e = -\beta\varepsilon^2 + \ln Q_s$	Q_s (mg/g) β (mol²/kJ²)

Table 2b
Two-parameter adsorption isotherm parameters

Model	Parameters		Inference [32]
Langmuir	k_L (L/mg)	0.0043	<1 High-affinity
	q_L (mg/g)	5,000	High adsorption capacity
	R_L	0.0227	$0 < R_L < 1$ favorable
	R^2	0.9767	
Freundlich	n_F (g/L)	1.952	1–10 favorable
	k_F (L/g)	143.2	>1 Higher affinity and heterogeneity
	R^2	0.9927	
Temkin	b_T (J/mol)	4.845	
	k_T (L/g)	2.04E-05	High adsorption capacity
	R^2	0.9613	
Dubinin–Radushkevich	Q_s (mg/g)	4,919	
	β (mol²/kJ²)	0.043	High adsorption capacity
	R^2	0.8863	

Freundlich isotherm adsorption condition observed in our study. The higher affinity and the heterogeneity behavior were confirmed from the values of k_F [37].

The influence of implied synergy between adsorbent and adsorbate in the adsorption process is described in the Temkin isotherm model. The basic assumption behind this model is that the heat of adsorption of the pollutant decreases linearly, which ends in increases in surface coverage. The model parameters such as b_T, k_T were calculated from the slope and the intercept of Fig. S1c and given as 4.845×10^{-5} and 2.04×10^{-5}, respectively. The fit of the model was also assured by the higher R^2 (0.9613) value [38].

Dubinin–Radushkevich model is a more generic expression that gives an idea about the porosity of the biomass dose, adsorption energy, and energy sharing on heterogeneous surfaces. A discriminating behavior of this model is temperature-dependent. The activity coefficient β (0.043 mol²/kJ²) and adsorption capacity (4,919 mg/g) were calculated from Fig. S1d [39]. The linear regression correlation R^2 values are in the order of Freundlich (0.9927) > Langmuir (0.9767) > Temkin (0.9613) > Dubinin–Radushkevich (0.8863).

3.9. Kinetics analysis

The pollutant removal mechanism from the Azadirachtin insecticide wastewater and the possible rate controlling parameters are explained through kinetic models. The linear form of kinetic equations is listed in Table 3a and its model parameters are summarized in Table 3b.

Usually, the first-order kinetic model, pseudo-first-order kinetic model, second-order model, pseudo-second-order kinetic model and Elovich models were used to understand the surface reaction kinetics [40]. The existence of intercept indicated the unfit of the first-order kinetic model to the treatment process. The concealed values of experimental and predicted q_e values expressed the unsuitability of the second-order kinetic model. However, the pseudo-first-order kinetic model exhibited a good correlation among the q_e experimental and predicted. The calculated regression coefficients (Fig. S2a) were high for all the different initial concentration values ($0.966 > R^2 > 0.99$) (Table 3b) [41].

The plot for the pseudo-second-order kinetic model is shown in Fig. S2b. The slopes and intercept values listed

in Table 3b indicate the pollutant's transport behavior towards the adsorbent. The equilibrium uptake of the adsorbent was escalating with the initial concentration due to the pollutant load. The higher R^2 values support the model's assumption that adsorption is due to chemisorption by proving that the adsorption data are well represented by pseudo-second-order kinetics [36].

Elovich equation primarily helps to explain the adsorption phenomena by highly heterogeneous adsorbents (Fig. S2c). The larger values of model parameters α_E (>1) and the smaller value of β_E (<1) are the indicators of heterogeneity being of the adsorbent and the non-occurrence of chemisorption, respectively. A curve for an adsorbent was noticed to be linear with a good correlation coefficient [42].

The rate-controlling step of the treatment process was identified with the aid of kinetic diffusion models, that is, the intraparticle diffusion model [40]. The intraparticle diffusion model was used to check the contributions of each diffusion step in the overall mass transfer mechanism. In the drawn plot (Fig. S2d), the line slips to cross through the origin. This behavior indicates that along with intraparticle diffusion, film diffusion also dominates the treatment process to some extent. The correlation coefficient ($R^2 > 0.98$) was in good agreement with the model parameters [43].

Table 3a
Linear form of kinetic models

Models	Linear equation
Pseudo-first-order kinetic model	$\log\left(q_e - q_t\right) = \frac{k_1}{2.303}t + \log q_e$
Pseudo-second-order kinetic model	$\frac{t}{q_t} = \frac{1}{k_2 q_e}t + \frac{1}{k_2 q_e^2}$
Elovich kinetic model	$q_t = \frac{1}{\beta_E}\ln\left(\alpha_E\beta_E\right) + \frac{1}{\beta_E}\ln t$
Intraparticle diffusion model	$q_t = k_{id}t^{0.5} + I$

4. Conclusion

The results of the current study demonstrated that the freshwater algae biomass, *Ottelia alismoides* could be exploited for the pollutant removal from the industrial Azadirachtin insecticide wastewater. The recommended conditions to reach the maximum pollutant removal are summarized as acidically modified 0.15 g of biomass of 22 mesh size; at initial pH 5 and 30°C used for 1 L of effluent. The maximum adsorption capacity of the adsorbent was calculated as 500 mg/g using adsorption isotherm parameters. The isotherm model values confirmed the affinity between the pollutants and adsorbent and the suitability of the material as an adsorbent. The surface and diffusion kinetic model parameters affirmed the heterogeneous nature of the adsorbent and the non-occurrence of the chemisorption. Both the film diffusion and the intraparticle diffusion exhibited its rate-controlling step of the treatment process.

Symbols

b_T	—	Temkin heat of sorption, J/mol
C_0, C_e, C_t	—	Concentration of the solute, at t = 0, at equilibrium and time 't' in the effluent, mg/L
I	—	Thickness of the boundary layer, mg/g
k_F	—	Adsorption capacity from Freundlich model, L/g
k_{id}	—	Kinetic rate constant in the intraparticle diffusion model, mg/g $min^{0.5}$
k_L	—	Langmuir adsorption constant, L/mg
k_T	—	Temkin isotherm constant, L/g
k_1	—	Rate constant for the pseudo-first-order sorption, min^{-1}
k_2	—	Rate constant of the pseudo-second-order kinetic equation in, g/mg min
m	—	Total mass of adsorbent, g
n_F	—	Adsorption intensity from Freundlich model, g/L
q_t, q_e	—	Total quantity of pollutant adsorbed at time 't' and equilibrium, mg/g
q_L	—	Monolayer adsorption capacity from Langmuir model, mg/g

Table 3b
Kinetic model parameter values

Initial conc. (mg COD/L)		2,000	4,000	6,000	8,000	10,000
	R^2	0.966	0.98	0.99	0.977	0.978
Pseudo-first-order	k_1	0.0115	0.00921	0.00922	0.00921	0.00921
	q_e (eqn)	1,330	2,495	3,589	4,721	5,768
	R^2	0.989	0.987	0.990	0.991	0.985
Pseudo-second-order	q_e (eqn)	1,269	2,733	5,025	3,800	15,600
	k_2	0.0131	0.0122	0.00995	0.0132	0.00641
	R^2	0.917	0.94	0.917	0.92	0.884
Elovich	α_E	143	297	387	504	534
	β_E	0.0041	0.0022	0.0015	0.0012	0.0010
	R^2	0.982	0.983	0.989	0.987	0.99
Intraparticle diffusion	k_{id}	78.87	147.1	215.6	275	335.4
	I	33.81	126.6	80.25	126.3	45.87

Q_s	—	Maximum adsorption capacity, mg/g
R	—	Gas constant, 8.314 J/mol K
R^2	—	Correlation coefficient
R_L	—	Separation factor
t	—	Time, min
T	—	Absolute temperature, K
V	—	Volume of the effluent, L
α_E	—	Initial adsorption rate in the Elovich model, mg/mg
β	—	Activity coefficient, mol^2/kJ^2
β_E	—	Desorption constant in the Elovich model, g/mg
ε	—	Polanyi potential, J g/mol mg

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Supplementary information

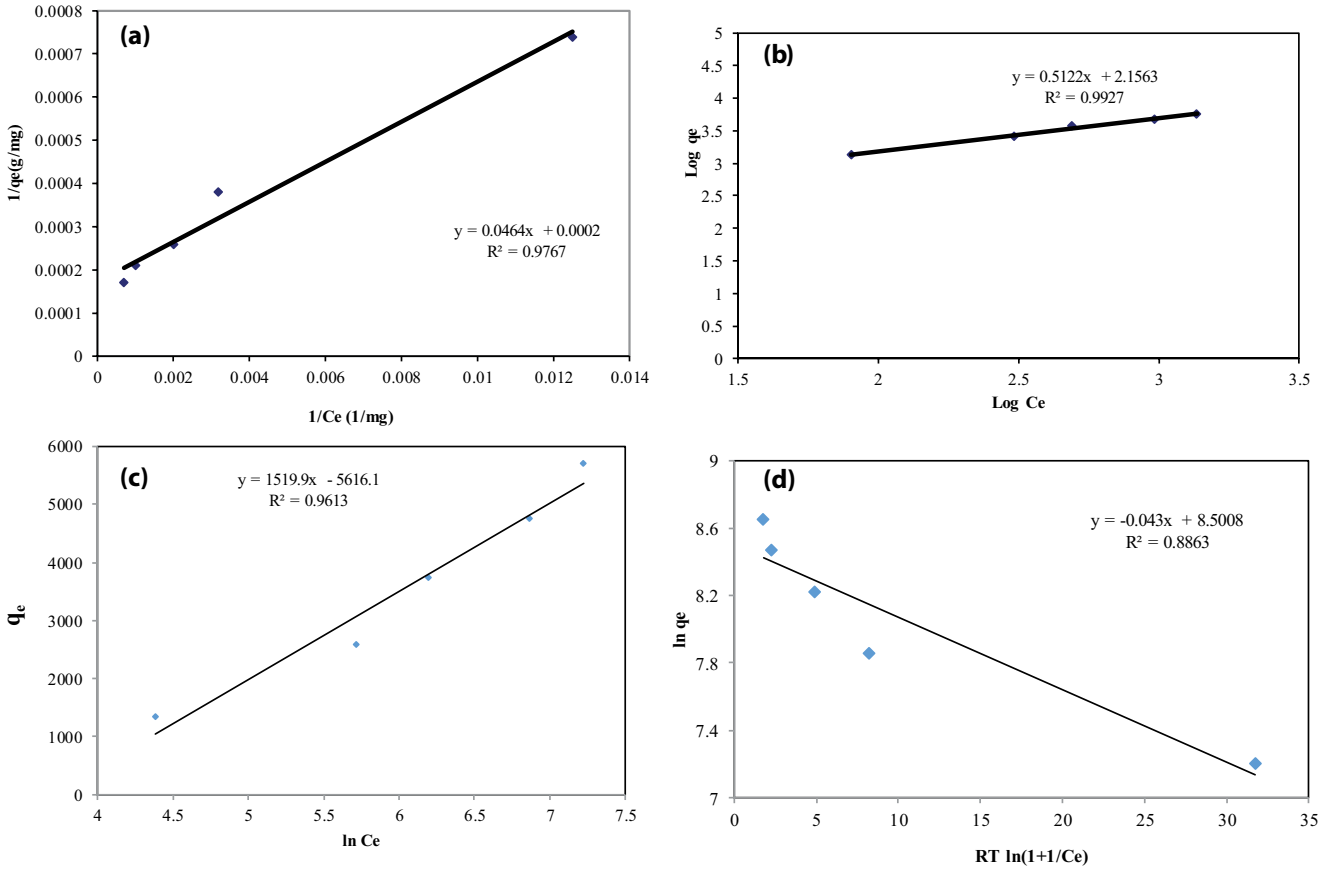

Fig. S1. (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin–Radushkevich adsorption isotherm.

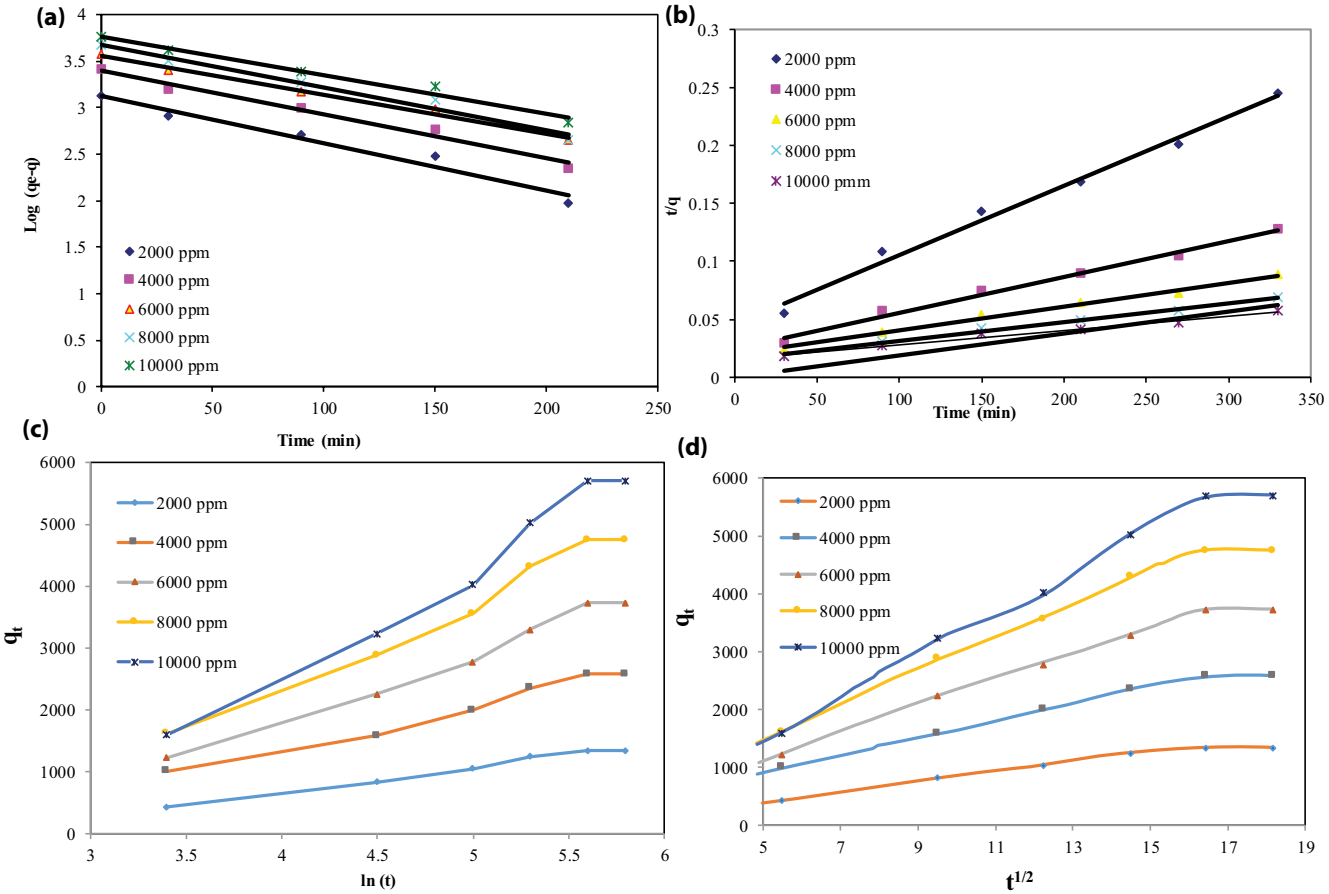

Fig. S2. (a) Pseudo-first-order, (b) pseudo-second-order, (c) Elovich, and (d) intraparticle diffusion kinetic model.