RESEARCH ARTICLE

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Application of Azolla for 2, 4, 6-Trichlorophenol (TCP) Removal from Aqueous Solutions

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Background & Aims of the Study: The 2, 4, 6-Trichlorophenol (TCP) is a phenolic compound which it can produce adverse effects on human and environment. Therefore, the removal of these compounds is necessary. The aim of this study is the investigation of TCP removal by using Azolla filiculoides biomass.

Materials & Methods: The Azolla biomass was dried in the sunlight, and then it was crushed and sieved to particle sizes in range of 1-2 mm. Next treated with 0.1M HCl for a period of 5h. The Azolla was washed with distilled water and it was used as adsorbent. The effect of operating parameters such as pH, contact time, TCP concentration and adsorbent dose on the TCP removal efficiency was investigated. The residues concentration of TCP was measured by spectrophotometer in λ_{max} of 296 nm.

Results: In optimum condition (pH 3, contact time 120 min , adsorbent dose 10 gr/l and TCP concentration 10 ppm), Azolla was able to remove 95% of TCP from aqueous solutions. The equilibrium data follows the Langmuir isotherm and the proper kinetic model is pseudo-second model.

Conclusions: Adsorption process by Azolla filiculoides is an efficient method for removal of 2, 4, 6-Trichlorophenol from aqueous solutions.

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Background

Increasing of public concerns about environmental problems especially the water resources pollution has highlighted the treatment process of wastewater (1,2). Many wastewaters contain significant levels of organic contaminants, phenol and phenol derivatives belong to a group of common environmental contaminants (3,4). Chlorophenols are the name of a group of phenolic compounds that contain between one and five chlorines (5). Phenolic derivatives are extensively used in producing the certain artificial resins and in the synthesis of many drugs, dyes, weed killers, insecticides, and explosives (6). Chlorophenols can make the taste and odour problems even at concentrations below 0.1 mg/L and can lead to many adverse effects such as toxicity and carcinogenicity (8). Adsorption, chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, reverse osmosis and etc. have been used for removal of phenolic compounds from water and effluents (7, 9). The adsorption is the best method to remove of phenols. This removal process has some advantages such as high efficiency, easy handling, high selectivity, lower operating cost, easy regeneration of adsorbent and the minimum sludge production (8,10).

The chemistry and surface morphology of the adsorbent can influence on adsorption process. Therefore, it is necessary to find the adsorbents which are economical, easily available, strong affinity and high loading capacity (11). Some of materials such as activated carbon, red mud and rubber seed coat and etc. have been used for pollutant removal in other studies (12-14). Azolla is a floating water fern which it can grows rapidly on the water surface and can form a dense mat, therefore it can lead to many negative effects to aquatic life (15,16).

Therefore, use of Azolla as a biosorbent to remove phenol from the industrial effluent can help to solve both problems including phenol removal as well as weeds problem. Recently, dried and modified Azolla has been used as a proper biosorbent for the treatment of metal-bearing effluents (17,19). There are a few studies, which have suggested that Azolla is capable of removing dyes (20,22) and phenol compounds (12) from aqueous solutions, also. In this study, dried Azolla filiculoides was used as a biosorbent to remove 2, 4, 6-Trichlorophenol (TCP) as a target pollutant from aqueous solution.

Aims of the study: The aim of this current paper was to study the effects of biosorption of TCP on dried Azolla filiculoides using batch experiments under different experimental conditions, including pH, biosorbent dosage, contact time, temperature and initial TCP concentrations.

Materials & Methods

Adsorbent preparation:

Azolla filiculoides was collected from rice paddy in Sari city and the collected Azolla was prepared according to study of Zazouli et al (12). The resultant biomass was subsequently used in the sorption experiments.

Material:

2, 4, 6 Trichlorophenol was purchased from Sigma Aldrich Corporation. The desired concentration of TCP solution was prepared by dilution of stock solution (1000 mg/l). The general characteristic and chemical structure of TCP are presented in table 1 and Fig. 1.

Table1) characteristics of 2, 4, 6-Trichlorophenol (23).

C.I. name	Molecular weight	λ_{max} (nm)	Molecular formula
2,4,6-Trichlorophenol	197.45 g/mol	296 nm	$C_6H_2Cl_3OH$

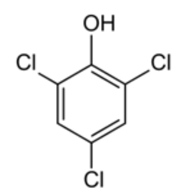


Figure 1) The chemical structures 2,4,6-Trichlorophenol (23)

Batch adsorption experiments:

It has been proven by literatures that the most effective variables on adsorption process are the pH, adsorbent dose, and contacts time and pollutants concentrations. The initial range of TCP concentrations were 10 to 100 mg/L. The effect of absorbent dosage (0.2-1.4 g), contact time (15,30,45,60,75,90,120,180,240 min) and pH (3,5,7,9,11) were investigated (24). The experiments were carried out in batch system in a 250 ml Erlenmeyer. In each adsorption experiment, the certain concentration of TCP solution poured into the flask. In every experiment, a certain concentration of TCP and specific dose of absorbent spilled into the flask and completely mixed with shaker at 180 rpm for 120 minutes. Then the samples were centrifuged at 3600 rpm for 10 minutes. Finally, the residual concentrations were measured by uv-visible (made in Hatch, DR5000) in λ_{max} of 296 nm. The amount of adsorbed TCP was calculated according to the following E_q 1 (25).

$$q_e = (C_o - C_e) V/m \quad (1)$$

Where q_e is the amount of adsorbed (mg/g), C_0 and C_e are the initial and equilibrium concentrations of liquid phase (mg/L) respectively, V is the volume of the solution (L) and m is the mass of the adsorbent.

Adsorption isotherms:

The adsorption system design is performed by the equilibrium adsorption isotherms. In this study, two widely used isotherm e.g. Langmuier and Freundlich were applied. The Langmuir isotherm is presented in the E_q 2 (33).

$$c_e / q_e = 1/q_m K_L + c_e / q_m \quad (2)$$

Where q_e is the amount of adsorbed TCP at equilibrium (mg/g); qm (mg/g) is the maximum theoretical biosorption capacity; C_e is the equilibrium concentration of the TCP in the solution (mg/L); and K_L (L/mg) is constant amount of biosorption energy.

The Freundlich equation is given by the following Eq. 3 (6, 26).

$$\text{Log } x/m = 1/n \log C_e + \log K_F \quad (3)$$

Where qe is the biosorbed TCP at the equilibrium (mg/g); C_e is the equilibrium concentration of the TCP in the solution (mg/L); K_F is a constant amount that indicative the biosorption capacity (2). Fig.5 shows the Freundlich and Langmuir equation obtained for the biosorption TCP onto dried A. filiculoides.

Adsorption kinetics:

The Examination of the adsorption rate process and potential rate controlling step is performed by kinetics models. In present work, obtained kinetic data from batch studies have been analyzed by using the pseudo second-order and pseudo First-order model. The pseudo-first-order rate equation is expressed as E_q 4 (25):

$$\text{Log } (q_e - q) = \log q_e - k_1 t / 2.3 \quad (4)$$

Where q_e and q are the amounts of adsorbed TCP per unit weight of adsorbent (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of adsorption (min^{-1}). Values of k_1 were calculated from the plots of log (q_e − q) versus (t) for different concentration.

Also the pseudo-second-order rate equation has been given by equation 5 (27):

$$dq / dt = k_2 (q_e - q)^2 \quad (5)$$

Where K_2 the second order rate constant (g mg $^{-1}$min^{-1}), q and q_e are the amount of the adsorbed on the adsorbent (mg/g) at equilibrium and at time t . The integration from E_q 6 (28):

$$t / q = 1/k_2 q_e^2 + 1/ q_e t \quad (6)$$

The plot of t/q against t of Eq (6) will give a linear relationship. The q_e and K_2 can be determined from the slope and the intercept of the plot.

Results

The Fig.2 indicates that the TCP removal efficiency has increased during the contact time 120 min. It reached to balance after this time. Therefore, the optimum contact time was 120 min. The adsorption rate decreases by increasing of the initial concentration, so the adsorption rate in concentration of 10 ppm was obtained two times more than 100 ppm. The results of effect the increasing TCP initial concentration are revealed in Fig. 3.

Effect of pH and adsorbent dosage:

The Fig 3, 4 shows the effect of pH and adsorbent dosage on adsorption rate. As can be seen the maximum adsorption rate was performed in acidic pH and it is decreased in alkaline pH.

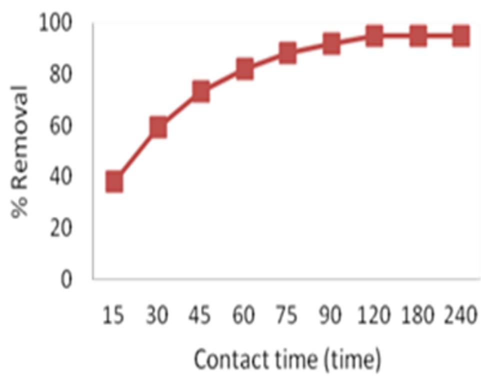


Figure 2) Effect of contact time on removal efficiency of TCP (pH = 5, adsorbent dosage 10 gr/1, TCP concentration: 10 ppm)

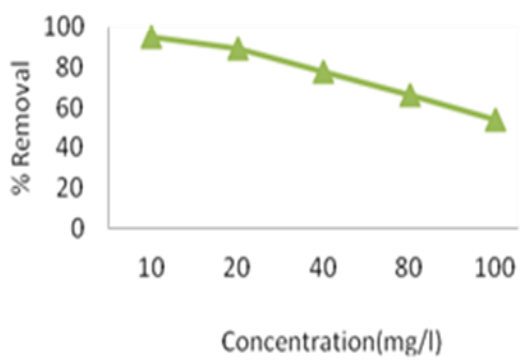


Figure 3) Effect of TCP concentration on removal efficiency of TCP

(Time = 120 min, dose: 10 gr/l, pH = 5)

The adsorption rate was increased by increasing of adsorbent dosage up to concentration of 10 g/L, and then was reached to equilibrium. As a result adsorption rate by increasing the adsorbent dosage was increased too.

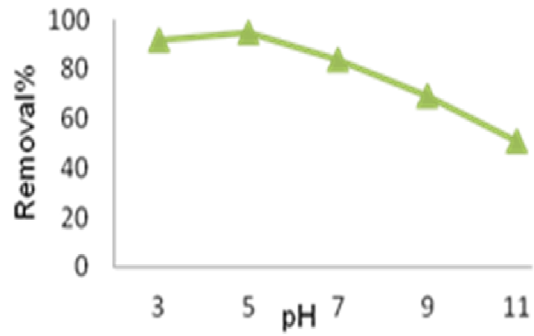


Figure 4) Effect of pH on removal efficiency of TCP (contact time = 120 min, dose: 10 gr/l, TCP concentration: 10 ppm)

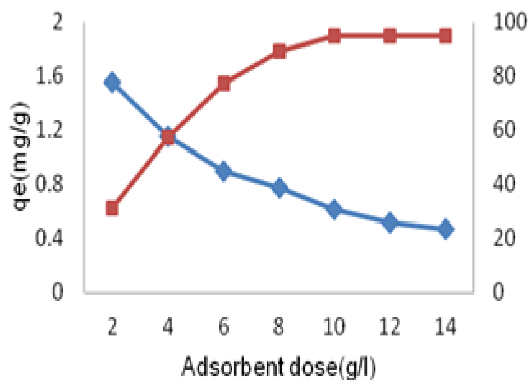
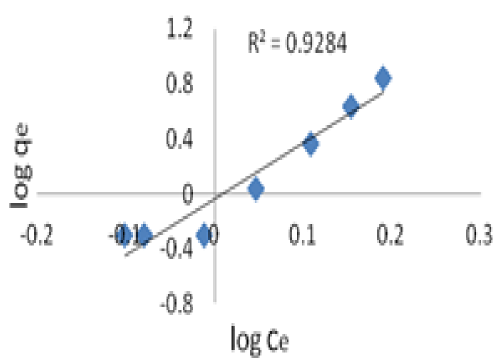


Figure 5) Effect of adsorbent dose on removal efficiency of TCP (contact time = 120 min, pH = 5, TCP concentration: 10 ppm)

Adsorption kinetics and isotherms:

The isothermal models and adsorption kinetics show in Fig. 5 and Table 2.



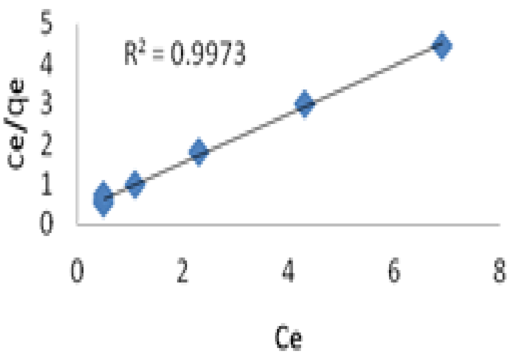


Figure 5) isotherm models: (a) Freundlich (b) Langmuir

Table 2) the adsorption kinetic model constants

pseudo second-order model				**pseudo First-order model**		
co(mg/l)	K= (g/mg min)	R^2	q	K= (1/ min)	R^2	q(mg/g)
10 1.89	0.09	0.984		0.064	0.918	1.56
25 4.1	0.12	0.994		0.079	0.944	3.7
50 6.2	0.14	0.998		0.085	0.961	5.9

Discussion

The results indicated that the increasing of the contact time gives rise the TCP removal efficiency due to increase the contact between adsorbate and adsorbent in the initial minutes. The TCP adsorption was rapidly decreased with time that it could be because of declining the TCP concentration and decreasing the active points on adsorbent surface area. There is a lot of empty sites on surface of adsorbent in early stages of adsorption and they are occupied by TCP molecules with time which it is consistent with several studies that it conducted on Chlorophenols removal by other absorbent (23, 29, 30). As shown Fig. 2, TCP removal efficiencies have been increased when their concentrations have been decreases. This phenomenon probably could be due to enhancing the contact of adsorbate with available sites of adsorbent. In other words, the adsorbent sites were decreased on the adsorbent. Therefore when the initial TCP concentration increases, the adsorbent sites filled earlier and the TCP removal efficiency was decreased (15). Indeed, the removal efficiency is increased by decreasing the initial concentration of TCP due to the being constant amount of adsorbent and available adsorb positions. It is consistent with other conducted studies (15,31). pH plays an important role in all process and adsorption capacity. The pH can influence on the different aspects of adsorption process containing the adsorbent surface charge, the degree of ionization, separation of functional groups on the adsorbent active sites and solution chemistry. Many researchers have reported that pH plays a main role in electrostatic force between adsorbent and TCP. In this study the maximum TCP removal was obtained in pH=5 which is similar to Liang Ren study on TCP removal by activated carbon (23). The increasing of the adsorbent dose can lead to gives rise adsorption efficiency because of increasing of the active surface of adsorbent. The results indicated that while efficiency has been increased with increasing adsorbent dose, however the adsorbed TCP per gram of adsorbent has been decreased and it probably is because of the active sites onto adsorbent that are not saturated yet. By adding the adsorbent dose, the total adsorbent capacity not to use completely and it would reduce the absorption rate per unit mass of the adsorbent (15). The R^2 of kinetic models suggested that the pseudo second- order model mechanism is predominant which means the uptake process follows the pseudo-second-order expression with Correlation coefficients were greater of 0.99. The lowest correlation coefficient in pseudo second- order model was better than the first order model correlation coefficients (25,27,32,33). The correlation coefficient (R^2) for Freundlich equation was obtained 0.9284 which it was lower than the R^2 value obtained from Langmuier equation and it can indicated that the better has been fitted the equilibrium obtained in this study (8,28, 34).

Footnotes

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Conflict of Interest:
The authors declare no conflict of interest.

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