

*Original Article***Application of *Azolla Filiculoides* biomass for 2-Chlorophenol and 4-Chlorophenol Removal from aqueous solutions**Mohammad Ali Zazouli<sup>1</sup> \* Davoud Balarak<sup>2</sup> Yousef Mahdavi<sup>2</sup>

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\* [dbalarak2@gmail.com](mailto:dbalarak2@gmail.com)**Abstract**

**Background and purpose:** The 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP) are phenolic compounds which they may have adverse effects on human and environment. Therefore, the removal of these compounds is necessary from water and wastewater. The aim of this study was the investigation of 2-CP and 4-CP removal by using *Azolla filiculoides* biomass.

**Materials and Methods:** The *Azolla* biomass was sun dried, crushed and sieved to particle sizes in range of 1-2 mm. Then treated with 0.1M HCl for 5h followed by washing with distilled water and it used as adsorbent. The residues concentration of 2-CP and 4-CP was measured by spectrophotometer in  $\lambda_{max}$  of 274 and 280 nm, respectively.

**Results:** The solute removed increased with increasing of contact time. The equilibrium time for 2-CP and 4-CP is 90 and 75, respectively. The removal efficiency of 4-CP is more than 2-CP. An increase in initial concentration of both compounds can lead to decrease the removal efficiency of them. The optimum pH to remove the both compound is 5. The equilibrium data is best fitted on Langmuir isotherm and the adsorption kinetic model follows pseudo-second model.

**Conclusion:** The results indicated that *Azolla* is an effective adsorbent for 2-CP and 4-CP removal from water and wastewater. [Zazouli MA. \*Balarak D. Mahdavi Y. Application of *Azolla filiculoides* biomass for 2-Chlorophenol and 4-Chlorophenol Removal from aqueous solutions. *IJHS* 2013; 1(2):43-55] <http://jhs.mazums.ac.ir>

**Key words:** *Azolla filiculoides* biomass, Adsorption, 2-chlorophenol, 4-chlorophenol, water treatment

## 1. **Introduction**

Chlorophenols are an important class of aromatic pollutants in industrial wastewaters and belong to a group of common environmental contaminants(1). Chlorophenols (CP) are widely found in the environment, for example during the chlorination of drinking water in municipal water treatment facilities; as by chlorine bleaching in numerous industries; as discharge from a range of incineration processes; and as common constituents of herbicides and pesticides on agricultural land.(2). Due to their toxicity and adverse effect upon human, the United States Environmental Protection Agency (EPA), has classified them as priority pollutants(3, 4).

Chlorophenols are used extensively in the manufacture of fungicides, herbicides, insecticides, pharmaceuticals, preservatives, glue, paint, fibers, leather, and as intermediates in chemical synthesis(5). Because of high toxicity, carcinogenicity, yet poor biodegradability, chlorophenols are among the priority contaminants of major environmental concern. Therefore it is desirable to develop efficient processes for the removal of these compounds from waste waters(6). Numerous approaches, including physical, chemical, and

biological processes, for the removal of phenols and phenolic compounds from industrial waste effluents have been employed. The traditional methods such as adsorption, chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, and reverse osmosis, etc. have been widely used for removal of phenols from aqueous solutions(7-9). Among them, removal of phenols by adsorption is the most powerful separation and purification method because this technique has significant advantages including high efficiency, easy handling, high selectivity, lower operating cost, easy regeneration of adsorbent, and minimized the production of chemical or biological sludge(8).

Adsorption process is strongly affected by the chemistry and surface morphology of the adsorbent. Therefore, new adsorbents, which are economical, easily available, having strong affinity and high loading capacity, have been required. A number of adsorbents such as activated carbon, red mud, rubber seed coat and etc. have been used for Phenolic compounds (10-13). Activated carbon is commonly used to remove organic compounds from industrial effluents because of its high removal efficiency. However, the cost associated with using activated carbon is relatively high and is not

applicable to industrial effluents containing low concentrations of contaminants(14-16). Hence, many cheap alternative adsorbents have been tested to remove organic compounds from industrial effluents. Recently much attention has been focused on the use of biosorbent materials, such as fungal or bacterial biomass, and natural biopolymers, including peat, wheat shells, fly ash, wood sawdust and dried algal biomass, for the removal of material (17-19). *Azolla*, a floating water fern, grows quickly over the water surface, forming a dense mat, and therefore poses many negative effects to aquatic ecology(20, 21). However, using *Azolla* as a bioabsorbent to remove phenol from the industrial effluents would be a “win-win” solution for both environmental problems as it would be effective in phenol compounds removal and an essentially noxious weed would find an alternative use as remediation material. Recently, non living *Azolla* has been used as a potential biosorbent for the treatment of metal-bearing effluents (22-24).

However, a few reports have also suggested that *Azolla* is capable of removing dyes(25-27) and phenol compounds(20) from aqueous solutions. In this study, dried *Azolla Filiculoides* was used as a biosorbent to remove 2-Chlorophenol and 4-

Chlorophenol as a target pollutant from aqueous solution. The aim of this research was to study application of *Azolla Filiculoides* biomass for 2-Chlorophenol and 4-Chlorophenol Removal from aqueous solutions using batch experiments under different experimental conditions, including pH, biosorbent dosage, contact time, temperature and initial 2-Chlorophenol and 4-Chlorophenol concentrations.

## **2. Materials and Methods**

### **1.2. Adsorbent preparation**

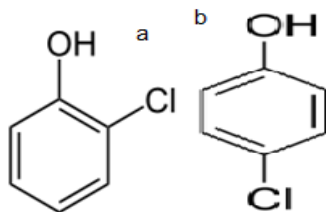
*Azolla filiculoides* was collected from rice paddy in Sari County; then it was dried in the sunlight, and was crushed and sieved to particle sizes in the range of 1–2 mm. The biomass was treated with 0.1 M HCl for a period of 5 h and it was washed with distilled water and finally was dried in the shade(20). The resultant biomass was subsequently used in sorption experiments.

### **2.2. Material**

The 2-CP and 4-CP was purchased from Merck Co. The desired concentration of 2-Chlorophenol and 4-Chlorophenol solution was prepared by dilution of stock solution (1000mg/l). The general characteristics and chemical structures of 2-Chlorophenol and 4-Chlorophenol are presented in table1 and Fig1, respectively.

**Table 1.** The characteristics of 2-Chlorophenol and 4-Chlorophenol (28-30)

C.I. name	Molecular weight g/mol	$\lambda_{\max}$ (nm)	Molecular formula
2-Chlorophenol	128.56	274	C <sub>6</sub> H <sub>5</sub> ClO
4-Chlorophenol	128.56	280	C <sub>6</sub> H <sub>5</sub> ClO

**Fig 1.** The chemical structures a:2-Chlorophenol b:4-Chlorophenol(30)

### 3.2. Batch adsorption experiments

The literature review indicated that the most important effective variables on adsorption are including pH, adsorbent dose, and contact time and pollutants concentrations. Therefore, the initial 2-CP and 4-CP concentrations were selected (10, 25, 50, 100, 200 mg/l). The effect of adsorbent dosage (0.2-1.4g), contact time (10, 20, 30, 45, 60, 75, 90, 120, 180, 240 min) and pH (3, 5, 7, 9, 11) were investigated (30). The experiments in batch system were carried out in a 250 ml Erlenmeyer flask Meyer. In each adsorption experiment, certain with certain concentration of 2-Chlorophenol

and 4-Chlorophenol solution were added into the flask. The desired condition was adjusted and then the specific dose of adsorbent was added. Studied samples were mixed with shaker at 180 rpm for 60 minutes. Then the samples were centrifuged at 3600 rpm for 10 min. Finally, the residual concentrations were measured using uv-visible in  $\lambda_{\max}$  of 274 and 280 nm for 2-CP and 4-CP respectively. The amount of adsorbed 2-CP and 4-CP was calculated according to the following equation (31).

$$q_e = \frac{(C_0 - C_e) V}{m} \quad (1)$$

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),  $V$  is the volume of the solution (L), and  $m$  is the mass of the adsorbent.

#### 4.2. Adsorption isotherms

The equilibrium adsorption isotherm is importance in the design of adsorption systems. Although several isotherm equations are available, two important isotherms were selected in this study the Langmuir, Freundlich isotherms. The Langmuir isotherm is the equation2 (33).

$$\frac{ce}{qe} = \frac{1}{q_m K_L} + \frac{ce}{q_m} \quad (2)$$

Where  $q_e$  is the amount of sorbate biosorbed at equilibrium (mg/g);  $C_e$  is the equilibrium concentration of the sorbate or the sorbate unadsorbed in the solution (mg/L);  $q_m$  (mg/g) is the maximum theoretical biosorption capacity and  $K_L$  (L/mg) is a measure of biosorption energy, indicating the affinity between biosorbent and sorbate. The Freundlich equation is given by the following equation3 (3, 32).

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

where  $q_e$  is the sorbate biosorbed at the equilibrium (mg/g);  $C_e$  is the equilibrium concentration of the sorbate or the unabsorbed sorbate in the solution (mg/L);  $K_F$  is a constant, indicative of biosorption capacity(33).

Fig shows the Freundlich and Langmuir equation obtained for the biosorption of 2-Chlorophenol and 4-Chlorophenol onto dried *A. filiculoides*.

#### 5.2. Adsorption kinetics

Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step. In the present work, the kinetic data obtained from batch studies have been analyzed by using pseudo second-order, pseudo First-order model. The pseudo-first-order rate equation is expressed as equation 4 (31).

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

Where  $q_e$  and  $q$  are the amounts of 2-CP and 4-CP adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively, and  $k_1$  the rate constant of adsorption ( $\text{min}^{-1}$ ). Values of  $k_1$  were calculated from the plots of  $\text{log} (q_e - q)$  versus  $t$  for different concentrations. The pseudo-second-order rate equation is expressed as equation5 (34).

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

Where  $K_2$  is the rate constant of pseudo-second-order sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $q$  and  $q_e$  are the amount of solute sorbed at any time and at equilibrium (mg/g) respectively. The integration from equation6 (35).

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (6)$$

If the second-order kinetic equation is applicable, the plot of  $t/q$  against  $t$  of Eq (6) should give a linear relationship. The  $q_e$  and  $K_2$  can be determined from the slope and the intercept of the plot.

### 3. Results

#### 1.3. Effect of contact time

The adsorption rate of 4-CP and 2-CP increased by increasing the contact time,

however the equilibrium point was reached 15 minute earlier for 4-CP. The optimum contact time for 4-CP and 2-CP was obtained in 75 and 90 min, respectively; although there was no significant difference in 75 and 90 min for 2-CP. The effect of contact time on removal efficiency of each compound is presented in Fig2.

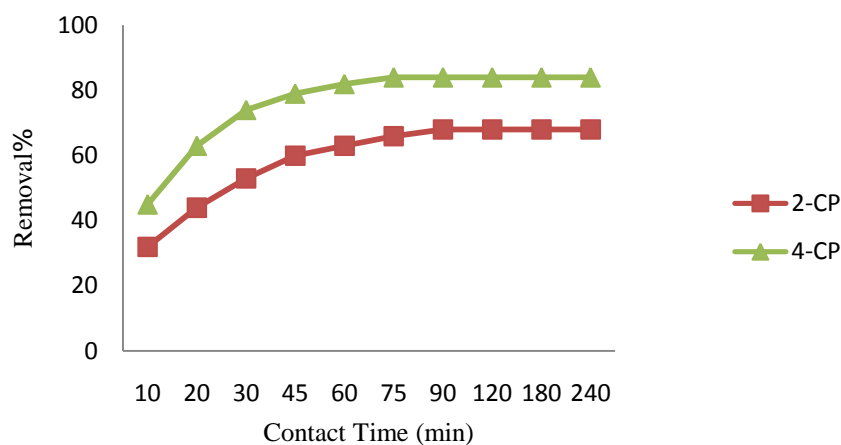


Fig2. Effect of contact time (pH = 5, adsorbent dosage 10gr/l, 2-CP and 4-CP con: 10mg/l) 3.2.

#### 2.3. Effect of pH and adsorbent dosage.

The Fig 3&4 are shown the effect of pH and adsorbent dosage on adsorption rate. As can be observed, the maximum removal efficiency was occurred in acidic pH. Adsorption rate is not significant difference in acidic pH, so that there is only 3% difference in adsorption efficiency in pH of 3 and 5 and the optimum pH is 5. However, the adsorption efficiency decreased rapidly

with increasing of the pH from acidic to alkali ranges. The adsorption efficiency increased by increasing of the adsorbent dose up to 10gr/l and 12gr/l for 4-CP and 2-CP, respectively. It reaches to equilibrium after those doses. Although the adsorption efficiency increases by increasing in adsorbent dose, however the adsorption rate per gr of adsorbent dose ( $q_e$ ) decreases.

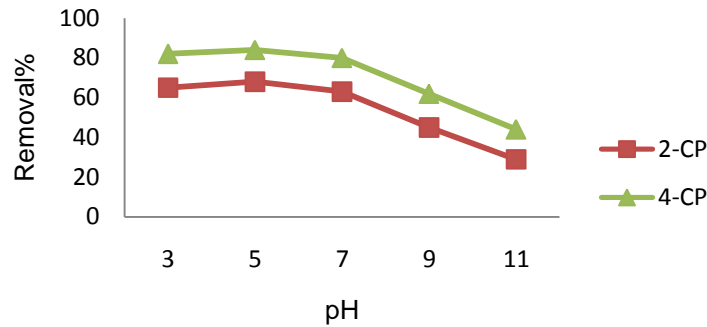


Fig3. Effect of pH (contact time = 75 for 4-CP, 90 for 2-CP, dose 10 gr/l, con:10mg/l)

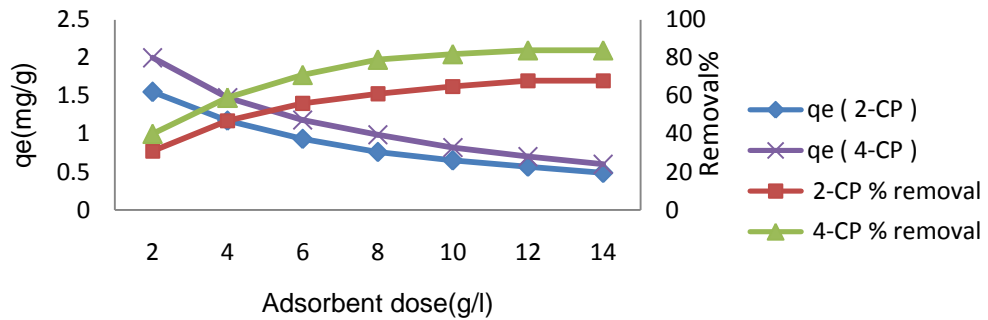


Fig4. Effect of adsorbent dosage (contact time = 75 for 4-CP, 90 for 2-CP, PH = 5, con: 10mg/l)

### 3.3. Effect of initial 2-CP and 4-CP concentration.

The biosorption of CP on dried *A. Filiculoides* decreased significantly with increasing solution 2-CP and 4-CP

concentration from 25 to 200 and remained approximately constant from 10 to 25 with maximum of 85, 71 removed for 4-CP and 2-CP respectively. The obtained results are presented in Fig 5.



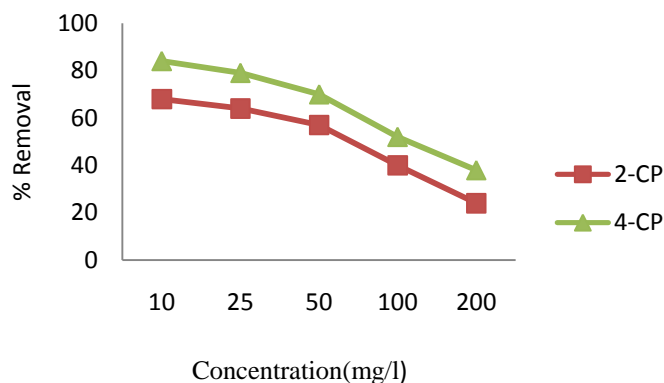


Fig 5. Effect of solute concentration (time = 75 min for 4-CP, 90 for 2-CP, dose: 10 gr/l, pH = 5)

**4. 3. Adsorption kinetics and isotherms.** The isothermal models and adsorption kinetics in Fig. 5 and Table 2, 3.

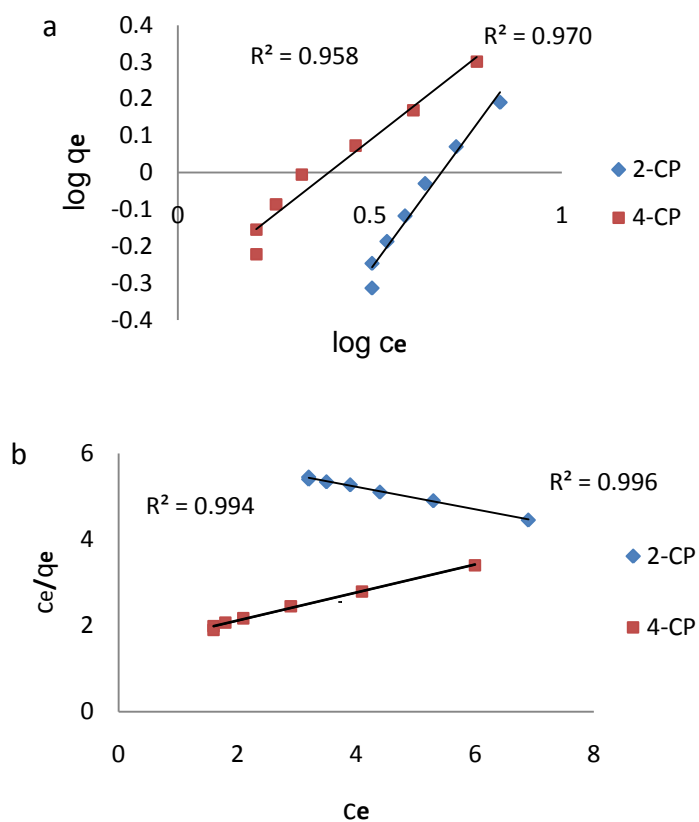


Fig6. Isotherm models: (a) Freundlich (b) Langmuir



**Table2.** The adsorption isotherms constants for the 4-CP, 2-CP removal

	Langmuir model			Freundlich model		
	b(ml/g)	R <sup>2</sup>	q <sub>m</sub>	K <sub>F</sub>	R <sup>2</sup>	1/n
2-CP	1.11	0.996	7.8	57.6	0.958	1.17
4-CP	1.04	0.994	8.24	51.9	0.97	1.29

**Table3.** The adsorption kinetic model constants for the 4-CP, 2-CP removal

	pseudo second-order model			pseudo First-order model			
	co(mg/l)	k <sub>2</sub> (g/mg min)	R <sup>2</sup>	q	k <sub>1</sub> (1/min)	R <sup>2</sup>	q(mg/g)
2-CP	10	0.09	0.989	0.071	0.926	1.27	
	25	0.11	0.993	0.082	0.945	3.6	
	50	0.12	0.996	0.09	0.959	5.42	
4-CP	10	0.045	0.991	0.079	0.943	1.84	
	25	0.078	0.996	0.094	0.951	4.36	
	50	0.098	0.999	0.104	0.964	6.8	

#### 4. Discussion

With regarding the results, the 4-CP, 2-CP removal efficiency increased by increasing of contact time which it is due to more contact between pollutants and adsorbent. In the initial minutes the 4-CP, 2-CP was rapidly adsorpted. Adsorption decreased with time which it on Phenolic compounds removal by several adsorbents(31, 35). The adsorption rate of 4-CP is 20% more than 2-CP. one of the most important factors affecting the biosorption of CP on dried *A. filiculoides* was the acidity of the solution. The pH of the solution influences not only the surface charge of the biosorbent and the dissociation of functional groups of the active sites on the surface of the biosorbent, but also the aqueous chemistry of the CP.

can be due to declining of 4-CP, 2-CP concentration and decreasing of active points on adsorbent surface area. In the early stages of adsorption, there are a lot of empty spaces and they are occupied by 4-CP, 2-CP molecules with time which it is consistent with several studies that they conducted. The difference adsorption rate for 2-chlorophenol and 4-chlorophenol depends on different solubility of these compound which due to the position of chlorine on ring of 2-CP that can lead to more stability against ionization and the less solubility of 2-CP. The percent removal decreased with increasing in pH. As equation7 (36).

$$CP_0 = \frac{CP_T}{1+10^{(pH-pKa)}} \quad (7)$$

(Where  $CP_0$  is the concentration of unionized CP species,  $CPT$  is the total concentration of CP taken,  $pH$  (equilibrium  $pH$ ) after adsorption and  $pK_a$  is (8.35), the concentrations of ionized CP species (chlorophenolate) were calculated. Equation 7 expressed that the number of ionized CP is decreased by an increasing in  $pH$  and it can lead to reduce the adsorption efficiency (36). This is implied in the study on 2-CP removal by low-cost adsorbent which is conducted by namasivayam & Kavitha (36). The adsorption efficiency decreased by increasing of initial concentration of phenol compound, however the adsorption capacity increased (30). This probably occurs due to that by increasing of the surface charge on the adsorbent, the adsorption sites of top surfaces of adsorbent are saturated and the removal efficiency decreased. The reason of the rising the adsorption capacity by increasing the initial phenolic compound concentrations is due to the increasing of collusion and contact between adsorbent and adsorbate (30). It is consistent with other conducted studies (3, 13). The adsorption rate increased by increasing of adsorbent dose which it is due to increasing of the active surface of adsorbent. The results showed that although efficiency increased with increasing adsorbent dose, however the 4-CP, 2-CP adsorbed per gram of adsorbent decreased because the active sites of adsorbent are not saturated. increasing of adsorbent dose, the total capacity of the adsorbent surface points not used completely and this reduces the absorption rate per unit mass of the adsorbent (11). Lower biosorption

capacity of CP at a higher dosage of biosorbent is probably due to the decrease of the surface area of the biosorbent by the overlapping or aggregation during the sorption (18). The  $R^2$  of kinetic models suggested that the pseudo second-order model mechanism is predominant. It means the uptake process follows the pseudo-second-order expression with Correlation coefficients were always greater of 0.99. The lowest correlation coefficient in pseudo second-order model was better than the first order model correlation coefficients (31, 34, 37-39). The Freundlich equation is based on the hypothesis of multi-layer biosorption. Langmuir isotherm assumes monolayer coverage of a sorbate on to the solid surface of adsorbent, uniform energy of sorption, and no transmigration of sorbate in the plane of the surface. the correlation coefficient ( $R^2$ ) for Langmuir equation always greater than 0.99, which was slightly more than the  $R^2$  value obtained from the Freundlich equation indicating that the Langmuir model better fitted the equilibrium obtained in this study (5, 8, 35). Conclusion: The present study shows that the *Azolla Filiculoides* is an effective adsorbent for the removal of 2-CP and 4-CP from aqueous solutions. Adsorption equilibrium follows Langmuir isotherm. Kinetics of adsorption follows second-order model. The complete removal of phenolic compounds from wastewater can be achieved by using appropriate dosage of the adsorbent,  $pH$  and contact time from wastewater.

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