

## Survey of Efficiency Agricultural Weast us adsorbent for Removal of P-Cresol from Aqueous Solution

**Abstract:** This study examined the feasibility of removing P-Cresol from aqueous solutions using canola stalk. The effects of P-Cresol concentration, Contact time, biomass dosage and pH on adsorption of P-Cresol by canola biomass were also evaluated. Pseudo first order and Pseudo second-order, intraparticle diffusion models were adopted to evaluate experimental data and thereby elucidate the kinetic adsorption process. Additionally, this study used the Langmuir, Freundlich, Redlich–Peterson and Temkin isotherms to describe equilibrium adsorption. The adsorption percentage of P-Cresol increased as contact time and biomass dosage increased. Conversely, the adsorption percentage decreased as P-Cresol concentration increased. The equilibrium data is best fitted on Langmuir isotherm and the adsorption kinetic model follows pseudo-second model. It is evident from the literature that canola biomass have shown good potential for the removal of isomeric phenol from aqueous solution.

**Keywords:** Adsorption, Canola stalk, P-Cresol, Isotherm, Kinetics

**Introduction:** Organic compounds constitute a very large group of pollutants in the wastewater(1). Very often small amounts of synthetic organic compounds (including phenol and its derivatives, pesticides, aliphatic and aromatic hydrocarbons, dyes and surfactants among most representatives) are detected in water streams(2, 3). P-Cresol is an isomeric phenol with a methyl substituent at the para position relative to hydroxy group(4). P-Cresol has a wide variety of uses including as disinfectants, fumigants, explosives, in the manufacturing of synthetic resins, in photographic developers, etc(5). It is a naturally occurring metabolic product that is formed from tyrosine by bacteria under anaerobic conditions(6). It is highly toxic and even at a very low concentration it may act as a promoter for stomach tumors(7). It is corrosive to the eyes, the skin and the respiratory track. It may cause adverse effects on the central nervous system, cardiovascular system, lungs, kidney, and liver resulting in CNS depression. Exposure at higher levels may result in lowering in consciousness and death(8, 9). Environmental Protection Agency (EPA) has classified p-cresol as pollutant of group C (possible human carcinogens)(10, 11). Therefore, to save our aqueous ecosystem, it has been essential to reduce p-cresol concentration in wastewater to acceptable level before safe disposal to water bodies(12). Several conventional physiochemical techniques are available in the literature to treat wastewater. These include chlorination, ozonation, membrane process, solvent extraction, flocculation, coagulation, etc(13, 14). Most of them suffer from serious drawbacks such as high cost, tendency of the formation of secondary hazardous byproducts, incompleteness of purification(15). Adsorption process is one of the most effective and economically feasible methods for the removal of Phenolic compounds from aqueous solutions(16). The high cost of activated carbon sometimes makes its use limited(17). So many researchers have tried to search for alternative materials, which are relatively inexpensive, and at the same time with reasonable adsorptive efficiency(18). The canola stalk is a lignocellulosic waste widely produced in Iran and around the world due to the growth of canola for the production and consumption of vegetable oils(19, 20). Therefore, the canola stalk is easily available and, due to its characteristics, has been used in several studies for pollutant removal(21-23). The aim of the present study was the investigation of the ability of canola in P-Cresol removal from aqueous solution and the effect of various parameters including contact time, pH, adsorbent dose and initial P-Cresol concentration and isotherm and kinetic studies was investigated.

## Materials and Methods

**The characteristics of P-Cresol:** The used P-Cresol (4-methylphenol) was the analytical grade which were purchased from Sigma-Aldrich CO (purity 99%). its molecular weight is 108.14 mg/mol and chemical fomula is  $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ . The stock solution (1000 mg/L) was prepared and desired concentration of P-Cresol solution was prepared by dilution of stock solution. A calibration plot (absorbance versus concentration of p-cresol) was drawn and used for estimating the concentration of unknown p-cresol concentration. The plot was linear ( $R^2 = 0.992$ ) between 0 and 20 mg/L p-cresol solution. The test samples drawn from experiments with higher concentrations of p-cresol were adequately diluted and then the absorbance was determined. Samples were taken from the reactor at a predetermined time intervals for analysis.

**Adsorbent characterization:** The specific surface area of dried Canola was determined by the BET-N<sub>2</sub> method using an ASAP 2000 apparatus based nitrogen adsorption-desorption isotherms at 77K. The surface images of dried Canola before and after adsorption process were captured by a Philips XL30 scanning electron microscope (SEM).

**Preparation procedure of adsorbent:** In this study, the Canola was used as low cost natural or agricultural wastes for P-Cresol removal from aqueous solutions. The stalks of Canola(C) were collected from research farm of Tabriz agricultural school. The stalks were washed several times with water to remove the contaminant, dried in the oven at 105°C for 5 h. The biomass was then treated with 0.1M HCL for 2 h followed by the washing with distilled water and then was oven dried at 105°C for 5 h. After drying, adsorbent were sieved to obtain particle size of 18 mesh prior to being used for adsorption studies(24).

### Batch adsorption experiments:

The batch adsorption system was employed in present study and the most effective factors for adsorption process including contact time (10-150 min), pH (3-11), adsorbent dose (0.5-8 g L<sup>-1</sup>) and initial concentration of P-Cresol (10- 200 mg/L) were assessed.

The optimum pH was determined by varying the pH in range of 3-11 and keeping constant of other variables (contact time, adsorbent dose and initial P-Cresol concentration). The experiments were preformed in 200 milliliter beaker with a constant concentration of P-Cresol. Then this mixture was shaken with a shaker device of enforce model with 180 rpm and the room temperature of 20 – 25°C. In the next step, the optimum adsorbent dose was estimated by keeping constant of contact time and initial day concentration and also the obtained optimum pH. After determination of the optimum pH and adsorbent dose, the various concentrations of the P-Cresol in the specified times of contact was investigated. The effect of solution pH on the retention of p-cresol on the studied adsorbents was investigated by adding 0.1 M NaOH or HCl (for pH adjustment) to the stock solution containing the aromatic compound. The concentration of p-cresol in influent and effluent was measured using DR5000 UV/Vis spectrophotometer (HACH, USA) at 280 nm wavelength(8). All the adsorption measurements were carried out at room temperature in a stirred batch system thermostatically controlled with an external circulating bath. Before these experiments, kinetics studies were performed to determine the equilibration time of the systems.

All the adsorption measurements were done in triplicate. The amount adsorbed was determined by the following equation(25):

$$q_t = (C_0 - C_t)W/V$$

Where  $q_t$  is the amount ( $\text{mg g}^{-1}$ ) adsorbed at time  $t$ ,  $C_0$  is the initial concentration ( $\text{mg/L}$ ),  $C_t$  is the concentration at time  $t$  ( $\text{mg/L}$ ), and  $V$  is the volume ( $\text{L}$ ) of the adsorbate solution and  $W$  is the weight ( $\text{g}$ ) of the adsorbent.

### 3. Results and Discussion

Scanning electron microscopy (SEM) images were used to analyze the surface structure of Canola (Fig. 1). Fig. 1(a) clearly shows the pore textural structure of dried Canola before use. However, the Fig. 1(b) indicated that the clear pore textural structure is not observed on the surface of dried Canola after use which it could be due to either agglomeration on the surface or the invasion of P-Cresol into the pores of dried Canola. It was found that the adsorbent has Heterogeneous surface structure with deep pores. The specific surface area of modified Canola was determined in the size of  $32 \text{ m}^2/\text{g}$ . The similar results were obtained for sorption of Acid blue 113 and Cr+6 from aqueous solutions onto Canola, also(20, 21).

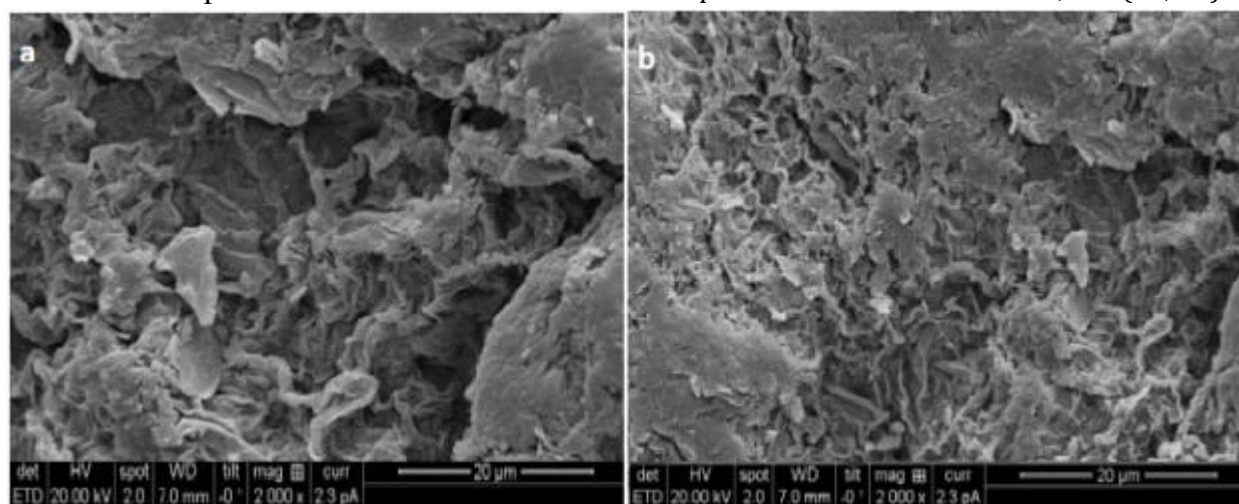


Fig. 1. The SEM image of dried Canola: (a) before use; (b) after use

**Effect of contact time and initial concentration on P-Cresol adsorption:** Fig. 2 depicts the effect of contact time on the removal of P-Cresol at various initial concentrations (25–200  $\text{mg/L}$ ). The saturation curves rise sharply in the initial stages, indicating that there are plenty of readily accessible sites. Eventually, a plateau is reached in all curves indicating that the adsorbent is saturated at this level. It can be seen from Fig. 2 that the contact time needed for P-Cresol solutions with initial concentrations of 25–200  $\text{mg/L}$  to reach equilibrium was 75 min. It was also seen that an increase in initial P-Cresol concentration resulted in increased P-Cresol uptake. The removal curves are single, smooth and continuous, indicating the formation of monolayer coverage of the P-Cresol molecules onto the outer surface of the adsorbent. The adsorption capacity at equilibrium ( $q_e$ ) increased from 6.19 to 35.6  $\text{mg/g}$  with an increase in the initial P-Cresol concentrations from 25 to 200  $\text{mg/L}$ . Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent(26). First, the adsorbate migrates through the solution, i.e., film diffusion, followed by solute movement from particle surface into interior site by pore diffusion and finally the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle. This phenomenon takes relatively long contact time(27, 28).

**Effect of pH:** The pH of the solution plays an important role in the adsorption capacity. The effect of initial pH of P-Cresol solution on the percentage removal was studied by varying

the initial pH under constant process parameters (4 g/L of adsorbent at initial P-Cresol concentration 20 mg/L). The results are shown in Fig. 3. The uptake of P-Cresol increased with decreasing initial pH and was the greatest at pH 3. The pH primarily affects the degree of ionization of the P-Cresol and the surface properties of Canola. At low pH values, the functional groups of chitin would be protonated and result in a stronger attraction for negatively charged ions in the adsorption medium. P-Cresol being weakly acidic would be partially ionized in solution(8). These ions will be negatively charged and will be directly attracted due to electrostatic forces by the protonated amino groups of the chitin. As the pH increased, the overall surface charge of the Canola became negative and adsorption decreased.(24, 29)

**Effect of Adsorbent Dose:** The dependence of adsorption of the P-Cresol on the concentration of dried Canola was investigated by varying the quantity of the adsorbent from 0.5 to 8 g/L in 50 mg/L solution of the P-Cresol while keeping other parameters (contact time, pH, initial P-Cresol concentration, temperature) constant. As shown in Fig. 4, adsorption capacity decreased from 41.6 to 6.11 mg/g for an increase in adsorbent mass from 0.5 g to 8 g, whereas the percentage removal increased from 41.6 % to 97.5% with the same increase in adsorbent mass. This observation is usually attributed to the increase in the adsorbent pore surface areas and availability of more adsorption sites with increasing mass of adsorbent(30, 31).

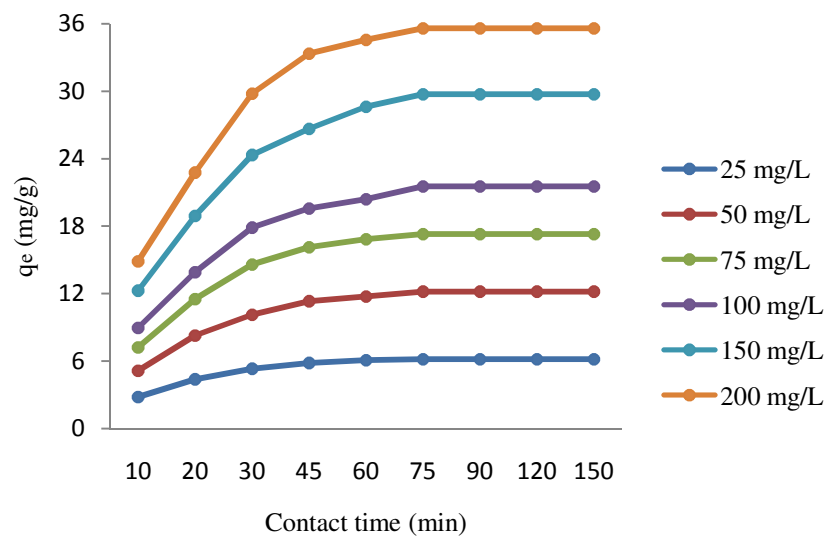


Fig.2. Effect of contact time and initial P-Cresol concentration on removal efficiency (pH = 3, adsorbent dose 4 g/L, Temp: 30 °C)

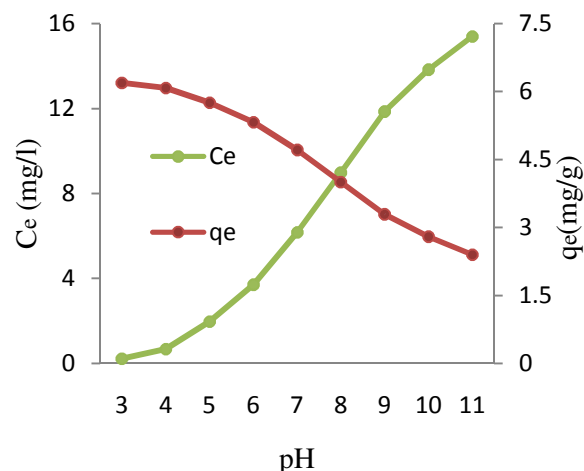


Fig. 3. Effect of pH on P-Cresol removal efficiency ( $C_0 = 25$  mg/L, adsorbent dose of 4 g/L, Time = 75 min and Temp: 25 °C)

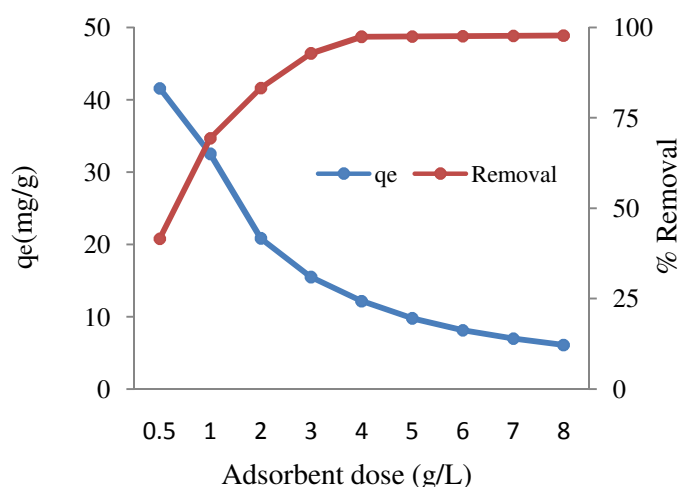


Fig.4: Effect of biomass dose on P-Cresol biosorption ( $C_0 = 50$  mg/L, pH=3, Contact time=75 min and Temp: 25 °C)

## Adsorption isotherms

Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were used to describe the relationship between the amount of P-Cresol adsorbed and its equilibrium concentration in solutions. The Langmuir isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform adsorption on the surface and no transmigration in the plane of the surface. The linear form of the Langmuir isotherm can be represented by the following equation(32):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} \times \frac{C_e}{q_m}$$

Where  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $q_e$  (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent,  $q_0$  and  $b$  are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The Langmuir plots for P-Cresol adsorption onto Canola biomass are obtained in Fig. 5, and the parameters are shown in Table 1. The correlation coefficients of the isotherms are all higher than 0.995 at the different concentration, thereby indicating that the Langmuir isotherm fits the equilibrium data very well. The applicability of the model suggests monolayer coverage of the adsorbate at the outer surface of the adsorbent is significant. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor ( $R_L$ ) which is defined by(33):

$$R_L = \frac{1}{1 + bC_0}$$

Where  $b$  is the Langmuir constant and  $C_0$  is the highest P-Cresol concentration (mg/L). The value of  $R_L$  indicates the type of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). The value of  $R_L$  was found to be 0.32-0.64 and this again confirmed that the Langmuir isotherm was favorable for adsorption of P-Cresol onto the activated carbon under the conditions used in this study.

Freundlich model is an empirical equation assuming heterogeneous adsorptive energies on the adsorbent surface, which can be written as(34, 35):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

Where  $q_e$  is the equilibrium P-Cresol concentration on the adsorbent ( $\text{mg g}^{-1}$ );  $C_e$ , the equilibrium P-Cresol concentration in solution ( $\text{mg L}^{-1}$ ); and  $K_F$  is the Freundlich constant. In this function, it is assumed that the sorbent has a surface with a non-uniform distribution of sorption heat. This equation was primarily proposed on a purely empirical basis for adsorption phenomena occurring on gas–solid interfaces, although it can be theoretically derived for an adsorption model in which the heat of adsorption varies exponentially with surface coverage. The slope of plot  $1/n$  ranging 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

Tempkin considered the effect of some indirect sorbate/adsorbate interactions on the adsorption isotherm. This isotherm assumes that; the heat of adsorption of all the molecules in a layer decreases linearly with surface coverage of adsorbent due to sorbate–adsorbate interactions. This adsorption is characterized by a uniform distribution of binding energies. The linear form of the Tempkin isotherm equation is represented by the following equation(36):

$$q_e = B \ln A + B \ln C_e$$

Where  $B = RT/b$ ,  $T$  is the absolute temperature in K,  $R$  the universal gas constant ( $8.314 \text{ K}^{-1} \text{ mol}^{-1}$ ),  $A$  the equilibrium binding constant and the constant  $B$  is related to the heat of adsorption.

Another isotherm which was used for the prediction of adsorption behavior is the Redlich–Peterson model. Redlich–Peterson equation included three adjustable parameters into an

empirical isotherm. This equation is widely used as a compromise between Langmuir and Freundlich systems.

The equation for this model is(37):

$$\ln \left[ \frac{k_R C_e}{q_e} - 1 \right] = \ln aR + \beta \ln C_e$$

Where  $K_R$  and  $\beta$  are the R-P constants. When the value of  $\beta$  is equal to 1, the above equation is reduced to the Langmuir isotherm, while it reduced to a Freundlich isotherm, in case the value of the parameter  $\beta$  is much bigger than 1.

Table 1 lists the parameters of the isotherm models along with the regression coefficients ( $R^2$ ) The  $R^2$  values in Table 1 reveal that the Langmuir isotherm fits the experimental results better than other model, implying that the adsorption of P-Cresol onto Canola biomass follows the mechanism of monolayer adsorption (chemisorption) on a homogenous surface. Although the Langmuir and Redlich-Peterson equations have similar correlation coefficients, the Langmuir is a simpler equation and therefore easier to use. Consequently, it was selected to predict  $q_e$  values in the present work.

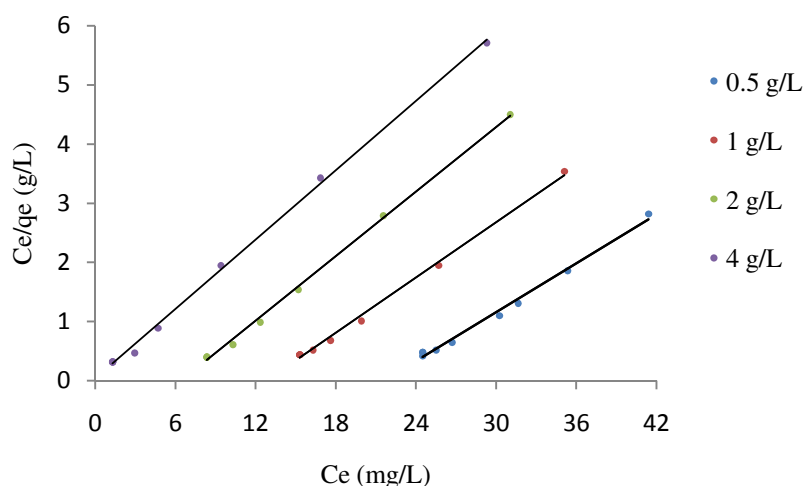


Table 1: The adsorption isotherms constants for the removal P-Cresol onto Canola biomass

| Dose (g/l) | $q_e$ exp (mg/g) | Langmuir model |        |       | Freundlich model |       |       | Temkin model |       |       | Redlich–Peterson model |       |         |       |
|------------|------------------|----------------|--------|-------|------------------|-------|-------|--------------|-------|-------|------------------------|-------|---------|-------|
|            |                  | $q_m$          | $K_L$  | $R^2$ | $n$              | $K_F$ | $R^2$ | $B$          | $A$   | $R^2$ | $k_R$                  | $aR$  | $\beta$ | $R^2$ |
| 0.5        | 46.22            | 41.81          | 0.0045 | 0.997 | 3.71             | 9.14  | 0.876 | 29.12        | 0.245 | 0.741 | 14.4                   | 0.172 | 0.98    | 0.984 |
| 0.1        | 34.71            | 32.17          | 0.0067 | 0.999 | 3.22             | 12.45 | 0.849 | 21.45        | 0.384 | 0.796 | 17.7                   | 0.346 | 0.95    | 0.976 |
| 0.2        | 20.82            | 19.74          | 0.0079 | 0.998 | 2.64             | 14.66 | 0.854 | 17.24        | 0.514 | 0.823 | 21.2                   | 0.593 | 0.96    | 0.965 |
| 0.4        | 12.17            | 12.45          | 0.0094 | 0.996 | 1.95             | 16.73 | 0.832 | 11.69        | 0.694 | 0.804 | 23.4                   | 0.845 | 0.99    | 0.989 |

Fig.5: Langmuir plots for the P-Cresol adsorption onto Canola biomass.

## Adsorption kinetics

209 In order to examine the mechanism and rate-controlling step in the overall adsorption process,  
210 three kinetic models, pseudo-first-order, pseudo-second-order and intra-particle diffusion, are  
211 adopted to investigate the adsorption process.

212 The pseudo-first-order equation can be expressed as the following equation(38):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$$

213 Where  $q_e$  and  $q_t$  (mg/g) are the P-Cresol adsorption capacity at equilibrium and at time  $t$  (min),  
214 respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo-first-order.

215 The parameters  $k_1$  and  $q_e$  could be calculated from the slope and intercept of the plots of  $\log(q_e$   
216  $q_t)$  versus  $t$  and are given in Table 2. The values of the correlation coefficient  $R^2$  obtained at all  
217 the studied concentrations are low, in the range 0.741–0.862. Furthermore, the experimental  
218 values of  $q_e$ , exp (mg/g) are far from the calculated  $q_e$ , cal (mg/g). This suggests that the pseudo-  
219 first-order kinetic model is not suitable to describe the adsorption process.

220 On the other hand, the pseudo-second-order kinetic model can be expressed in linear form as  
221 follows(39):

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$$

223 where  $k_2$  (g/mg min) is the rate constant of the pseudo- second-order. The  $q_e$  and  $k_2$  values  
224 can be obtained from the slope and intercept of plots of  $t/q_t$  versus  $t$  which are illustrated in Fig.  
225 6. The good linear plots of  $t/q_t$  versus  $t$  at different concentrations with the correlation  
226 coefficients ( $R^2$ ) higher than 0.997 suggest that adsorption of P-Cresol onto canola biomass  
227 predominantly follows the pseudo-second-order kinetic model. Besides, the calculated data  
228 ( $q_e$ , cal) agree well with the experimental data ( $q_e$ , exp). The parameters are listed in Table 2. The  
229 same conclusion was found in the literature on the adsorption of P-Cresol by lemna minor and  
230 azolla filiculoides biomass.

231 The two models above cannot identify the diffusion mechanism during the adsorption process, so  
232 the experimental data are tested by the intra-particle diffusion model, which can be expressed by  
233 following equation(40):

$$q_t = k t^{0.5} + C$$

234 Where  $q_t$  (mg/g) is the amount of P-Cresol adsorbed at time  $t$  (min),  $k$  ( $\text{mg/g min}^{1/2}$ ) is the intra-  
235 particle diffusion rate constant and  $C$  is the intercept.

236 The adsorption of a solute from solution by porous adsorbents is essentially related to three  
237 consecutive steps. The first step is the external surface adsorption or the instantaneous  
238 adsorption. The second step is the gradual adsorption stage where intra-particle diffusion is rate-  
239 limiting. The third step is the final equilibrium stage where intra-particle diffusion started to  
240 slow down due to the extremely low adsorbate concentrations left in the solutions. One or  
241 more of these three steps control the adsorption rate. The parameters are listed in Table 2 and  
242 shows a double straightline nature. Initially, it is postulated that P-Cresol is transported to the

external surface of canola biomass through film diffusion within a very short time. The first linear part could be due to the entry of P-Cresol molecules into the canola biomass particle by intra-particle diffusion. The second linear part represents the final equilibrium stage. As given in Table 2, it is obvious that values of  $k$  increase from 2.14 to 7.36  $\text{mg/g min}^{1/2}$  when the initial P-Cresol concentrations increase from 25 to 200  $\text{mg/L}$ .

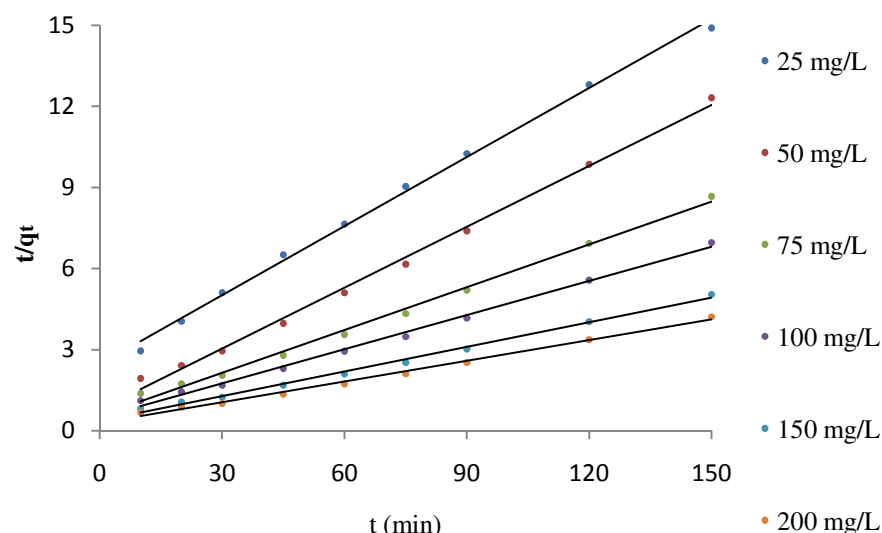


Fig 6: Pseudo-second-order kinetic plots for P-Cresol adsorption onto Canola biomass at Different concentrations.

Table 2: Adsorption kinetic constants P-Cresol adsorption onto Canola biomass

| $C_0$<br>(mg/L) | $q_e$ exp<br>(mg/g) | Pseudo-first order |       |       | Pseudo-second order |       |       | Intraparticle diffusion |       |       |
|-----------------|---------------------|--------------------|-------|-------|---------------------|-------|-------|-------------------------|-------|-------|
|                 |                     | $K_1$              | $q_e$ | $R^2$ | $K_2$               | $q_e$ | $R^2$ | $K$                     | $C$   | $R^2$ |
| 25              | 6.196               | 0.446              | 3.251 | 0.782 | 0.0914              | 5.994 | 0.997 | 2.14                    | 1.212 | 0.956 |
| 50              | 12.17               | 0.149              | 7.144 | 0.741 | 0.0689              | 11.49 | 0.998 | 3.84                    | 3.176 | 0.967 |
| 75              | 17.30               | 0.0929             | 12.45 | 0.862 | 0.0341              | 16.42 | 0.998 | 4.45                    | 2.459 | 0.972 |
| 100             | 21.55               | 0.0551             | 15.64 | 0.793 | 0.0172              | 20.85 | 0.999 | 5.98                    | 4.193 | 0.981 |
| 150             | 29.73               | 0.0468             | 21.19 | 0.821 | 0.0035              | 29.11 | 0.999 | 6.29                    | 5.648 | 0.945 |
| 200             | 35.61               | 0.0119             | 26.38 | 0.842 | 0.0056              | 36.24 | 0.998 | 7.36                    | 6.198 | 0.963 |

**Conclusions:** The results obtained from batch equilibrium experiments indicated that the conditions affecting the biosorption of P-Cresol on Canola biomass included initial solution pH, biosorbent dosage, contact time and initial P-Cresol concentration. Low pH and initial P-Cresol concentration favored the biosorption of P-Cresol. With increase in biosorbent dosage and Contact time, the removal efficiency is also enhanced. The results indicated that the Langmuir model provided the best correlation of the experimental data. Pseudo-second-order model was best applicable to the sorption data. The study showed that Canola biomass can be used successfully to uncontaminate the environment.

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