

STUDIES OF BIOSORPTION KINETICS OF PHENOL BY ORANGE PEEL AND TEA WASTE

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In this paper, eco-friendly bio sorbents (orange peel and tea waste) were used for removal of phenol from aqueous solution. Physio-chemical characterization of the orange peel and tea waste before and after phenol bio sorption were analysed using Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), energy dispersive atomic X-ray spectroscopy (EDAX) and Fourier transform infrared spectroscopy (FTIR). Orange peel and tea waste were washed and dried in order to study the effect of pH, bio sorbent dose (m) and contact time (t) in the adsorption process of phenol. Maximum removal percentage of phenol was found to be 34.8% at optimum dosage 8g/l, pH 10 and contact time 4h for orange peel and 27.2% at optimum dosage 5g/l, pH 5.8 and contact time 4h for tea waste. The maximum adsorption capacities were found to be 70 mg/g and 120 mg/g for removal of phenol with orange peel and tea waste respectively. On the basis of bio sorption kinetic models, second order reaction best fitted the experimental data.

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1. Introduction

Phenol and phenolic compounds are extensively discharged by different industries such as petroleum refinery, pharmaceutical, petrochemical, textile, paper & pulp, dye, cosmetics and synthetic coal fuel conversion plant, etc.[1]. The effluents of these industries are highly toxic and disposal of these wastes is very important for sustainable development. Presence of these compounds may cause vomiting, pulmonary oedema, hepatic injury, kidney injury, paralysis, heart damage, paralysis and death [2]. According to WHO (2008), concentration of phenol in drinking water should not exceed 0.001 mg/l [3]. Permissible limit of phenol should not exceed 1.0 mg/l for their discharge into surface water and 5.0 mg/l for discharge into public sewers, land for irrigation and on marine coastal areas [4]. Due to high toxicity, high oxygen demand and low biodegradability, a conventional biological treatment process is not very effective in treating a phenol wastewater. Several physical and chemical methods are available such as adsorption, chemical oxidation, precipitation, ion exchange, ozonation, coagulation, ultra-filtration, electrochemical oxidation and photo-degradation to remove phenol from wastewater [5, 6]. These treatment methods are expensive and have operational issues such as maintaining constant intensity of light radiation for photo-degradation process and increase of iron content in coagulation process if ferrous sulphate is added. Adsorption of the molecules onto various adsorbents is a very good and eco-friendly technique due to its environmental friendly behaviour, cost-effectiveness and abundance of adsorbents. Despite being the most effective adsorbent, the use of activated carbon increases the cost of adsorption systems. Some earlier research worked on low cost, non-conventional adsorbents such as coir pith, banana pith, coconut husk, saw dust,

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biogas residual slurry, bagasse and paddy straw, industrial solid wastes such as fly ash and coal, red mud, wool fibre, cotton fibre, chitosan, hardwood, neem husk, gypsum, tamarind fruit shell and cashew nut shell [7-12]. The aim of this study is to remove phenol from aqueous solution by using orange peel and tea waste as bio sorbents. Orange peel and tea waste principally consist of holocellulose (cellulose and hemicelluloses), lignin, chlorophyll pigments and other low molecular weight hydrocarbons[13,14]. Orange peel and tea waste are waste material which is easily obtained in any local markets. Orange peel and tea waste have been characterized to evaluate its physio-chemical properties and phenol adsorption on the surface by varying different parameters such as pH, dosage and contact time. Finally, experimental data were analysed by different kinetic models such as pseudo first and second order and Weber Morris kinetic model.

2. Experimentation

2.1. Chemicals used

Phenol (C_6H_5OH), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from S.D. Fine Chemicals, Ltd., New Delhi, India. Test solutions were prepared by diluting 1 mg/l of stock solution with double-distilled water. Synthetic wastewater having a range of phenol concentrations (50 to 1000 mg/l) was prepared by diluting the stock solution with double-distilled water.

2.2. Preparation of Orange peel and Tea waste bio sorbents

Orange peel and tea waste were collected from a local market in Bhopal. These wastes were washed with water several times to remove soluble lighter materials before being washed with double-distilled water (orange peel cut into small pieces). After that orange peels and tea waste were dried in open sun for two days and kept inside a hot air oven at temperature of 80°C for 24 h [15]. The peel biomass was grinded and sieved to small particles and kept in storage for further use. BET surface and pore volume were measured by Micromeritics Chemisorb 2720 instrument [16]. Samples were first gold coated using a sputter coater, (Edwards S150). SEM-EDAX was analysed by JEOL, model JSM-5300, model 435 VP, Japan. Gold sputtering provided conductivity to the samples. Morphology of orange peel and tea waste was studied by using SEM simultaneously with an EDAX spectrometry for elemental analysis. FTIR spectrometer (3000 Hyperion with Vertex 80, Germany) was employed to determine the presence of functional groups. KBr-Pellet (pressed-disk) technique has been used for this purpose. The thermal degradation characteristic of the biosorbent was studied using the TGA analyser (DuPont Hi-Res TGA 2950, USA). The above characterization methods were adopted from the other researcher [12].

2.3. Method of Analysis

A stock solution was prepared by diluting a known amount of phenol with double-distilled water. From this stock solution, different concentrations of 50, 100, 250, 500, 750 and 1000 mg/l were prepared. The final concentration of phenol in solution were determined at 280 nm (This is a fixed wavelength range for analysis of phenol by chromatographic method) wavelength using high performance liquid chromatography (HPLC) supplied by waters (India) Pvt. Ltd., Bangalore. A mixture of 40% methanol, 60% HPLC grade water and 1% acetic acid was used as a solvent or mobile phase; its composition and temperature play a major role in this analysis. In this system C_{18} column (4.6 mm × 150 mm) was used with flow rate of solvent at 0.5 ml/min.

2.4. Batch adsorption study

For batch adsorption study, different amounts of orange peel or tea waste were added separately into 100 ml of a known concentration of phenol in 250 ml conical flasks. These flasks were kept in orbital shaker (Metrex Scientific Instruments, New Delhi) at 303 K temperature at 150 rpm (rotation per minute). Samples were withdrawn from the shaker after attaining the optimum time. The contents were centrifuged using a research centrifuge (Remi Instruments, Mumbai) at 1000 rpm for 5 minutes. After centrifugation, supernatant liquid was analysed by

HPLC. The solution pH was maintained by the addition of dilute 2 N HCl and 1 N NaOH solutions.

The percentage of phenol removal from the solution was calculated as:

$$\% \text{ phenol removal} = 100 (C_o - C_t)/C_o \quad (1)$$

And the amount of phenol adsorbed by bio sorbent was calculated as

$$q_t = (C_o - C_t) V/w \quad (2)$$

Where, C_o is the initial concentration of phenol (mg/l), C_t is the concentration of phenol (mg/l) after equilibrium time, V is the volume of the solution (L) and w is the mass of the bio sorbent (g)

2.5. Statistical analysis

All experiments were conducted in triplicate and statistical analysis was performed by using IBM SPSS statistics software program. Analysis of variance was done by the one-way ANOVA procedure. T-tests were used to determine significant difference in the value of k_f , $q_{e,cal}$, $q_{e,exp}$, K_s , h , K_{id1} and K_{id2} between phenol-orange peel and phenol-tea waste adsorption systems.

3. Results and Discussion

3.1. Physio-chemical characterisation of biomass

Physico-chemical and textural characterization of the blank and some of the characteristics of phenol-loaded orange peel and tea waste were discussed. The average particle sizes of orange peel powder and tea waste were found to be 0.35 mm and 0.57 mm respectively. No ash was found in blank or phenol-loaded orange peel or tea waste. The proximate analysis for the presence of moisture, volatile matter and fixed carbon contained in the orange peel and tea waste (blank and phenol loaded) is shown in Table 1. Some characterisations of the orange peel and tea waste are presented in Table 2.

The distribution of elements (carbon, oxygen, calcium, magnesium, silica and sodium) in orange peel and tea waste for blank and phenol loaded samples are shown in Table 3.

Table 1. Proximate analysis of orange peel and tea waste

	Orange peel		Tea waste	
	Blank	Phenol loaded	Blank	Phenol loaded
Moisture	10.03%	1.02%	8.08%	0.84%
Volatile matter	15.39%	10.13%	11.21%	8.14%
Fix carbon	70.87%	78.66%	68.87%	70.01%

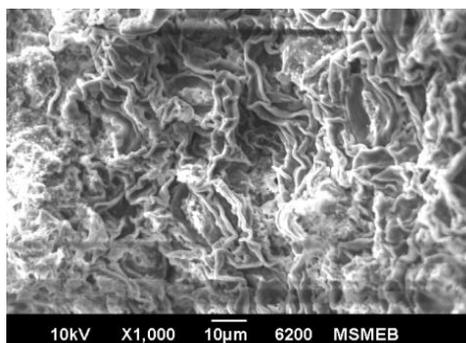
Table 2. Characterisations of orange peel and tea waste

	Orange peel	Tea waste
Bulk density, kg/m ³	321	555
Heating value, MJ/kg	4.51	5.11
BET surface area, m ² /g	391.07	261.35
BET average pore size, Å	12.23	7.23
Total pore volume, cm ³ /g	0.2135	0.2532

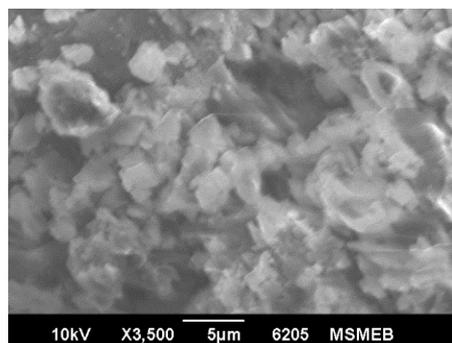
Table 3. Distribution of elements in orange peel and tea waste

Elements	Orange peel		Tea waste	
	Blank	Phenol loaded	Blank	Phenol loaded
Carbon, %	58	67.7	48.8	60.29
Oxygen, %	24.09	25.08	15.98	26.55
Calcium, %	2.94	0.84	3.84	2.5
Magnesium, %	5.96	2.23	11.2	2.1
Silica, %	7	2.62	8.62	3.4
Sodium, %	2	1.7	5.7	2.2

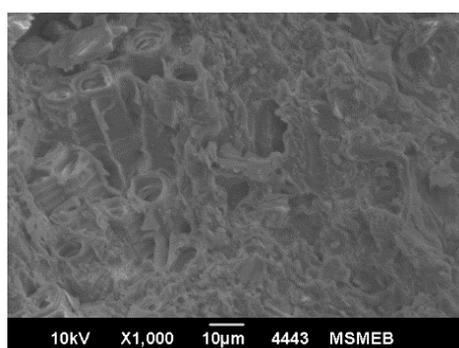
The obtained SEM micrographs are shown in Fig. 1 for blank and phenol-loaded orange peel powder and tea waste. Blank-orange peel powder and tea waste show random types of irregular and porous surfaces. Insignificant differences in surface texture between blank and phenol-loaded orange peel powder and tea waste are observed at low magnification. However, at higher magnification more bright spots are observed in phenol-loaded orange peel powder and tea waste which may be due to the filling of pores.



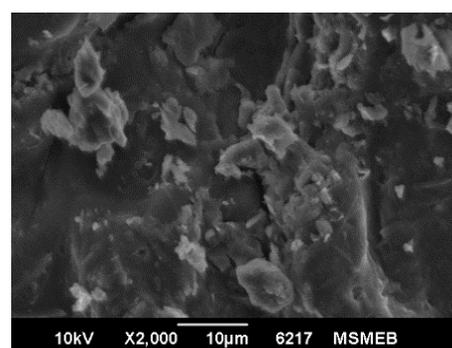
(a) Fresh tea waste



(b) phenol-loaded tea waste



(c) Orange peel powder



(d) phenol-loaded orange peel powder

Fig. 1. SEM images of blank and phenol loaded tea waste and orange peel.

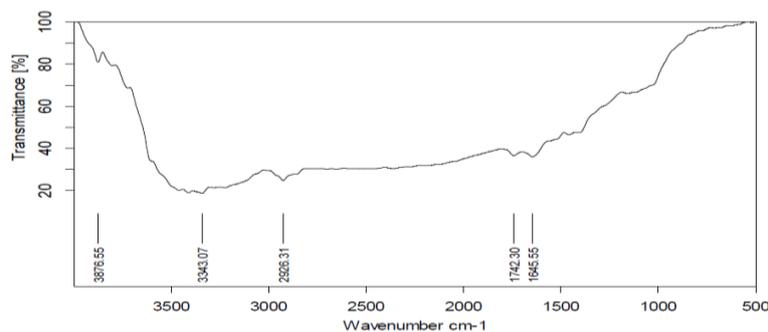


Fig. 2. FTIR of orange peel powder

To determine the interaction between phenol with functional groups present in the orange peel and tea waste, surfaces were shown in FTIR analysis. The infrared spectra of the OH stretching region of blank orange peel powder at natural pH is shown in Fig. 2. The infrared spectra of blank orange peel powder display many peaks in the region $1645.55\text{--}3876.56\text{ cm}^{-1}$. These bands are assigned to OH stretching vibrations of the surface. Figure 2 shows peaks at 1645.55 cm^{-1} , 1742.30 cm^{-1} , 2926.31 cm^{-1} , 3343.07 cm^{-1} and 3876.56 cm^{-1} . Some of these peaks may be due to the water-hydrogen bonded OH units and non-hydrogen bonded OH units. The peaks found for blank-orange peel powder and tea waste disappeared completely in phenol-orange peel powder and phenol-tea waste spectra (not shown figure here) due to the adsorption process.

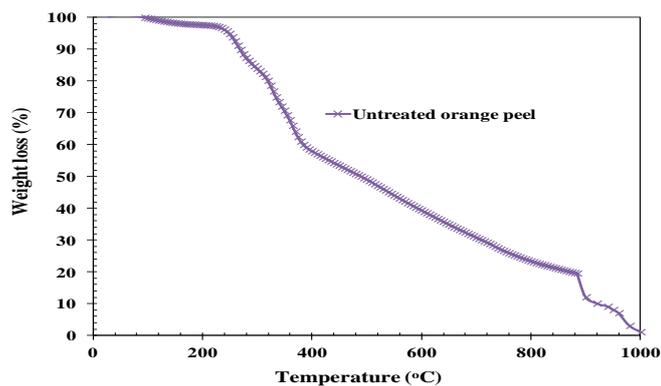


Fig. 3. Thermogravimetric analysis of orange peel powder

Fig. 3 shows the TG traces for the orange peel powder. Weight loss and the evolution of some light weight molecules were found to be 8-15% at a temperature range of 25 to 250°C . The samples were dried at 105°C . Due to the loss of the surface tension bound water of the particles, the rate of weight loss was found to increase with temperature from 200 to 840°C for orange peel powder. Oxidation of orange peel powder at this temperature range results in a gradual weight loss from 10 to 80%.

3.2. Effect of solution pH

The effect of pH on phenol removal of orange peel powder and tea waste by varying pH 2-12 is shown in Fig. 4. Removal of phenol increases with an increase in pH of the solution and the optimum removal efficiency found at pH 10 for orange peels and pH 6 for tea waste. Further increase in pH leads to a decrease in phenol removal efficiency. Orange peel contains various functional groups, such as carboxyl, amino, hydroxyl groups, which could also be affected by the pH of solutions. Therefore, nature of phenol molecules and orange peel properties as well as electrostatic attraction could play a very important role in phenol adsorption on orange peel and tea waste. Similar trends were observed for in the removal of dyes and As (III) by orange peel [15],

[17]. The highest removal of phenol was observed in the pH range of 5 to 9 and this was also found from another similar research in the extraction of phenol by iron oxide [18]. So the optimum pH was 10 for orange peel and 6 for tea waste and it was used in further studies.

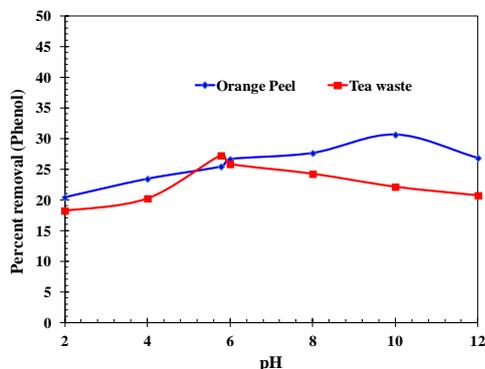


Fig. 4. Effect of pH on the percent removal of phenol onto orange peel powder and tea waste, $C_o=500\text{mg/l}$ and $t=24\text{h}$, $T=303\text{K}$

3.3. Effect of bio-sorbent dosage

Fig. 5 shows the effect of bio sorbent loading on the phenol removal ranging from 0 to 10 g/l, while other parameters were kept constant at $C_o = 500 \text{ mg/l}$, $T = 303 \text{ K}$, $t = 24\text{h}$, pH 10 for orange peel and pH 6 for tea waste. The phenol removal efficiency increases from 20 % at $m=1 \text{ g/l}$ to 34.8 % at $m=8 \text{ g/l}$ with orange peel powder and 18 % at $m=1 \text{ g/l}$ to 27.2 % at $m = 5\text{g/l}$ with tea waste. From Fig. 5, it seems that as the bio sorbent dose increases, phenol removal efficiency increases. This may be due to the presence of more available active sites in bio sorbent [11]. But after optimum conditions were reached, phenol removal efficiency decreases due to the saturation of the active sites present on available bio sorbent. Thus, $m=8 \text{ g/l}$ was chosen as the optimum bio sorbent dose for orange peel powder and 5g/l for tea waste bio sorbent.

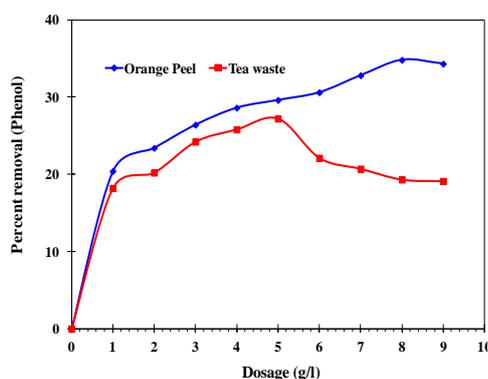


Fig. 5. Effect of dosage on the percent removal of phenol on the orange peel

3.4. Effect of contact time

Figure 6 shows the effect of contact time (0-24 h) on the q_t values as C_o varies from 50 to 1000 mg/l at $m=8\text{g/l}$ and 5 g/l , pH 10 and $T = 303 \text{ K}$ for orange peel and tea waste. The amount of phenol adsorption increases with contact time and attains equilibrium at about 4 h as shown in Fig.6. The sorption process can be considered very fast as there is rapid uptake of phenol to the sorbent within the first 4 h of adsorption and thereafter, it becomes slower near the equilibrium due to a large number of vacant surface sites are available for the adsorption during the initial period [11]. Also repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase play a role in diminishing the sorption rate. The reason for the repulsive force may be

due to increase in temperature in the adsorption process. Similar findings were reported in the removal of phenol from aqueous solution by cassava peel and chemically modified cassava peels[19]. In this study it was found that uptake of phenol decreases with increase in temperature. This is due to increase in temperature increases the average kinetic energy of phenolium ions which will cause the repulsive force between the phenolium ions and positively charged cassava peel surface.

Another finding shows that concentration of phenol drops sharply in less than 3 hours by using different grade activated carbon as adsorbent [20].

Phenol molecules were initially absent in the bio sorbent, but after some time the uptake of the phenol molecules by the bio sorbent is given in Eq. 3 [11].

$$q_t = q_e [1 - \exp(-k_f t)] \quad (3)$$

Where, q_e amount of the adsorbate adsorbed on the bio sorbent under equilibrium condition and k_f is the pseudo-first-order rate constant.

The pseudo-second-order kinetic model as shown in Eq. 4 is given [21].

$$q_t = \frac{tk_s q_e^2}{1 + tk_s q_e} \quad (4)$$

The Marquardt's percent standard deviation (MPSD) error is given in Eq. 5 [22].

$$MPSD = 100 \sqrt{\frac{1}{n_m - n_p} \sum_{i=1}^m \left(\frac{q_{e,i,exp} - q_{e,i,cal}}{q_{e,i,exp}} \right)^2} \quad (5)$$

In error function equation, the subscripts 'exp' and 'calc' represent the experimental and calculated values, n_m is the number of measurements, and n_p is the number of parameters in the model. The possibility of intra-particle diffusion was explored by Weber and Morris model expressed in Eq. 6 [23].

$$q_t = k_{id} t^{1/2} + I \quad (6)$$

Where, k_{id} is the intra-particle diffusion rate constant, value of I is the thickness of the boundary layer.

Fig. 6 (a-b) shows the effect of contact time (0–24 h) on the q_t values for $C_o = 50$ -1000 mg/l at $m=8$ g/l, 5 g/l, $T=303$ K for orange peel powder, tea waste. In the first hour, fast adsorption of phenol occurred at all C_o and thereafter, the adsorption rate decreased gradually and the adsorption reached equilibrium. However, at C_o (50-1000 mg/l), 4 h contact time was found to be the equilibrium time in which minimum of the residual concentrations than those obtained after 24 h contact time. Therefore, after 4 h contact time, a steady state approximation was assumed and quasi-equilibrium was formed. Fig. 6 (a-b) shows that q_e increases with an increase in C_o . The C_o provides the necessary driving force to overcome the mass transfer resistance of phenol between the aqueous phase and the solid phase. The increase in C_o also enhances the interaction between adsorbate molecules and the vacant sorption sites on the adsorbent and the surface functional groups. Intra-particle diffusion to be the rate-controlling step for the uptake of phenol onto granular activated carbon for $C_o = 50$ -1000 mg/l [12]. If the Weber and Morris plot of q_t versus $t_{0.5}$ satisfies the linear relationship with the experimental data, the sorption process is supposed to be controlled by intra-particle diffusion only [23]. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process.

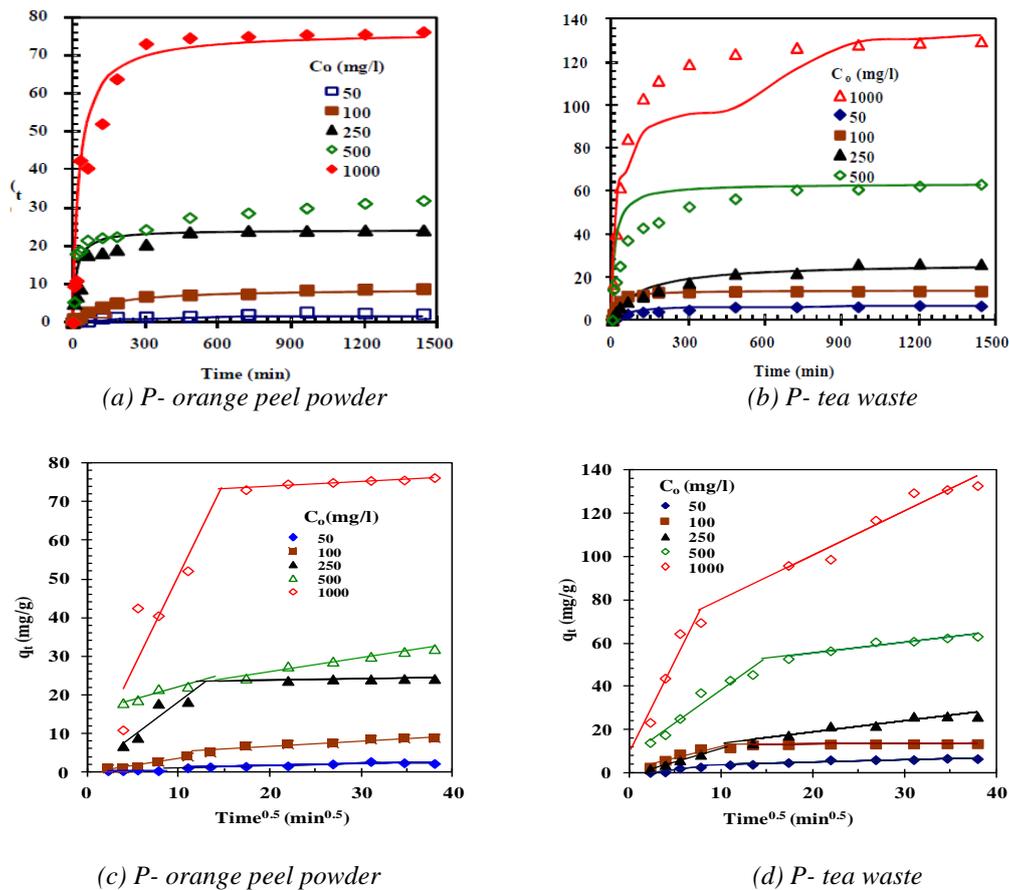


Fig. 6. Effect of contact time on the adsorption of phenol by orange peel powder and tea waste.

Experimental data points given by the symbols and the lines predicted by the pseudo-second-order model. Weber and Morris intra-particle diffusion plot for the removal of phenol by orange peel powder and tea waste at $T=303\text{ K}$, $m=5$ and 8 g/l .

Fig. 6 (c-d) presents the plots of q_t versus $t_{0.5}$ for the phenol and the parametric values are given in Appendixes A and B. In this figure, the data points are related by two straight lines. The curvature from the origin to the start of the first linear portion (not shown in figure) represents the boundary layer diffusion and/or external mass transfer effects and also indicates that pore diffusion is not the sole rate determining step. The first linear portion depicts macro-pore diffusion with general attainment of equilibrium. The second linear portion represents the slower meso-pore diffusion which gets slowed down due to low residual adsorbate concentration and larger pore-diffusion resistance[24]. The slopes of the linear portions are defined as rate parameters ($k_{id,1}$ and $k_{id,2}$) and are characteristics of the rate of adsorption in the region where intra-particle diffusion is rate controlling. It seems that the intra-particle diffusion of phenol into meso-pores (second linear portion) is the rate-controlling step in the adsorption process. The portion of the plots are nearly parallel ($k_{id,2}=0.029\text{--}0.0350\text{ mg/g min}^{0.5}$ for orange peel and $k_{id,2}=0.022\text{--}2.052\text{ mg/g min}^{0.5}$ for tea waste), suggesting that the rate of adsorption of phenol into the meso-pores of orange peel powder and tea waste is comparable at all C_o . Slopes of first portions ($k_{id,1}$) for phenol removal are higher for higher C_o . This corresponds to an enhanced diffusion of phenol through macro-pores, and is attributed to the greater driving force at higher C_o .

The multi-phasic nature of intra-particle diffusion plot confirms the presence of both surface and pore diffusion. In order to predict the actual slow step involved, the kinetic data was further analysed using Boyd kinetic expression (not shown here). The linearity of the plot of B_t versus time was used to distinguish whether surface and intra-particle transport controls the adsorption rate. It was observed that the relation between B_t and t (not shown here) was non-linear

($R^2=0.805-0.964$ for orange peel powder and $R^2=0.884-0.927$ for tea waste) at all concentrations, confirming that surface diffusion is not the sole rate-limiting step. Thus, both surface and pore diffusion seem to be the rate-limiting steps in the adsorption process and the adsorption proceeds via a complex mechanism. Average values of D_e as calculated for both adsorbents are nearly the same: 6.15×10^{-11} and $4.40 \times 10^{-12} \text{ m}^2/\text{s}$, respectively, during the sorption of phenol onto orange peel powder and tea waste.

Two kinetic models, namely pseudo-first-order and pseudo-second-order, were used to investigate the sorption process of phenol onto orange peel powder and tea waste. Pseudo-first order model does not hold good for the adsorption of phenol onto orange peel powder and tea waste. Kinetic parameters along with the MPSD and the correlation coefficient for the non-linear fitting of the data with pseudo-second-order kinetic model are listed in Appendix A. The calculated correlation coefficient is very close to unity. MPSD error function values as shown in Table 1 are also quite low. Therefore, the sorption kinetics can be approximated favourably by the pseudo-second-order kinetic model for phenol. It may be seen that the initial sorption rate (h) continuously increased with an increase in C_o . This is because of the increase in driving force due to an increase in C_o . A comparison of maximum adsorption capacity (q_m) values of orange peel powder and tea waste is given in Appendixes A and B. It shows that the orange peel powder and tea waste exhibits a reasonable capacity for phenol adsorption from aqueous solutions. Another finding in the adsorption of phenol from aqueous solution on a low-cost activated carbon produced from tea industry waste follows pseudo second order kinetics [25].

Mean differences were considered significant at the $p < 0.05$ level. Since p value is greater than 0.05 there is no statistical significance in the value of k_f , $q_{e,cal}$, $q_{e,exp}$, K_s , h , $q_{e,cal}$, K_{id1} and K_{id2} between phenol-orange peel and phenol-tea waste adsorption systems. By one way ANOVA it was found that C_o has no significant effect in the value of k_f , $q_{e,exp}$, K_s , h , and K_{id2} .

4. Conclusions

The waste orange peel powder and tea waste act as effective bio sorbents for the removal of phenol from aqueous solution. The maximum adsorption capacities were 70 mg/g and 120 mg/g for removal of phenol onto orange peel and tea waste. Equilibrium time for this adsorption process was achieved in 4h. From the kinetic study it is observed that the biosorption process is a pseudo-second-order rate reaction. It was found that removal efficiency of phenol using orange peel and tea waste is not much higher compared to other commercial adsorbents. However due to its availability, free of cost, eco-friendly nature, uses of waste material; it can be a better option for bio sorption process.

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