

Removal of Phenol from Aqueous Solution Using Sugar Beet Pulp Activated Carbon

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In this study, activated carbon was obtained from sugar beet pulp by applying low-temperature carbonization at 350 °C. Removal of phenol from aqueous solutions was investigated by applying chemical activation process to activated carbon with HCl and NaOH. For adsorption of phenol removal from aqueous solutions; effects of pH, adsorbent dosage, phenol concentration, temperature and contact times were investigated. The highest removal efficiency was achieved as 63 % at pH of 7 for NaOH-treated activated carbon at 0.1 g adsorbent dosage, 100 mg/L phenol concentration, 1 hour contact time, and room temperature. Results of the experiments showed that the adsorption kinetics obey pseudo-second order kinetic model, respectively.

1. Introduction

Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for many applications. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants due to their potential harm to human health (Hameed and Rahman, 2008). According to the World Health Organization regulation, 0.002 mg L⁻¹ is the permissible limit for phenol concentration and the wastewater containing phenolic compounds must be treated before their discharge into water streams to avoid legal problems (Rodrigues et al., 2011).

In the past years, extensive researches have been undertaken to develop alternative and economic adsorbents produced from a variety of starting materials such as wastes and agricultural residues, wood, bentonite, and polymers (Dursun et al., 2005). Sugar beet pulp is one of these low-cost sorbents and a by-product of the sugar refining industry, which exhibits a large capacity to bind metals. This material is cheap and is essentially used as animal feed. Sugar beet pulp is a natural polysaccharide and is composed of 20 % and more than 40 % of cellulosic (Dronnet et al., 1997); and pectic substances, (Kartel et al., 1999; Aksu and Işoğlu, 2005).

Sugar beet pulp carbon obtained from different methods to use as an adsorbent was studied for removing heavy metals in earlier works, such as (Aksu and Işoğlu, 2005) on Copper removal, as well as Cadmium (Özer and Tümen, 2005), Chromium; Altundoğan, 2005) and phenol (Beker et al., 2010). There are also some studies of phenol adsorption by sugar beet pulp carbon, but little attention has been paid to the investigation of pH, adsorbent dosage, phenol concentration, temperature and contact times dependence of adsorption process and evaluating equilibrium, and kinetic parameters of the system, which are important in the design of treatment systems (Dursun et al., 2005). This study was carried at low temperature as 350 °C and also demonstrates that activated carbon can be specifically expressed as green carbon.

This study presents the adsorption characteristics of sugar beet pulp activated carbon for removing phenol from aqueous solutions. The binding capacity of activated carbon for phenol was shown as a function of initial pH, adsorbent dosage, phenol concentration, temperature and contact times in this study.

2. Materials and Methods

2.1 Preparation of sugar beet pulp carbons

Sugar beet pulp was collected from Central Region of Anatolia. Sugar beet pulp first washed with distilled water to remove impurities like dust, then air-dried at room temperature, ground in a ball-mill, sieved and stored in a dark room. Sugar beet pulp with a mean particle size was carbonized at 350 °C in a furnace. After being carbonized, samples were first activated with 1 M HCl or NaOH by agitating for 2 hours at room temperature to obtain two different activated carbons and then all the carbonized samples were washed several times with hot water to remove residual chemicals until the pH became neutral. The samples were finally filtered with black label filter paper and classified as ACSP-I, and ACSP-II, represents HCl, and NaOH treatment, respectively.

2.2 Adsorption studies

Analytical reagent grade phenol ($\geq 99\%$, Sigma Aldrich), HCl (37%, Merck), and NaOH (99.8 - 100.5%, Sigma Aldrich) were used in the experimental runs. Stock solution of phenol (1000 mg/L) was prepared by dissolving a weighed amount of phenol in distilled water. The experimental test solutions were prepared by diluting the respective stock solution of phenol with distilled water and mixing them in the desired proportion.

Adsorption experiments were carried out in batch processes by agitating 50-500 mg of activated carbon samples with 50 mL of phenol solution in a thermostated bath with a shaker. The parameters varied in the experiments from 1 to 9 for pH, from 20 to 100 mg/L with an increase of 20 mg/L for phenol concentration, 0.025 g and from 0.1 g to 0.5 g with an increase of 0.1 g for adsorbent dosage, from 20 to 120 min with an increase of 20 min for contact time and from 20 to 40 °C with an increase of 10 °C for temperature. The effect of different treatment agents onto activated carbons was investigated using by HCl and NaOH. Thus, 0.1 M HCl and 0.1 M NaOH buffer solutions was used in order to adjust solution pH. The pHs of the solutions were measured regularly using a Thermoscientific Orion 3 Star pH-meter and kept constant by adding HCl and NaOH solutions during the all batch adsorption experiments. The concentration of phenol was determined using by a Jasco V-530 UV/visible spectrophotometer at λ_{max} , 270 nm (Beker et al., 2009). The final phenol concentration was measured from the standard calibration curve. The amount of phenol adsorbed per unit mass (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_f)}{C_0} \quad (1)$$

$$q_t = \frac{|(C_0 - C_f)V|}{m} \quad (2)$$

where q_e and q_t are the amounts of phenol absorbed at equilibrium and time t ; C_0 and C_f are the initial and final phenol concentrations (mg/L) respectively. m is the adsorbent dosage (g) and V is the volume of solution (L) (Alam et al., 2009).

The phenol removal efficiency (η) was defined as:

$$\eta_{wa} = \left(\frac{C_0 - C_e}{C_0} \right) 100 \quad (3)$$

3. Results and Discussion

3.1 Adsorption studies

The adsorption of phenol was studied within pH range of 1-9 and adsorbent dosage, initial phenol concentration, contact time and temperature were kept constant at 0.1 g, 100 ppm, 1 hour and room temperature, respectively. Figure 1 shows the influence of solution pH and according to the results, maximum removal efficiencies were determined at pH 6 as 58.36% and 59.42% for ACSP-I and ACSP-II respectively. The phenol removal rose with the increase of the pH up to 6, decreased after it. Therefore, at pH values lower than 6 the surface of activated carbon is charged positively and the activated carbon surface is charged negatively at pH values higher than 6. Consequently, at pH higher than 6 phenol molecules are in their dissociated and anionic forms, and the activated carbon surface is negatively charged.

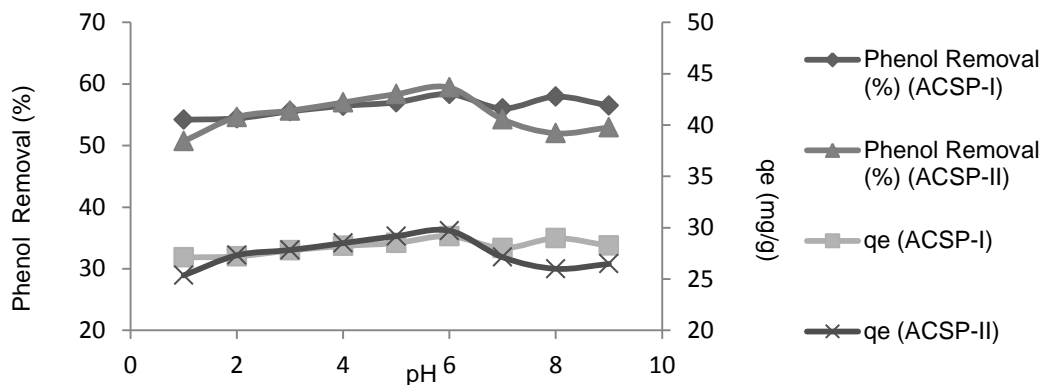


Figure 1: Effect of pH on henol removal onto ACSP I and ACSP II

The anionic form of phenol molecules and the presence of OH⁻ groups on the activated carbon surface are determinant to the characteristics of the adsorption processes (Rodrigues et al., 2011). At basic pH (>7), phenol adsorption became difficult due to the repulsion of the accumulation for negatively charged hydroxyl ions around the adsorbent surface.

The effect of the adsorbent dosage on the uptake of phenol was studied using of 50 mL of 100 mg/L phenol aqueous solutions. A sample of activated carbon was added, which mass ranged from 0.025 to 0.5 g. In all experiments, the temperature was kept at 298 K. Figure 2 shows the results of the study related to the effect of the adsorbent dosage on the phenol adsorption process. Phenol removal is dependent on the mass of activated carbon present in the solution and it increased when the adsorbent dosage increased. This growth can be attributed to the additional number of adsorption sites, which resulted from the increment on the adsorbent dosage. On the other hand, the total adsorbed amount of phenol (q_e) decreased as the adsorbent dosage increases. This is related to the aggregation or overlapping of adsorption sites due to overcrowding of adsorbent particles, which resulted in a decrease in total adsorbent surface available to the phenol. Interaction of particles could also desorb some sorbate molecules, since these molecules could be bound weakly and reversibly to the surface activated carbons. Therefore, at high adsorbent dosage, some adsorption sites remained unsaturated during the adsorption process because they were not accessible (Rodrigues et al., 2011). The adsorbent dosage was maintained at 0.1 g in all the subsequent experiments, which was considered that 0.5 g and 0.1 g has similar percentage of removal.

The effect of initial phenol concentration on the adsorption of phenol was determined within constant pH (6), adsorbent dosage (0.1 g/50 mL), contact time (1 hour) and room temperature. Solutions of phenol concentration at 20, 40, 60, 80, and 100 mg/L were studied and the results are given in Figure 5. As shown in Figure 3, the adsorption of phenol by activated carbons increased as the initial phenol concentration increased. Increasing the initial phenol concentration would increase the mass transfer driving force and therefore the rate at which phenol molecules pass from the bulk solution to the particle surface (Banat et al., 2000). This would result in higher phenol adsorption.

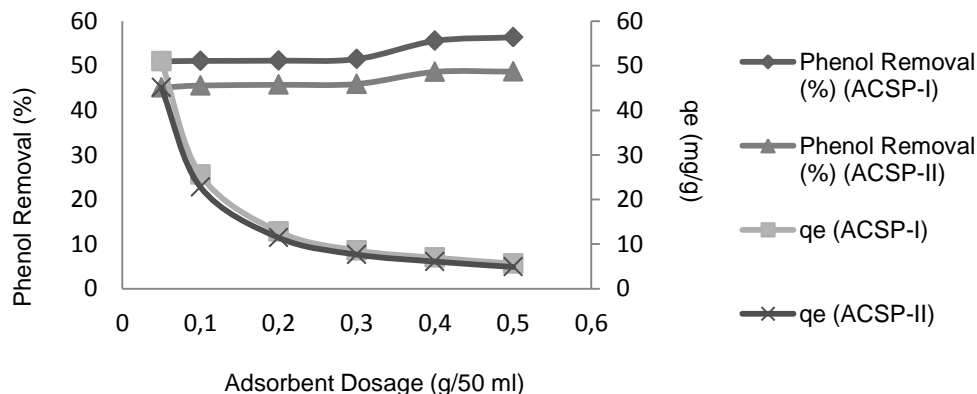


Figure 2: Effect of adsorbent dosage on phenol removal onto ACSP-I, and ACSP-II

In the case of lower concentrations, the ratio of phenol to the available sorption sites was low and lower adsorption yields were obtained. At higher concentrations, the numbers of phenol ions were relatively higher than available sites for adsorption. The maximum removal was achieved at both 100 mg/L as 45.71 %, and 47.14 % for ACSP-I, and ACSP-II, respectively.

The effects of temperature at 20, 30, and 40 °C and contact time at 20, 40, 60, 80, and 120 minutes were studied together at optimum pH (6), adsorbent dosage (0.1 g) and phenol concentration (100 mg/L). The experimental results are represented in Figure 4 and as illustrated, phenol removal decreased according to increasing contact time and temperature except ACSP-I at 30 °C. ACSP-I and ACSP-II had the highest removal at 30 °C as 47.6 % and 23 %, respectively.

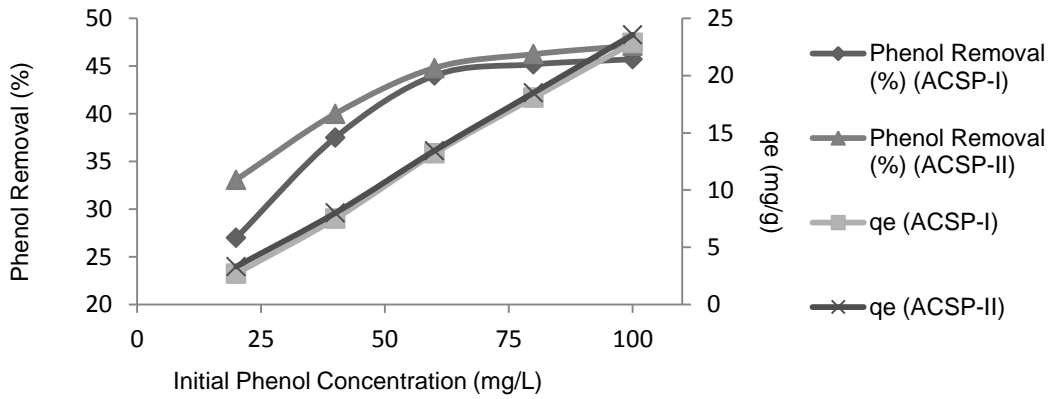


Figure 3: Effect of initial phenol concentration on phenol removal onto ACSP-I, and ACSP-II

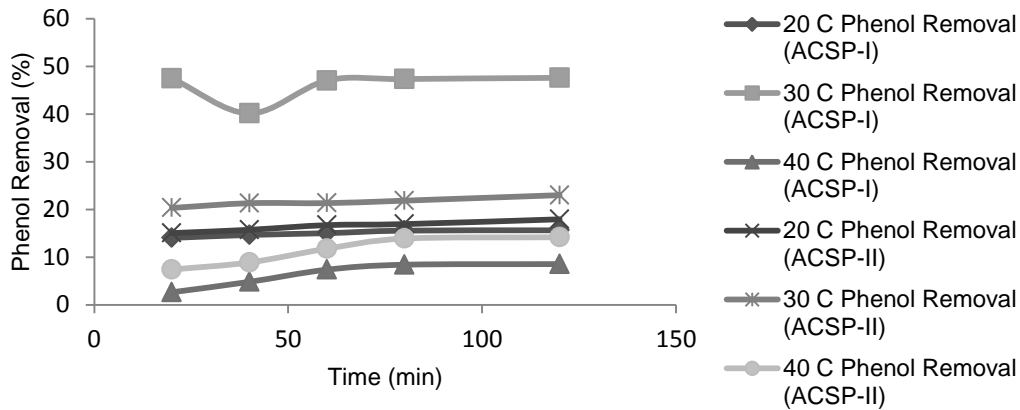


Figure 4: Effect of temperature and contact time on phenol removal onto ACSP I and ACSP II

The adsorption process reached equilibrium after 80 min. After 80 min, the remaining surface sites were difficult to be occupied because of the repulsion between the solute molecules of the solid. When the amount of phenol being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of phenol desorbed from the adsorbent, phenol removal reached a constant value (Ahmad and Rahman, 2011).

3.2 Kinetic modeling of phenol adsorption

Adsorption mechanism depends on transportation process as well as physical and chemical properties of adsorbent (Duranoğlu et al., 2012). The kinetics of adsorption of phenol on activated carbons was studied using two simplified kinetic models, including pseudo-first-order [Eq(4)] and pseudo-second order equations Eq(5)].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Here k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constants of the pseudo-first-order and second-order adsorption kinetics, respectively. Integrating Eqs(6) and (7) for the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ gives (Aroğuz and Gülen, 2008),

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (7)$$

Kinetic parameters calculated from linear plots of both models and correlation coefficient values are given in Table 1. Correlation coefficients of pseudo-second-order model indicated better correlation coefficients. According to results, linear plots of pseudo-first-order kinetic model did not fit the data, while pseudo-second-order plots fitted data very well. Therefore, it can be stated that phenol adsorption onto produced carbon consist of chemical adsorption due to the fact that pseudo-second-order kinetic model suggests that adsorption process involved chemisorption mechanism (Duranoğlu et al., 2012).

4. Conclusions

The removal of phenol from aqueous solution by activated carbons produced from sugar beet pulp and treated with HCl or NaOH has been investigated under different experimental conditions in batch model. The amount of adsorption increased with increasing adsorbent dosage and pH until 6. The equilibrium time of adsorption was found to be 80 min at room temperature. The kinetic of adsorption process was best described by the pseudo-second-order rate equation. In conclusion, the use of activated carbons from sugar beet pulp as a green adsorbent could be alternative for the high cost adsorbents due to its low cost and good efficiency for removal of phenol from aqueous solutions.

Table 1. Comparison of first order and second order adsorption rate constants calculated for different temperatures

Temperature	Parameters					
	20 °C		30 °C		40 °C	
	ACSP-I	ACSP-II	ACSP-I	ACSP-II	ACSP-I	ACSP-II
Pseudo-first-order						
k_1	0.048	0.018	0.037	0.011	0.039	0.050
q_e	3.033	2.729	2.667	1.621	8.669	14.723
R^2	0.849	0.857	0.959	0.903	0.890	0.850
Pseudo-second-order						
k_2	0.036	0.011	0.027	0.018	0.001	0.003
q_e	8.064	9.523	24.390	11.904	7.936	9.346
R^2	0.999	0.995	1	0.998	0.972	0.972

References

- Hameed B.H., Rahman A.A., 2008, Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material, J of Haz Mat, 160, 2-3, 576-581.
- Rodrigues L.A., Caetano Pinto da Silva M.L., Alvarez-Mendes M.O., dos Reis Coutinho A., Thim G.P., 2011, Phenol removal from aqueous solution by activated carbon produced from avocado kernel seeds, Chem Eng J, 174, 1, 49-57.
- Ahmad M.A., Rahman N.K., 2011, Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon, Chem Eng J, 170, 1, 154-161.

- Aksu Z, İšođlu I.A., 2005, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, *Process Biochemistry*, 40, 9, 3031-3044.
- Alam Md.Z., Ameer E.S., Muyibi S.A., Kabbashi N.A., 2009, The factors affecting the performance of activated carbon prepared from oil palm empty fruit bunches for adsorption of phenol, *Chem Eng J*, 155, 1-2, 191-198.
- Altundogan H.S., 2005, Cr(VI) removal from aqueous solution by iron (III) hydroxide-loaded sugar beet pulp, *Process Biochem.*, 40, 3-4, 1443-1452.
- Aroguz A.Z, Gulen J, Evers R.H, 2008, Adsorption of methylene blue from aqueous solution on pyrolyzed petrified sediment, *Bioresource Technol.*, 99, 6, 1503-1508.
- Banat F.A., Al-Bashir B., Al-Asheh S., Hayajneh O., 2000, Adsorption of phenol by bentonite, *Environmental Pollution*, 107, 3, 391-398.
- Beker U., Ganbold B., Dertli H., Duranođlu Glbayir D., 2010, Adsorption of phenol by activated carbon: Influence of activation methods and solution pH, *Energy Conversion and Management*, 51, 2, 235-240.
- Dronnet V.M., Renard C.M.G.C., Axelos M.A.V., Thibault J.F., 1997, Binding of divalent metal cations by sugar-beet pulp, *Carbohydr Polym*, 34, 1-2, 73-82.
- Duranođlu D., Trochimczuk A.W., Beker U., 2012, Kinetics and thermodynamics of hexavalent chromium adsorption onto activated carbon derived from acrylonitrile-divinylbenzene copolymer, *Chem Eng J*, 187, 1, 193-202.
- Dursun G., Cicek H., Dursun A.Y., 2005, Adsorption of phenol from aqueous solution by using carbonised beet pulp, *J of Haz Mat*, 125, 1-3, 175-182.
- Kartel M.T., Kupchik L.A., Veisov B.K., 1999, Evaluation of pectin binding of heavy metal ions in aqueous solutions, *Chemosphere*, 38, 11, 2591-2596.
- Ozer A., Tumen F., 2003, Cd(II) adsorption from aqueous solution by activated carbon from sugar beet pulp impregnated with phosphoric acid, *Fresen. Environ. Bull.*, 12, 9, 1050-1058.