

Removal of Phenol from Aqueous Solutions by Adsorption onto Polymeric Adsorbents

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ABSTRACT: Phenolic compounds are one of the most representative pollutants in industrial wastewater, and efficient removals of them have attracted significant concerns. In this study, several commercial and new synthetic polymers (acrylonitrile, 1,3-butadiene, and styrene copolymer (ABS), styrene, acrylonitrile copolymer (SAN), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), poly(*tert*-butyl acrylate) (*pt*BA)) with special functionalities were evaluated for their ability to remove phenol from an aqueous solution. Equilibrium studies were conducted in the range of 20–100 mg/L initial phenol concentrations, 3–11 pH solutions, and a temperature range of 25–65°C. The results showed that (styrene, 1,3-butadiene) copolymer (SAN) gave the best adsorption capacity among all of the polymers tested. The solution

temperature, phenol concentration, and agitation rate played a significant role in influencing the capacity of the adsorbents toward phenol molecules. An increase in solution temperature led to a significant increase in the adsorption capacity of SAN. The percentage of adsorption decreased when initial concentration of phenol increased. However, the percentage removal of phenol was observed to increase with agitation. Removal of phenol using polymeric microbeads is difficult to investigate under high and low pH values because it requires a lot of acid or base to adjust the pH values in the adsorption media. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1908–1913, 2010

Key words: wastewater; phenol removal; polymers; adsorption isotherm

INTRODUCTION

Wastewater treatment due to organic pollutants remains a serious environmental and public problem. Moreover, faced with more and more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors. Aromatic compounds (including phenolic derivatives and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses.¹ They are common contaminants in wastewater and many of them are known to be toxic or carcinogenic. Phenols and chlorinated phenols are considered as priority pollutants since they are harmful to organisms even at

low concentrations.^{2,3} Strict legislation on the discharge of these toxic products makes it then necessary to develop various efficient technologies for the removal of pollutants from wastewater. Conventional methods for the removal of phenolic pollutants in aqueous solutions can be divided into three main categories: physical, chemical, and biological treatment.⁴ Different technologies and processes are currently used. Biological treatments,^{5,6} membrane processes,^{7,8} advanced oxidation processes,^{9,10} chemical and electrochemical techniques,^{11,12} and adsorption procedures^{13,14} are most widely used for removing metals and organic compounds from industrial effluents. Among them, physical adsorption method is generally considered to be the best, effective, low cost, and most frequently used method for the removal of phenolic pollutants. Adsorption is a well-known equilibrium separation process. It is now recognized as an effective, efficient, and economic method for water decontamination applications and for separation analytical purposes. The adsorbents may be of mineral, organic, or biological origin: such

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as activated carbons, zeolites, clay, silica beads, etc. However, the high initial cost and the need for a costly regeneration system make the activated carbon less economically viable as excellent adsorbent.^{15,16} Therefore, the search for low cost and easily available adsorbents has led many researchers to search more economic and efficient techniques of using the natural and synthetic materials as adsorbents. Natural zeolites,¹⁷ clays,¹⁸ and tree minerals^{19,20} gained a significant interest among scientist, mainly due to their valuable properties such as ion exchange capability. Large deposits of natural zeolites in many countries such as Greece, UK, Italy, Mexico, Iran, and Jordan provide local industries some promising benefits such as cost efficiency since they are able to treat wastewater contaminated with heavy metal at low cost. Clay is one of the potential alternatives to activated carbon as well. Similar to zeolites, clay minerals are also important inorganic components in soil. Their sorption capabilities come from their high-surface area and exchange capacities. The negative charge on the structure of clay minerals gives clay the capability to attract metal ions. Other low-cost adsorbents, such as agricultural wastes,²¹ and fly ash^{22,23} have been studied less extensively due to their local availability.

In recent years and because of its better mechanical strength and feasible regeneration under mild conditions, polymeric adsorbents have increasingly been used for efficient removal of specific organic compounds from contaminated water.²⁴ To attain large adsorption capacity for a specific organic compound, chemical modification of the polymeric adsorbents is often adopted by introducing some special functional groups onto the matrix of the adsorbent.^{25–27} These introduced functional groups will modify the chemical composition of the adsorbent surface and hence improve the adsorption.^{28,29} In this work, several commercial and synthetic polymers with special functionalities have been introduced to study their behavior as adsorbent materials for phenols. These polymers represent an interesting and attractive alternatives because of their particular structure, chemical stability, high reactivity, and excellent selectivity toward aromatic compounds and metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido, or amino functions) in polymer chains (Fig. 1).

MATERIALS AND METHODS

Materials

Polymers

Acrylonitrile, 1,3-butadiene, and styrene copolymer (ABS) and styrene, acrylonitrile copolymer (SAN)

were purchased from commercially available sources (Finland). Poly(vinyl chloride) (PVC) were kindly gifted from the World Plastics (Jordan). Poly(methyl methacrylate) (PMMA) and poly(*tert*-butyl acrylate) (ptBA) (Merck, Germany) were synthesized according to the method described in details in earlier publications.^{30,31} All solvents were purchased as HPLC grade and dried using molecular sieves or distilled over Na under nitrogen atmosphere. Phenol (Merck, Germany) was utilized as the organic pollutant without further purification. The phenol concentrations were determined spectrophotometrically using UV-Vis-spectrophotometer (Jasco, model V-530). Solution pH was measured with digital pH meter (WTW-Wissens, Germany).

Methods

Sets of batch kinetic experiments have been carried out to investigate the behavior of some synthetic polymers in adsorbing phenol from aqueous solutions. The experimental procedures can be summarized as follows: A stock solution (1000 mg/L) of phenol was prepared by dissolving (1.0 g) of solid phenol in 1000 mL of distilled water. Different concentrations ranged from 20 to 100 mg/L were prepared by dilution of the stock solution (in distilled water) in 500-mL Erlenmeyer flasks. For each series of experiments, a mixture of 0.5 g of polymer and a 500 mL of the prepared phenol solution, with a particular concentration, was prepared in closed 500-mL Erlenmeyer flasks. Before starting the experiment, a 2.5 mL sample was taken from the solution. This sample was centrifuged and then analyzed using UV-Vis-spectrophotometer (at a wavelength, $\lambda = 270$ nm) to determine the starting (initial) concentration of phenol in the solution. Except for the experiments conducted for studying the effect of temperature, the mixture was then subjected for continuous shaking (GFL, model 3005) at 250 rpm for 25 h to attain uniform composition (homogeneous solution) and to enhance the adsorption process. Then, time recording was started immediately after starting shaking. The first 2.5 mL sample was taken after 0.5 h. Further samples were taken after different time intervals (1.5, 2.5, 3.5, 5.5, 9.5, and 15.5 h). Each sample was analyzed by measuring the phenol concentration.

The percentage of absorbance (%) was calculated according to the following formula:

$$\% \text{ of absorbance} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t are the concentration of phenol (mg/L) in the solution at time equal 0 (initial) and a certain time t , respectively.

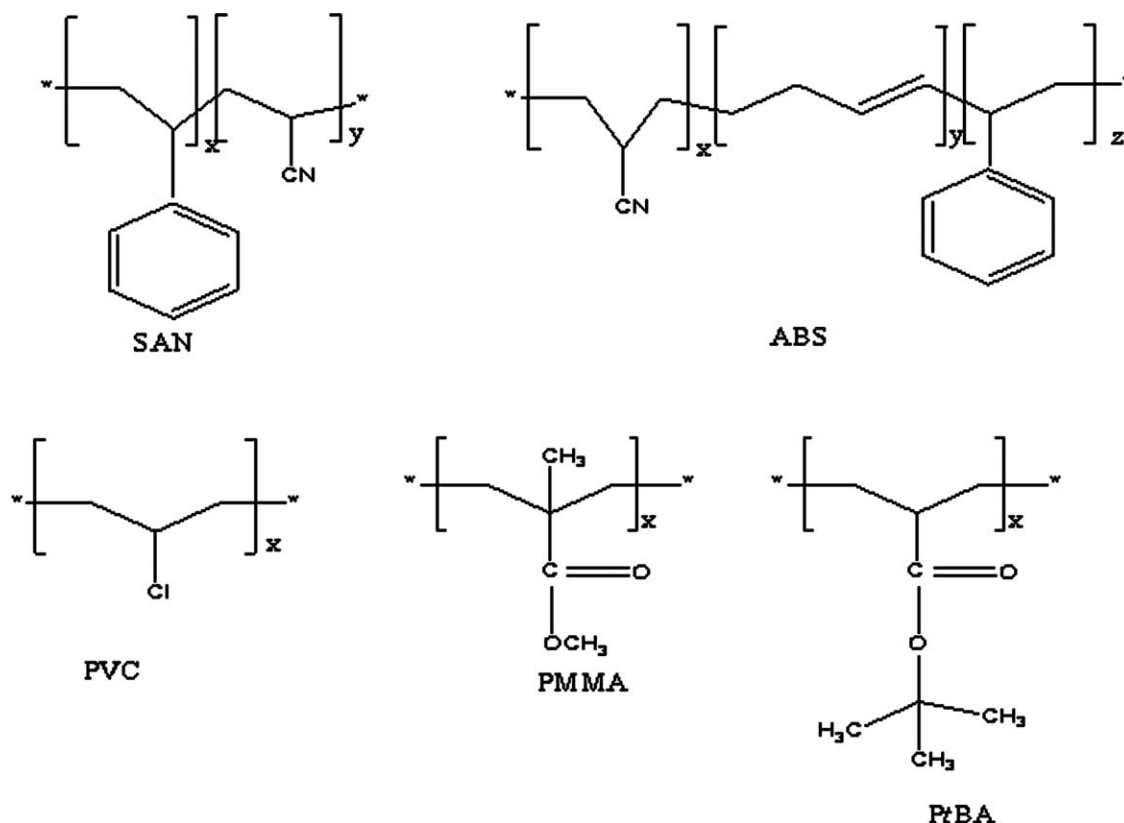


Figure 1 Structure of the polymers under study.

The amount of phenol sorbed by sorbent (q) in the sorption system was calculated using the mass balance as follows:

$$q = \frac{V(C_0 - C_e)}{m} \quad (2)$$

where V is the solution volume (L), C_e is the concentration of phenol (mg/L) in the solution at equilibrium, and m is the amount of adsorbent (g).

All experiments were performed at room temperature, except for these needed to study the effect of temperature part. Furthermore, the pH value of the prepared solutions was adjusted to pKa except in the experiments of the pH dependency investigation.

Effect of contact time

The contact time of adsorbent and adsorbate plays an important role in adsorption process. Sets of experiments were carried out to determine the capacity of the polymers for the adsorption of phenol. To each 0.5 g of the investigated polymers, 500 mL solution containing 40 mg/L of phenol was added (in 500 mL Erlenmeyer flasks). The prepared solutions were shaken for 48 h. 2.5 mL samples were taken at different time intervals to study the effect of the contact time on the adsorption process.

Regeneration method of adsorbed polymers

Regeneration of adsorbed polymers has been achieved by using a vacuum regeneration absorption system. This uses a vacuum pump to lower the pressure in the adsorber to below the vapor pressure of the adsorbed phenol, which causes the phenol to boil off at the temperature that is ambient within the adsorbent, instead of at higher temperature. In the process of boiling, the temperature of the adsorbent will actually go below the normal outside ambient temperature.

Effect of initial concentration

Adsorbent concentration is of great importance in adsorption process. To investigate the effect of the concentration of phenol in the solution, a set of kinetic experiments were carried out at a constant amount (0.5 g) of SAN polymer (it showed the best adsorption capacity, see later), and 500 mL phenol solutions containing varying concentrations (20–100 mg/L). The experiments were performed by shaking the solution for 3.5 h (period needed to reach the equilibrium). The experimental results were used for isotherm studies.

Effect of pH

The pH of the solution is an important parameter affecting the adsorption process. The effect of pH on

the removal of phenol was studied by conducting experiments at different pH values (3.3, pK_a and $pH = 11$), 0.5 g SAN, initial phenol concentration 40 mg/L, and 3.5 h contact time. Solutions of (0.05 mol/L) NaOH and/or HCl were used for pH adjustment.

Effect of temperature

The effect of temperature on adsorption equilibrium was studied experimentally by shaking the mixture (0.5 g) of SAN polymer and 40 mg/L phenol solution for 3.5 h at various temperatures (25, 45, and 65°C). Temperature was controlled by using water bath (The Shel Lab Models WS17).

Effect of agitation rate

To study the effect of agitation rate on the adsorption process, a set of experiments were carried out. To each 0.5 g of the investigated polymers, 500 mL solution containing 40 mg/L of phenol was added (in 500 mL Erlenmeyer flasks). The experiments were performed at 25°C without and with agitation (at 250 rpm). 2.5 mL samples were taken at different time intervals (0.5 h, 1.5 h, 2.5 h, ...etc).

RESULTS AND DISCUSSION

Effect of contact time

The adsorption processes were studied as a function of time to determine the point of equilibrium from adsorption of phenol onto different polymers. These experiments were carried out at pH 7 that is without pH adjustment and at room temperature. Figure 2 shows the adsorption uptake versus the adsorption time (*PtBA* is not shown in Figure 2 since it showed almost no adsorption respond). The amount of phenol adsorbed (mg/g) increased with increase in time until equilibrium was reached. The amount of phenol adsorbed at equilibrium reflected the maximum adsorption uptake of the adsorbent under the operating conditions applied. The results revealed that the phenol adsorption was fast at the initial stages of the contact period, and thereafter, it become slower near the equilibrium. This was due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Among all polymers under investigation, SAN showed the best adsorption capacity, which may be attributed to the fact that it contains acrylonitrile group that has a good affinity for the formation of hydrogen bonding with phenols. Moreover,

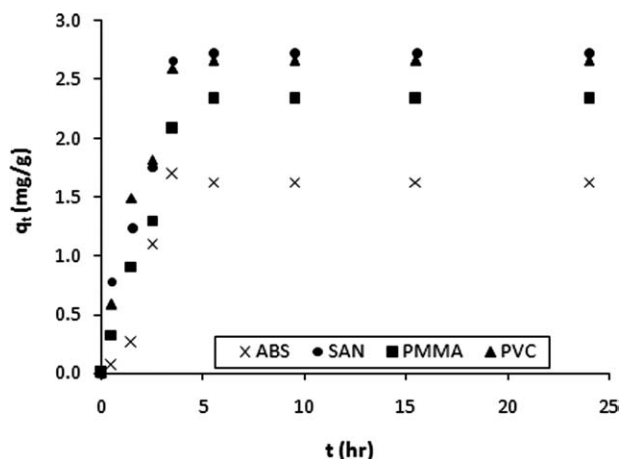


Figure 2 Effect of contact time on phenol adsorption on various polymers at $C_{\text{pho}} = 40 \text{ mg/L}$, $T = 25^\circ\text{C}$, and $pH = 7$.

SAN copolymer has a glass transition temperature greater than 100°C owing to the acrylonitrile units in the chain, so making the material resistant to boiling water. SAN will be chosen for further experiments since it gives relatively higher adsorption values at the beginning and at the equilibrium state as can be depicted from Figure 2. It is worth mentioning that the available experimental data on the sorption capacity of the phenolic species from aqueous solutions by natural and synthetic polymers were in a very wide range (20 μg –200 mg), the initial concentration of the phenolic species in solution being in the range 10 $\mu\text{g/L}$ –500 mg/L.³² In our case, the adsorption capacity for the phenolic species is really high, compared with the literature values.

Effect of initial concentration

Assessment of the initial concentration on the adsorption of phenol on SAN polymer, which gave the best adsorption capacity (Fig. 2), was carried out by varying the adsorptive concentrations from 20 to 100 mg/L at room temperature for 24 h, the results are shown in Figure 3. It can be seen that the adsorption of phenol onto SAN polymer was strongly dependent on initial concentration. The percentage of adsorption decreased when initial concentration of phenol increased. It is obvious from the previous findings that among all polymers under investigation, SAN showed the best adsorption capacity which may be attributed to the same reasons mentioned earlier.

Effect of solution temperature on phenol adsorption

The effect of temperature in the adsorption of phenol on SAN polymer is shown in Figure 4. The temperature was varied from 25 to 65°C at pH 7, contact

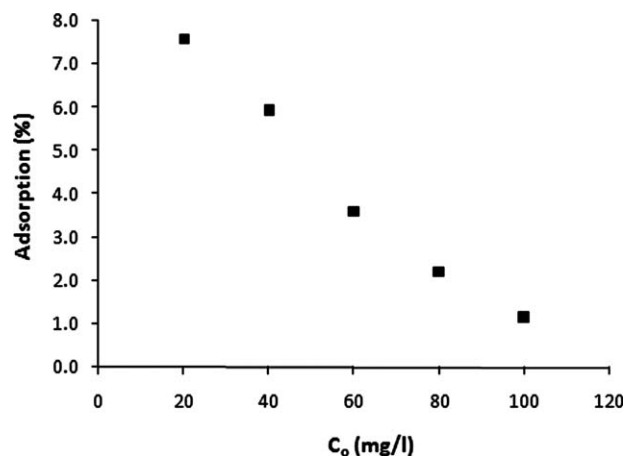


Figure 3 Effect of solution initial concentration on the adsorption of phenol on SAN polymer at $T = 25^\circ\text{C}$, and $\text{pH} = 7$.

time of 24 h, and phenol concentration of 40 mg/L. It can be seen that the adsorption of phenol ions increases with temperature. This indicates that there is a better adsorption at higher temperature. Increasing temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. The increase in amount of phenol adsorbed with an increase in temperature could be explained by the increase in the mobility of the phenol with increasing temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the polymer enabling phenol to penetrate further.

Effect of pH

Adsorption of phenol onto the polymers under investigation was studied at different pH to determine the optimum pH for the maximum removal of phenol. In these experiments, the accuracy of the phenol concentrations was very low by the pH changing when UV-Vis-spectrophotometer was used. However, removal of phenol using polymeric microbeads is difficult to investigate under high and low pH values because it requires a lot of acid or base to adjust the pH values in the adsorption media. Therefore, a value of $\text{pH} = 6.5$, which is very close to the pH value of wastewater, was used in this study.

Effect of agitation rate

The effect of agitation rate on the adsorption of phenol by SAN polymer is shown in Figure 5. The adsorption increased from 1.55% (without agi-

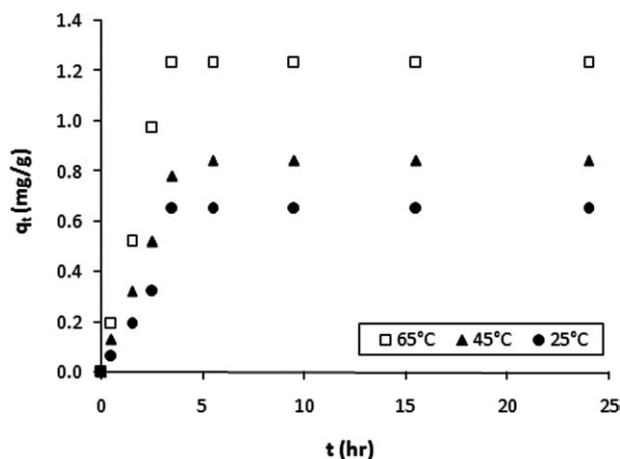


Figure 4 Effect of solution temperature on phenol adsorption on SAN polymer at $C_{\text{pho}} = 40$ g/L and $\text{pH} = 7$.

tation) to 6.49% (with agitation, 250 rpm). The increased value was about 5%. Mane et al.³³ proposed a mechanism for phenol removal from effluent which involved four steps: (i) migration of phenol molecules from the bulk solution to the surface of the adsorbent; (ii) diffusion through the boundary layer to the surface of adsorbent; (iii) adsorption at a site; and (iv) intraparticle diffusion into the interior of the adsorbent. The diffusion rate of phenol through the boundary layer to the surface of adsorbent becomes higher with agitation due to the decrease in the thickness and resistance of the liquid boundary layer and the enhancement of turbulence.³⁴

CONCLUSIONS

In this study, the adsorption potential of commercial and synthetic polymers was investigated for the removal of phenol from aqueous solutions. SAN gave

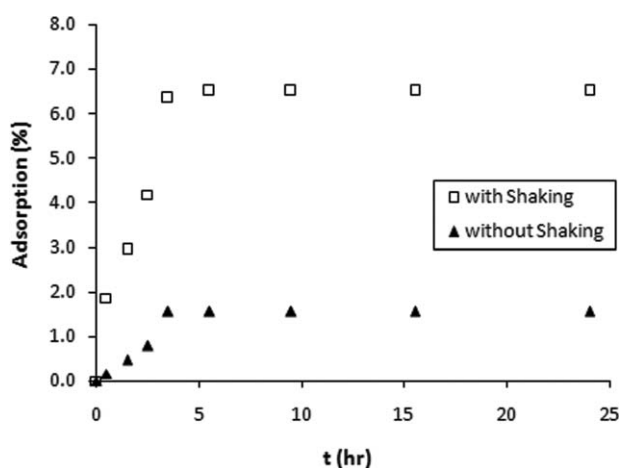


Figure 5 Effect of agitation rate on phenol adsorption on SAN polymer at $T = 25^\circ\text{C}$, $C_{\text{pho}} = 40$ g/L, and $\text{pH} = 7$.

the best adsorption capacity among all of the polymers tested. The solution temperature, agitation rate, and phenol concentration played a significant role in influencing the capacity of an adsorbent toward phenol molecules. An increase in solution temperature led to a significant increase in the adsorption capacity of SAN. By agitation, the removal of phenol was increased. However, the percentage of adsorption decreased when initial concentration of phenol increased. Removal of phenol using polymeric microbeads is difficult to investigate under high and low pH values because it requires a lot of acid or base to adjust the pH values in the adsorption media. The adsorption efficiency of the tested polymers for mono- or di-chlorophenols or other pollutants, which are inherently, exist in wastewater is under work. Moreover, synthesizing high-polar functional polymers with high-adsorption capacity is also under investigation.

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