



Removal of phenol from aqueous solutions using nano-chitosan

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| Article Info | Abstract |
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| <p>Article type: Research Article</p> <p>Article history: Received: August 2021 Accepted: August 2022</p> <p>Corresponding author: hassanrezaei1979@gmail.com</p> <p>Keywords: Nano-chitosan Phenol Adsorption Aromatic compounds</p> | <p>Phenol is one of the hydrocarbons identified as a priority pollutant by the US Environmental Protection Agency (EPA). Phenol and its derivatives have wide applications in a variety of industries and is known as an important pollutant in industrial wastewater. As conventional phenol removal methods are often expensive, there is a need for a low cost and environmentally friendly method to remove this pollutant. The purpose of this study is to examine the removal of phenol from aqueous solutions using chitosan nanoparticles. We experimented phenol removal in batch system with adsorbent dose (0.01- 0.4 g/l), pH (3-8), contact time (5-120 min), phenol concentration (5-50 mg /l) and temperature (15-40°C). Based on the results, the optimal levels of concentration, pH and adsorbent dose were 50 mg/L, 4 and 0.05 g/L as parameters for use in subsequent steps. After 35 minutes, the absorption system was in equilibrium and then there was no significant change in the phenol absorption, and after 60 minutes, the absorption rate decreased. Removal efficiency of phenol at 35°C demonstrated its highest amount. According to the findings, due to the characteristics such as degradability, regeneration ability, low cost, and acceptable adsorption efficiency, chitosan nanoparticles could be used to remove phenol from water contaminated with oil compounds.</p> |

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Introduction

Today's world is largely dependent on oil. Despite the fact that oil has provided considerable benefits, exploration, extraction and exploitation of oil resources in oil-rich countries like Iran have caused various environmental problems. One of the most important problems is contamination of water resources with oil compounds (Chen et al., 2016). The importance of water as the vital substance for life is an open secret, and the bottlenecks used by the increased population and the heightened pressure on water resources have

necessitated the conservation of these resources. Oil compounds are one of the most common pollutants of water. U.S. EPA has identified 16 oil compounds as the priority pollutants that should be removed from wastewater (Samanta et al., 2002). Phenolic acids that cause pollution particularly in groundwater are one of the most typical pollutants. Phenol with the chemical formula of C₆H₅OH and the molecular weight of 94.11 g/mol is a type of cyclic hydrocarbon, which is a colorless or white solid in its pure form. Phenol or hydroxybenzene is one of the hydrocarbons

inscribed into the list of priority pollutants by the U.S. EPA (Sullivan and Krieger, 2001). Phenol has a very high solubility in water and is inherently very toxic, colorless, permeable and crystalline (Kulkarni and Kawāre, 2013).

Phenol and its derivatives have wide applications in a variety of industries including paint, pesticides, and plastic & resin manufacturing industries; pharmacy; petroleum refining; petrochemical industries; coal mining; steel, aluminum, and lead industries; detergents; synthetic fabrics; and leather manufacturing. It is therefore considered an important pollutant in the wastewater of the above-mentioned industries. Although this substance fails to remain in the environment for a long time, its constant emission into the environment can be considered a serious threat for the environment (Malakootian & Asadi, 2011). Due to the mutagenic and carcinogenic effects of phenol and its compounds, its presence in the environment has caused considerable concerns (Kuipers et al., 2002). These pollutants can easily enter the surface and underground water through surface and deep streams, and then enter the food chain of plants, animals and human beings and consequently poison the living creatures (Rababah & Matsuzawa, 2002). Nowadays various approaches such as physicochemical methods including coagulation, sedimentation, filtration, radiation, adsorption on activated carbon and using other adsorbents have been suggested for the removal of aromatic and oil compounds (Christa Foley et al., 2008). In recent years, extensive efforts have been dedicated to remove these compounds. Given the development of the proposed methods, the adsorption process has been widely used in this regard (Vibo et al., 2007). A plethora of research has been carried out on natural coagulants to solve the problems associated with chemical coagulants. Chitosan is a substance having been suggested to this end (Folkard et al., 2001). In 1859, Rouget obtained chitosan from the deacetylation process of chitin in the presence of potassium hydroxide, and eventually in 1950, its structure was fully discovered (Shahidi et al., 1999). Chitin is

one of the most abundant bio-polymers after cellulose and is a natural polysaccharide and prominently found in crustaceans like crab and shrimp, insect cuticles, and fungal cell wall. Chitin and chitosan as natural amino-polysaccharides possessing multi-purpose specifications and unique structures are widely used in industry and medicine. High biocompatibility, acceptable biodegradability, low toxicity, and anti-bacterial and anti-allergenic properties are examples of their most prominent features (Mourya and Inamdar, 2008). The research presented by Rengaraj et al. (2002) can be referred to as one of the studies conducted on the removal of phenol by adsorption process. In their study, activated carbon prepared from date pits was used to remove phenol from water and sewage. The effect of phenol concentration, adsorbent dosage, contact time and pH was examined in this study. To this end, pH range was considered to be between 4 to 9. The adsorption equilibrium for the phenol concentration of 10-60 mg/l was determined during 3 hours. Studies have shown that active carbon prepared from the date pits can be used as a suitable adsorbent to remove phenol. Srivastava et al. (2006) used sugarcane bagasse ash and activated carbon to remove phenol. The effect of pH, contact time, initial phenol concentration, and adsorbent dosage parameters was studied. The initial concentration of phenol was considered to be 75-300 mg/l. The optimal conditions for removing phenol were: pH=6.5, adsorbance dose =10 mg/l, and equilibrium time=5 hours. The results indicated that sugarcane bagasse ash along with activated carbon could be effective in the process of phenol removal. Nadavala et al. (2009) investigated the biological removal of phenol and chlorophenol from aqueous solutions using calcium-chitosan alginate beads. The effects of pH, contact time, initial concentration and adsorption rate were examined. The highest adsorption capacity was obtained at the pH range 7. The results showed that calcium-chitosan alginate has a higher adsorption capacity for phenol than chlorophyll. Saitoh et al. (2011) investigated the removal of phenol

from water using chitosan-conjugated thermo-responsive polymers. The results showed that the maximum adsorption capacity for phenol obtained at pH=6, temperature=40 ° C, and equilibrium time= 2 hours. The proposed method is also used for removing phenol from sewage. Thiruganasambandham et al. (2013) used chitosan for treatment of sewage. In their research, sewage was treated under different operating conditions: stirring=1-3 min, pH =2.5-5.5, chitosan dose =0.3-0.6 g / l, and time =10-20 min. Their results revealed that under optimal condition, BOD, COD and opacity were eliminated to approximately 91%, 73% and 96%, respectively. The studies carried out by other scholars totally reveal that the removal rate of phenol would be different depending on the type of adsorbent. Regarding the type of the pollutant and also the environmental conditions that affect the activity of the adsorbent, the outcome of increased or decreased pH in the removal of phenol is also different. Increasing the initial concentration of the adsorbent and adsorbate up to a threshold level may augment the adsorption efficiency; however, further increase fails to have a significant impact. During the adsorption period there is also a threshold beyond which no significant increase in the adsorption rate is likely to be observed. To date, numerous studies have been conducted on the adsorption of phenol by using adsorbents such as activated carbon. However, adsorption of phenol by chitosan has rarely been studied on the global level. Accordingly, the present study used chitosan and its nanoparticles as adsorbents for the removal of phenol from aqueous solution. The result of this study can be useful for purification of water contaminated by oil compounds (e.g. aromatic compounds) in order to prevent the transmission of these compounds to the environment and living organisms.

Materials and Methods

Materials

Phenol (C₆H₅OH), hydrochloric acid (HCL), ammonium hydroxide (NH₄OH), potassium ferricyanide (K₃Fe (CN)₆), and

4-amino-antipyrin (C₁₁H₁₃N₃O) were purchased from Merck KGaA. In addition, the chitosan used in this study was offered by Sigma-Aldrich Corporation (identification code: 104564) and then converted to chitosan nanoparticles by mechanical method.

Methodology

The experiments were carried out in a discontinuous system under the same conditions, such that in each step one of the parameters (i.e. pH, phenol concentration, adsorbent content, contact time and temperature) changed while the others remained constant. The pH range (3, 4, 5, 6, 7, 8), the initial concentration of phenol (10, 20, 30, 40, 50 mg/l), adsorbent content (0.05, 0.1, 0.2, 0.3, 0.4 g), contact time (5, 15, 35, 60, 90, 120 min) and temperature range (15, 20, 25, 30, 35, 40 degrees Celsius) were subsequently determined. At first, the desirable pH for optimal adsorption efficiency was determined. Therefore, all experiments were carried out at this pH range. Then, when the equilibrium state was attained, the optimal phenol concentration and adsorbent content were determined as well. After obtaining the optimal values for the three aforementioned parameters and setting the conditions based on these values, contact time and temperature were also investigated. To prepare 1,000 ml of a mother solution, 1 g of phenol was poured into a 1000 ml volumetric flask and made up to the mark with distilled water. Then, dilution of the mother solution was used to prepare other solutions with 10-50 mg/l concentrations. The phenol used to produce a specific concentration of contamination in this study (state: solid, purity: 99.9%, MW: 94.1 g / mol) was purchased from Merck KGaA. Applying AZ86P3 pH meter manufactured in Taiwan, pH was adjusted using 0.5 N hydrochloric acid and ammonium hydroxide solutions. The test was carried out such that 100 ml of phenol solution with desirable concentration was poured in a 250 ml Erlenmeyer flask. Then, by adjusting pH of the solution, a certain amount of adsorbent was added to the solution and stirred at room temperature for

1 hour in a shaker to completely mix the adsorbent and phenol. The solution was then placed in a centrifuge rotating at 4000 rpm for 10 minutes. According to the methods presented in 'Standard Methods for the Examination of Water and Wastewater', the present study used S2000 UV / Vis spectrophotometer at 500 nm wave lengths to measure the phenol content. Data analysis was performed by Excel and SPSS (version 20) software.

Analysis of the phenol adsorption data in a discontinuous system:

The percentage of phenol removal in each experiment is calculated by the following equation (Rezaei, 2016).

Equation (1)

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

In this equation, C_0 and C_e refer to initial concentration and final concentration of phenol (mg/l), respectively. In the discontinuous adsorption analyses,

adsorption capacity at the equilibrium is one of the important parameters used to evaluate the adsorbent performance in adsorbing the desired compound. The adsorption capacity at the equilibrium can be obtained by equation 2 (Lin et al, 2009).

$$\text{Equation (2)} \quad q_e = \frac{(C_0 - C_e)V}{m}$$

where q_e = The amount of phenol ions adsorbed per unit mass of adsorbent (mg/g), C_0 = The initial concentration of phenol in the solution (mg/l), C_e = Phenol equilibrium concentration in solution (mg/l), V =Total solution volume (L), and m = Adsorbent mass (g).

Results

In order to determine the concentration of phenol by the spectrophotometer, the calibration curve was plotted at the concentrations of 1, 2, 4, 5, 10 and 20 mg/l. According to Figure 1, the correlation coefficient equals 0.94.

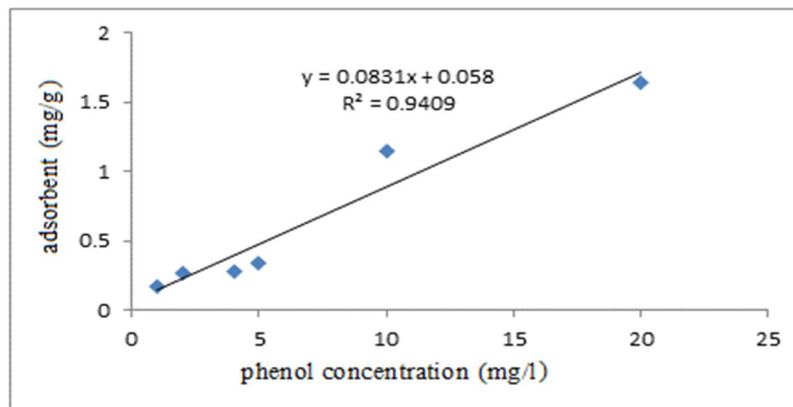


Figure 1. Phenol Calibration Curve. phenol absorption rate is based on its concentration.

The effect of initial pH

In this study, the effect of different pH levels (3, 4, 5, 6, 7 and 8) on the phenol adsorption was evaluated under initial concentration of 5 mg/l phenol, 0.2 g nano-chitosan, temperature of 25 °C and contact time of 60-min. The results showed that by increasing the pH value from 3 to 8, the phenol removal from the solution may decrease, indicating that phenol removal capability in acidic condition is much better than alkaline condition. pH 4 was proved to be the best at this stage. According to Fig.

2, the effect of different pH levels on the removal percentage showed that different pH levels have no significant effect on the adsorption efficiency ($p > 0.05$), thereby choosing the highest pH efficiency fails to have a significant difference; however, numerical analysis of the values showed that pH = 4 has the highest removal percentage compared to other pH levels (77.49%). Moreover, according to Fig. 3, the effect of different pH levels on the adsorption capacity showed that different pH levels have no significant differences,

and the variation in pH fails to cause any significant difference in the adsorption capacity. However, numerical analysis of

data showed that pH = 4 has the highest adsorption capacity compared to other pH levels (1.93).

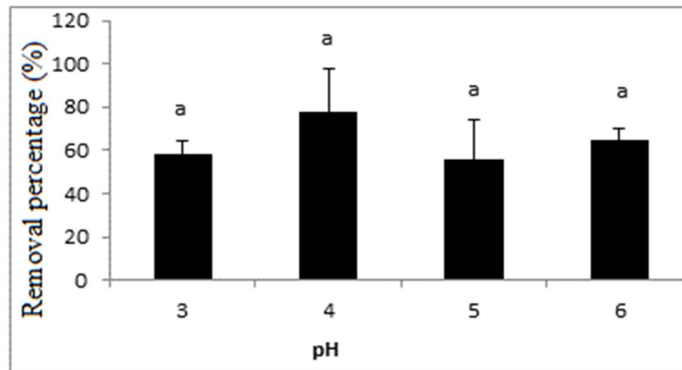


Figure 2. The effect of pH on the phenol removal percentage

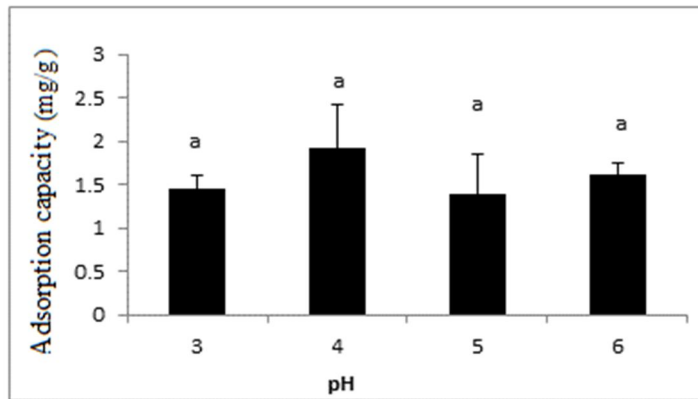


Figure 3. The effect of pH on the phenol adsorption capacity

The effect of adsorbent dose

By taking into account the lowest amount of adsorbent that can provide the highest adsorption, the range of nano-chitosan content, initial concentration, pH, temperature, and time was considered 0.05-0.4 g, 5 mg /l phenol, 4, 25 °C, and 60 min, respectively, in order to investigate the effect of different amounts of adsorbent on the phenol adsorption. The results showed that following the increased adsorbent dose, the phenol adsorption capacity might reduce due to nano-chitosan sediment. Statistical analysis revealed that different amounts of nano-chitosans have no significant effect on the removal percentage ($p > 0.05$), thereby selecting the maximum adsorbent efficiency fails to have any significant difference. However, numerical

analysis of the data showed that the highest percentage of phenol removal obtained at 0.1 g dosage, which is equal to 67.22% for nano-chitosan (Figure 4).

Also, according to Figure 5, the effect of various amounts of nanocytosans on adsorption capacity showed that different amounts of adsorbent have significant differences, so that variation in the amounts of nano-chitosan causes significant difference in the adsorption capacity ($P < 0.05$). Therefore, the highest and lowest adsorption capacity was related to the adsorbent dosage of 0.05 gr nano-chitosan (6.18) and that of 0.4 gr nano-chitosan (0.42), respectively; however, no significant difference was observed at 0.2, 0.3 and 0.4 g nano-chitosan.

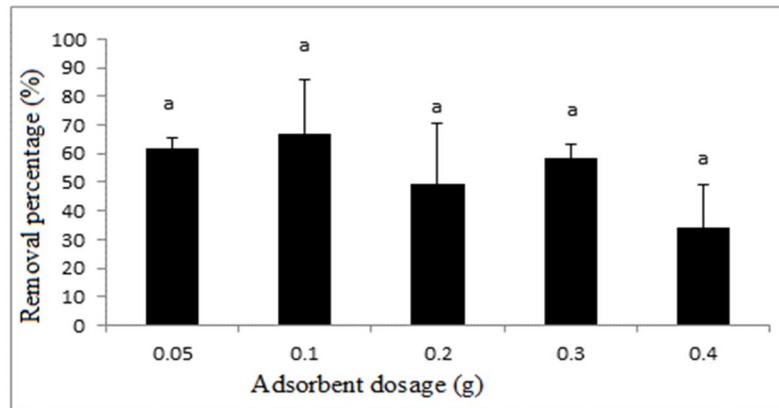


Figure 4. The effect of adsorbent dosage on the phenol removal percentage

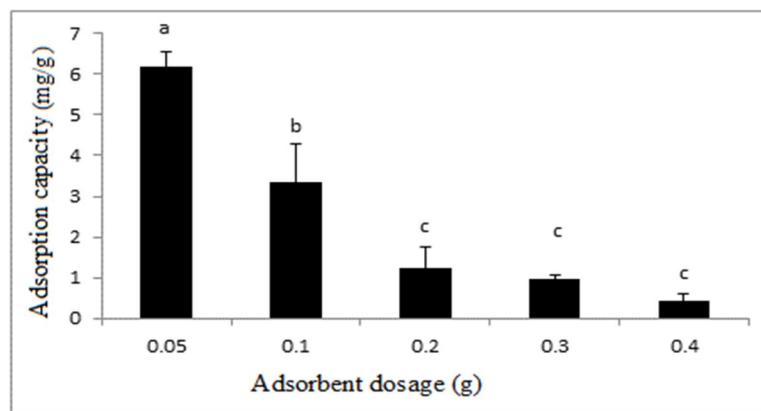


Figure 5. The effect of adsorbent dosage on the phenol adsorption capacity

The effect of initial concentration

The effect of initial phenol concentration in the range of 10 to 50 mg/l, pH = 4, adsorbent of 0.01 g, temperature of 25 °C, and time= 60 minutes was studied. The results indicated that increased phenol concentration leads to a continuous increase in the adsorption capacity. According to

Figure 6, the effect of different concentrations of phenol on the removal percentage showed that concentration fails to have a significant effect on adsorption efficiency ($P > 0.05$). Although numerical analysis showed that, the highest removal percentage is related to the concentration of 10 mg/l phenol (98.91%).

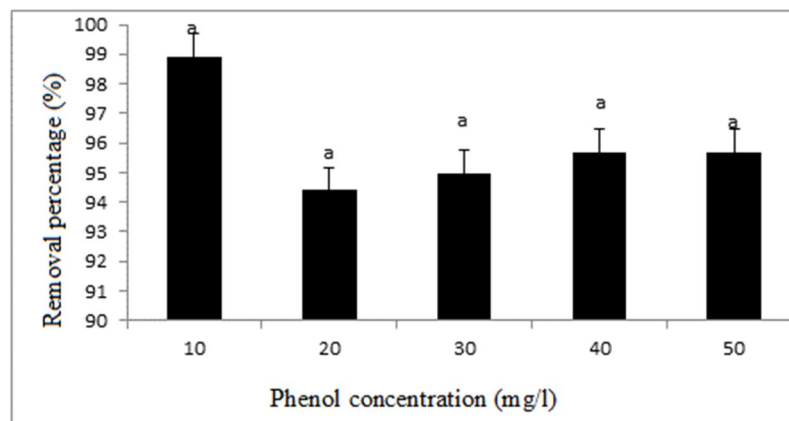


Figure 6. The effect of phenol initial concentrations on the percentage of phenol removal

Similarly, the effect of different concentrations of phenol on adsorption capacity in Figure 7 showed that different concentrations have significant differences. Put it another way, the variation in phenol concentrations causes a significant difference in adsorption capacity ($P < 0.05$).

Consequently, the highest and lowest adsorption capacities were related to the concentration of 50 mg/l phenol (478.53) and that of 10 mg/l phenol (98.91), respectively. In total, the optimum concentration of the phenol adsorption capacity was obtained at 50 mg/l phenol.

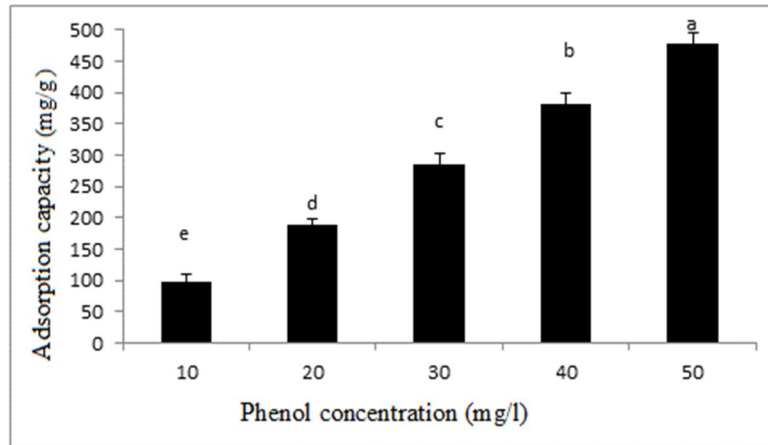


Figure 7. The effect of phenol initial concentrations on its adsorption capacity

The effect of contact time

Contact time is a highly important parameter in the adsorption and availability of the adsorbate on the active sites available for adsorbent. In the present study, after obtaining other optimal parameters of the phenol adsorption from aqueous solution to optimize the contact time of the adsorbent and adsorbate, the effect of contact time on the removal percentage and adsorption capacity in the range of 5 to 120 minutes at pH=4 and initial concentration of 50 mg/l and 0.01 g nano-chitosan at temperature of

25 °C was investigated. Statistical analysis of the effect of different times on adsorption efficiency and adsorption capacity, as demonstrated in Figs. 8 & 9, shows that different contact times fail to have any significant impact on the adsorption efficiency and capacity ($p > 0.05$). The numerical analysis, however, indicates that the highest removal rate (95.15%) and the highest adsorption capacity (475.75) are related to the contact time of 5 minutes.

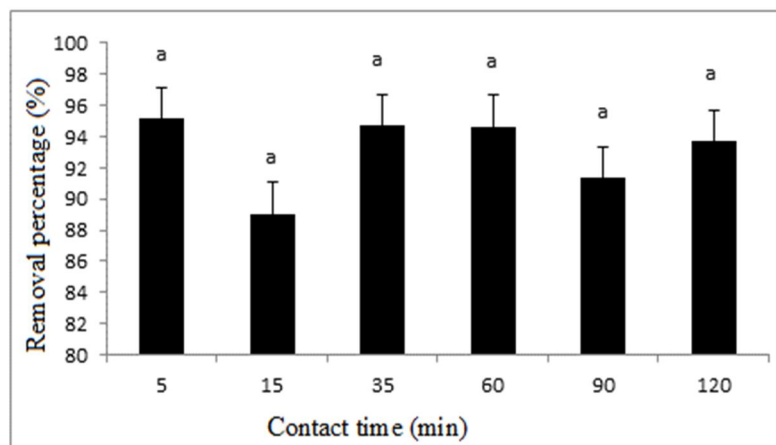


Figure 8. The effect of contact time on the phenol removal percentage

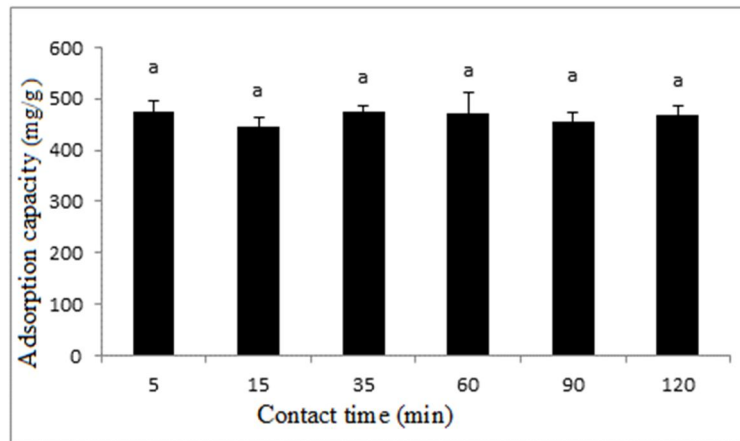


Figure 9. The effect of contact time on the phenol adsorption capacity

Temperature effect

Temperature parameter represents whether the process is endothermic or exothermic. To investigate the effect of the temperature, an adsorption process with a solution under the concentration of 50 mg/l phenol at pH=4, in the presence of 0.01 g of

adsorbent during 60 minute at 15, 20, 25, 30, 35, and 40 ° C was observed. According to Figs. 10 and 11, the results showed that by increasing the temperature from 15 to 40 ° C, the removal percentage and adsorption capacity generally increase and finally reach the highest amount at 35 ° C.

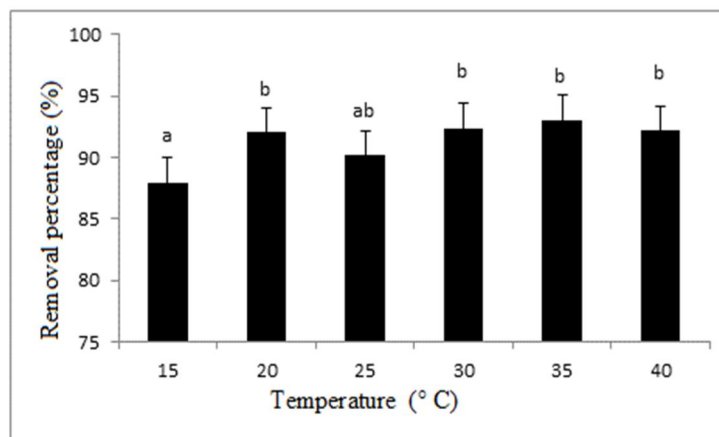


Figure 10. The effect of temperature on the phenol removal percentage

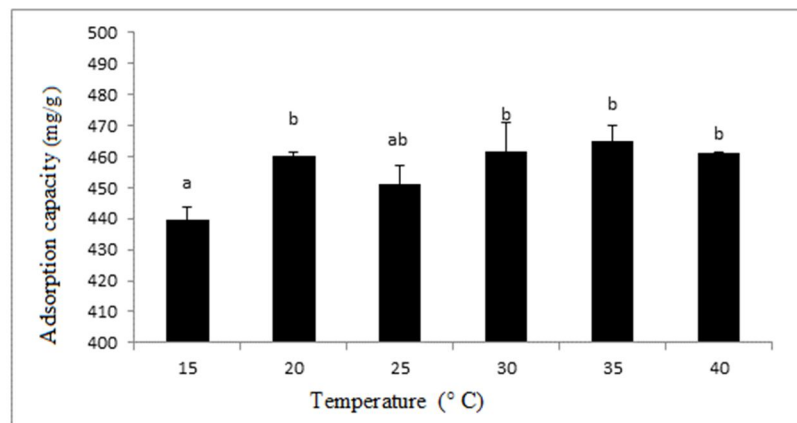


Figure 11. The effect of temperature on the phenol adsorption capacity

Discussion

PH effect

The pH of the adsorption medium is one of the key factors affecting the efficiency of the pollutant's adsorption by the adsorbents. It also affects the surface charge of the adsorbent, ionization of materials, and functional groups separation in adsorbent active sites (Jabbar et al., 2014). According to the findings, the highest phenol removal percentage was obtained at pH 4. Chitosan is a polymer that exhibits the best performance in an acidic condition (Corami et al., 2008). Although pH range of 3- 8 was selected to be investigated in this study, during the experiment sediments took place at pH levels higher than 6. At low pH levels, adsorbent charge was positive, and an electron exchange occurred between the adsorbent and the aromatic ring of the phenol, leading to increased adsorption energy between the adsorbent and the phenol. At high pH levels, phenol ionization was occurred and led to increased OH in the medium. On the other, when the adsorbent charge is negative, it leads to increased repulsive force between the adsorbent and the phenol (Senturk, 2009). In a study carried out by Chakraborty et al. (2011), nano-and micro-carbons were used to remove phenol from water through surface adsorption. They reported that at pH values greater than 5, the bonding between OH groups and the adsorbent surface creates a negative charge while at a pH below 5, the bond between H⁺ groups and adsorbent surface creates a positive charge and reduces the removal efficiency at pH levels higher and lower than 5. Their results are consistent with the results obtained in this study. In their study entitled 'Removal of phenol from aqueous solutions by adsorption onto activated carbon', Hameed et al. reported that in regard to the nature of phenol and ionization of its molecule, phenol competes with hydroxide ions to occupy adsorption surface in the environment with high pH, and adsorption capacity consequently decreases. In this study, pH 5 was considered to be the optimal pH level. Hashemi et al. (2014) investigated the pH

effects on the phenol adsorption using walnut green hulls as the adsorbent. Their results showed that the phenol adsorption efficiency has an inverse relation with increased pH level. As they asserted, it is due to the anionic structure of phenol and pH_{zpc} of the walnut green hull. pH_{zpc} is one of the parameters used in the adsorption process and represents the point of zero charge on the adsorbent surface, that is to say at pH level higher and lower than that point, the adsorbent surface has a negative and positive charge, respectively. In the study performed by Hashemi et al., pH_{zpc} of the walnut green hull was measured to be 7.3. Investigations revealed that the adsorbent surface is negatively charged at pH higher than pH_{zpc} . Accordingly, and also due to the fact that the surface of walnut green hull is negatively charged at pH higher than 7.3, increasing pH may enhance the number of negative charges. Also, given the anionic nature of the phenol, in this condition the electrostatic gravity between the adsorbent and the pollutant may decrease and the adsorption efficiency may reduce as well. The maximum phenol removal percentage at pH 4 was obtained to be 99.9, which is line with the results of the present study. Rengaraj et al. (2002) used the activated carbon prepared from the date pits to remove phenol from water and sewage. This study examined the effect of pH in the range of 4-9 on the phenol adsorption. The results showed that phenol adsorption may decrease with increasing pH. In this study, the optimum pH value was equal to 6, which fails to be consistent with the result in the present study.

Soni et al. (2017) investigated the effect of pH on phenol removal using nanocomposite particles of chitosan and activated carbon. The pH in this study ranged between 2 to 8; more to the point, the phenol adsorption decreased with increasing pH. The highest phenol removal percentage (78%) was observed at pH 4. These results are also supported by the present study. Lin et al. (2009) examined the effect of pH on phenol removal. They considered pH to be one of the most important parameters affecting the phenol adsorption process due to the effect of

adsorbate-adsorbent electric charge at different pH levels. They considered the pH range between 2 -11. In this process, the adsorption capacity decreased by increasing pH and it reached its highest point at pH 2. At low pH levels, the adsorbent charge was positive and an electron exchange occurred between the adsorbent and the aromatic ring of phenol occurred at this pH. In very low pH levels, hydrogen ions surrounded the adsorbent and increased the adsorption force between the adsorbent and the phenol. However, with increasing pH, the adsorption force between adsorbent and adsorbate reduced, and accordingly the adsorption capacity decreased as well.

The effect of the initial phenol concentration

The initial concentration of the pollutant is an important parameter to overcome the force inhibiting the solid-liquid mass-transfer. The removal efficiency of phenol at the concentrations of 10-50 mg/l with the contact time of 1h was investigated. According to the graph depicting the removal percentage, increasing the phenol concentration reduced the removal percentage so that by increasing the phenol concentration from 10 mg/l to 50 mg/l, the removal rate reduced from 98.91% to 95.69%. Reduced levels of the adsorbent due to increased phenol concentration can be considered to be the most important reason for this phenomenon. At higher concentrations, on the contrary, the adsorption capacity (q_e) increased, such that adsorption level augmented from 98.91 to 478.53, which can be due to the increased probability of contact between phenol and chitosan adsorbent. Soni et al. (2017) investigated the effect of phenol initial concentration on the removal percentage of phenol in aqueous solutions using nanocomposite particles of chitosan and activated carbon. The results suggested that by increasing the concentration from 2 to 8 milligrams per 10 milliliters of phenol solution, the removal percentage may enhance from 12.5% to 69%. As they explained, this phenomenon is due to the increased contact between phenol and adsorbent as the result of increased

concentrations. Qadeer and Rehan (2002) used activated carbon to remove phenol from aqueous solutions. They studied the effect of the concentration parameter in the range of 0.1 to 0.7 g/l. The results are representative of the fact that the removal percentage of phenol up to the concentration of 0.3 g /l was over 99%; however, this percentage decreased with rising concentration. As they pointed out, this is due to the reduced surface of the adsorbent by increasing the concentration of phenol. These results are consistent with the findings obtained in this study with respect to the removal percentage. Saitoh et al. (2011) dealt with the removal of phenol from water using chitosan-conjugated thermo-responsive polymers. They studied the effect of concentration parameter. The results are similar to the results yielded in the present study, which is the removal percentage increases by rising the phenol concentration.

The effect of adsorbent dosage

Investigating different amounts of adsorbent dosage on the phenol adsorption shed light on the fact that the highest removal percentage was obtained at 0.1 g /l chitosan, and this percentage reduced in less or greater amounts. Due to the constant concentration of phenol, increasing the adsorbent dosage augmented the adsorbed sites and hence reduced the concentration of phenol (El-Naas, 2010). However, the results of adsorption capacity revealed that the maximum adsorption capacity occurs at 0.05 g/l chitosan, and the amount of adsorption capacity may decrease with increasing adsorbent dosage. Although an increase in adsorbent dosage is expected to augment the active surface area and adsorption, the results of multiple experiments confirm the reverse causality. This can be due to the unsaturation of some active sites, which results in low adsorption (Ong et al., 2007). Chen et al. (2010) also stated that lack of increase in adsorption with an increase in the adsorbent dosage is due to the promoted competition between pollutant ions to access the active surface sites in higher concentrations of adsorbent. On the other, higher dosage of adsorbent in

a water unit leads to the overlapping of the adsorption sites and accumulation of them, resulting in a reduction in the total available sites and subsequently reduction in the adsorption of pollutants.

The accumulation of adsorbents expands the propagation pathway during the pollutant emission stage at active surfaces of the adsorbent, which results in lower adsorption (Hamid et al., 2007). Kulkarni et al. believe that reduced adsorption capacity at doses higher than the optimum level is because of decreased availability of adsorption sites due to adsorbent accumulation. Determination of the optimal dosage of the adsorbent is a parameter that due to the economic problems its minimum amount should be chosen in real condition considering the maximum adsorption capacity. Achak et al. (2009) examined the removal of phenolic compounds from olive mill wastewater using banana peel. In this study, the effect of various concentrations of adsorbent on the adsorption process in the constant concentration of 13.45 g /l of total phenolic compounds in 100 milliliters of plant wastewater was investigated. Concentrations considered for the adsorbent ranged from 10 to 50 g/l. Initially, adsorption rate increased with rising adsorbent dosage due to the availability of adsorption sites; however, the highest adsorption rate was not observed in the highest concentration of the substance. The adsorption rate increased up to 30 g /l, and then the amount and capacity of the adsorption reduced. As the authors asserted, this is due to the unsaturation of adsorption sites during the adsorption process, adsorbent deposition, and the establishment of equilibrium between adsorbent-adsorbate molecules. These results consist with the results of the present study, because as it was observed, the phenol adsorption capacity was reduced with increasing nano-chitosan content. Özkaya (2006) investigated the effect of different concentrations of activated carbon on the phenol adsorption. The results showed that adsorption efficiency increases with augmenting the adsorbent content; moreover, adsorption efficiency of 94% is obtained at 0.5 g / l adsorbent. This increase

in adsorption is due to the enhanced available adsorption sites. Reduced adsorption efficiency in doses greater than 0.5 g/l is probably due to the reduction of available levels because of the accumulation of solid particles. In the present study, at 0.1 g nano-chitosan and under optimal conditions, 67.02% of phenol was adsorbed from aqueous solution and the highest adsorption capacity was related to 0.05gr nano-chitosan, while in levels higher than 0.5 gr, the phenol removal efficiency and adsorption capacity reduced. According to a study by Kilik et al. (2011) on the adsorption of phenol from aqueous solutions using activated carbon, increased adsorbent mass resulted in reduced phenol adsorption capacity. This was probably due to the adsorbent accumulation and overlapping of the adsorption active sites. In the present study, similarly, rising the adsorbent dose to more than 0.05 g led to decreased capacity of phenol adsorption by nano-chitosan.

The effect of contact time

The time required for establishing equilibrium is assumed to be one of the key parameters needs to be taken into account in adsorption studies (Wang et al., 2010). In this study, the highest adsorption was achieved in the first 5 minutes, and adsorbent active sites failed to be fully occupied until the contact time of 35 minutes. Then, from the contact time of 35 minutes to 60 minutes, the adsorption rate was steady and in equilibrium. The high adsorption rate in the early stages of adsorption can be due to the high driving force and rapid transfer of phenol ions and adsorbent surface. Also, at the onset of adsorption, active sites on the adsorbent surface are not occupied (Ahmad et al., 2012). After 60 minutes, the adsorption rate partly reduces and then remains constant. This can be due to the separation of part of phenol during the desorption phase from adsorbent and reduced active sites (Taffarel et al., 2010). Senturk et al (2009) investigated the effect of contact time on the adsorption of phenol by bentonite. In this study, the adsorption process of the adsorbent and the solution of the adsorbate

took 60 minutes to reach an equilibrium. Huang et al. (2007) examined the effect of contact time on phenol adsorption. They considered 60 minutes as the time required to reach the equilibrium state. As they claimed, increased rate of adsorption over the first minutes is due to the special participation of the adsorbent groups and availability of active sites on the adsorbent surface. Also, the results of their study indicated that phenol adsorption may decrease after 60 minutes. The results of the present study also showed that after 1 h, the phenol adsorption rate decreases as well.

Temperature effect

With increasing temperature, the tendency of phenol molecules towards adsorbent and the binding of molecules to the adsorbent surface increase, thereby the adsorption may also rise. This augmentation in efficiency may be due to the adsorbent expansion and, as a result, increased active sites for the removal of phenol (Potgieter et al., 2009). Roostaei and Tezel (2004) examined the effect of the temperature on the phenol adsorption process. Their results showed that the adsorption capacity reduced between 40 °C to 25 °C and 40 °C to 55 °C. In the present study, on the contrary, increasing temperature from 15 to 40 degrees Celsius generally led to the increased adsorption capacity.

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Conclusions

According to the findings, it can be concluded that chitosan nanoparticles have high efficiency in the removal of phenol from aqueous solutions. The phenol adsorption capacity has a direct relationship with increased phenol concentration, decreased dosage of adsorbent, and increased temperature to a certain extent, while it has an inverse relationship with increased pH and contact time. Based on the results, the optimal levels of concentration, pH and adsorbent dose were determined as 50 mg/L, 4 and 0.05 g/L as parameters for use in subsequent steps. At the time of 35 minutes, absorption system was in equilibrium and then there was no significant change in the phenol absorption, and after 60 minutes, the absorption rate decreased. Removal efficiency of phenol at 35 °C demonstrated its highest amount. Also, based on the results, the highest phenol absorption capacity was 478/53. Furthermore, due to the chitosan characteristics such as biocompatibility, biodegradability, low cost, and its application for environmental protection and water treatment, applying this material as nano can be very effective. Therefore, it is recommended to use chitosan nanoparticles as natural adsorbents to remove oil compounds contaminating the water.

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