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Research on adsorption of phenols in wastewater with cyclodextrin

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Study of optimal process conditions of cyclodextrins (CDs) for treating wastewater containing phenol. adsorption time is 240 min, the pH value is 5 – 7, CDS dosage is 4 g/L, initial phenol concentration of 100 mg/L, adsorption temperature of 40˚C, the highest absorption efficiency can attainment 42,5 %. In the condition of 30˚C, adsorption phenol of wastewater by CDs process accords with the Freundliehadsorption model.

Key words: cyclodextrins (CDs), phenol of wastewater, adsorption.

INTRODUCTION

Typical cyclodextrins(CDs)[1-5],constituted by 6-8 glucopyranoside units, can be topologically represented as toroids with the large and the small openings of the toroid exposed to the solvent secondary and primary hydroxyl groups, respectively. Because of this arrangement, the interior characteristic of the toroid was changed from hydrophobic to less hydrophobic, as a result being able to host other hydrophobic molecules. In contrast, the exterior is sufficiently hydrophilic to impart CDs (or their complexes) into water.

The formation of inclusion compounds greatly modifies the physical and chemical properties of the guest molecule, mostly in terms of water solubility. This is the reason why CDs have attracted much interest in many fields, especially in pharmaceutical applications: since inclusion compounds of CDs with hydrophobic molecules are able to penetrate body tissues, these can be used to release biologically active compounds under specific conditions.

Phenolic compounds are highly toxic substances; they are a kind of industrial pollutants, mainly from oil refining, coal gas scrubbing, paper-making, ammonia and other chemicals production. Tap water containing microgram amounts of chlorophenols has significantly different smell; when taken by humans the chlorophenols accumulate and can cause poisoning symptoms; long-term consumption of phenol- polluted water can cause dizziness, itching, anemia and various neurological symptoms. At present, 6 kinds of phenolic compounds are involved in the national quality standards of water, the Environmental Protection Bureau of America involves 14 kinds of phenolic compounds, and our priority control involves 12 kinds of phenolic compounds in the pollutants: phenol and chlorophenols, cresol and nitro phenols. The phenol molecule diameter is around 0.59 nm, thus the phenol molecules can enter CDs of slightly larger diameter, so CDs have the ability of removing phenol pollutants from water. This paper studied the treatment of phenol wastewater by CDs in order to find out the best process conditions of wastewater treatment.

MATERIALS AND METHODS

Agents and apparatus

Phenol and CDs of analytical grade were used by Sinopharm Chemical Reagent Co. Ltd. Prior to usage; they were pretreated by vacuum drying. Three flasks, mechanical agitator, vacuum dryer, UV spectrophotometer were used in the study. More description should be listed like size, operational conditions etc.

Experimental apparatus

The experimental apparatus shown in Fig.1, included heater, mechanical agitator, temperature controller, and water bath.

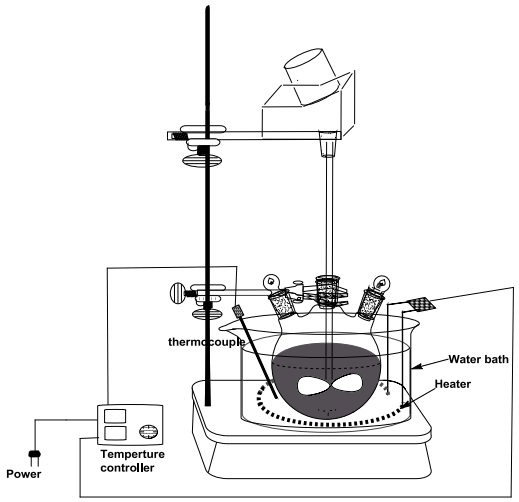

Fig. 1. Experimental apparatus of phenol in waste water by CDs.

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Adsorption efficiency

CDs were added to the phenol solution under mechanical stirring at a speed of 150 rpm for 30 min. After the adsorption equilibrium was reached, the solution and CDs were separated by a centrifugal separator. The supernatant was poured into the cell and analyzed at awave length of 270nm using a spectrophotometer. The calibration curve of phenol solution was prepared with a series of phenol concentrations. The phenol solution adsorption efficiency was expressed by the following equation[6-8]:

$$\eta = \frac{c_o - c_e}{c_o} \times 100\%$$

η - adsorption efficiency, %;

c_o - initial phenol concentration, mg/L;

c_e- phenol concentration in the supernatant at equilibrium, mg/L.

RESULTS AND DISCUSSION

Effect of different adsorption times on phenols removal by CDs[9,10].

An amount of 0.4 g of CDs, added to 100 mL of phenol solution of initial concentration of 100 mg/L, was operated at varied times at a temperature of 40°Cat a stirring speed of 150rpm. The effect of reaction time on phenol removal by CDs is plotted in Fig. 2.As can be seen from Fig.2, the removal efficiency of phenol by CDs adsorption increased with time. At a time of 160 min, the adsorption rate reached 34.5% and gradually increased till 300 min with phenol removal of 42.5%.Phenol removal on CDs was attributed to the cylindrical structure of CDs with cone. The cavity diameter of CDs was slightly larger than that of the phenol molecule, providing Van der Waals interaction between phenol and the hydrophobic groups of C-4, C-5 located in CDs. It is assumed in the literature that the removal of phenol by CDs is mainly due to the structure of CDs having inclusion ability for phenol. According to the current results, the optimal time of phenol removal by CDs is close to 240 min.

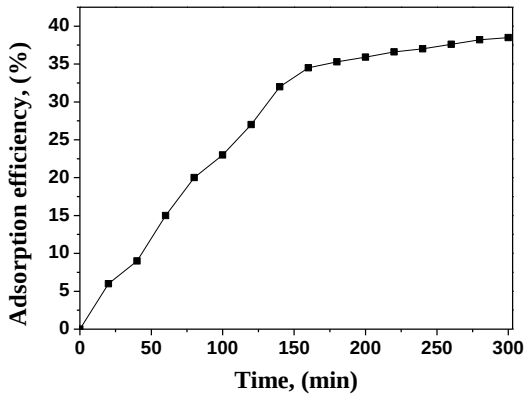

Fig. 2. Effect of different adsorption times on phenol removal by CDs.

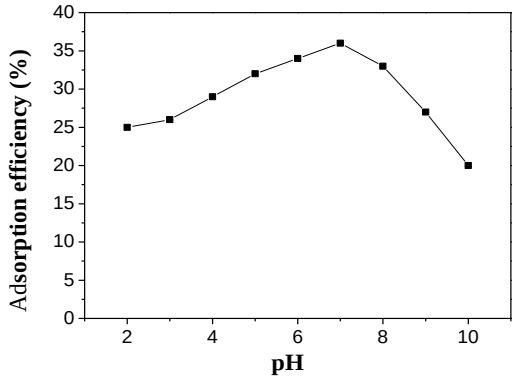

Fig. 3. Effect of pH on phenol removal by CDs.

Effect of pH on phenol removal by CDs

The reaction of 0.4 g of CDs, added to 100 mL of 100 mg/L phenol solutions with different pH, was performed at a temperature of 40℃for 60 min at a stirring speed of 150 rpm for 240 min. The results are plotted in Fig.3.

Fig.3 reveals that the pH value can affect phenol removal efficiency by CDs. Alkaline conditions are more unfavorable for phenol removal than acidic conditions. The phenol removal is 37.2% at pH=7, and decreases to 20.3% at pH=10. This is related to the hydrogen bond formation between phenol hydroxyl and hydroxyl group in CDs. With the increase of pH from neutral to alkaline, the formed sodium phenolate has a larger diameter than phenol, so that the sodium phenolate can not enter into the cavity of CDs, resulting in phenol desorption.

Effect of the initial concentration of CDson phenol removal[11,12]

Different amounts of CDS, such as 0.2 g, 0.3 g, 0.4 g and 0.5 g CDs were added to 100mL of the phenol solution with initial concentration of 100 mg/L at a temperature of 40℃, pH=6, stirring time 60 min, stirring speed of 150rpm, and adsorption time of 240 min. It follows from the results shown in Fig.4 that the increasing amount of CDs leads to improved removal of phenol. Larger amounts of CDs possess more active sites, resulting in higher adsorption. However, the larger amount of CDs consumed is related with ascending cost of water treatment, indicating that this process is not feasible for industrial application. With CDs concentration of 40 g/L, the solution becomes cloudy which interferes with the spectrophotometric analysis. As optimal concentration of CDs 4 g/L is considered.

Effect of phenol concentration on the adsorption efficiency of CDs

Amounts of 0.4 g CDs were added to 100 mL of aqueous phenol solutions with initial phenol concentration of 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L ata temperature of 40℃, pH=6, stirring time of 60 min, stirring speed of 150 rpm and adsorption time of 240 min, as shown in Fig.5.

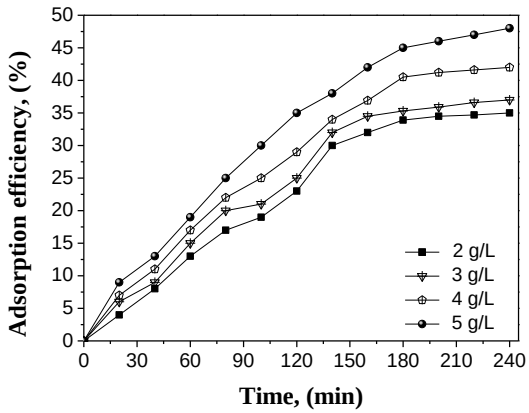

Fig. 4. Effect of initial CDs concentration on phenol removal.

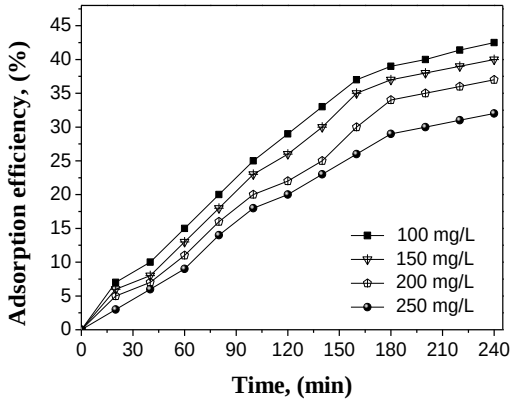

Fig. 5. Effect of initial concentration of phenol on its removal by CDs.

Fig.5 reveals that the adsorption efficiency of phenol byCDs decreases with increasing phenol concentration, the highest phenol removal efficiency was 42.5%.From the analysis of the figure, the adsorption rate in less than 160 min of time reached 30%, and at an adsorption time of 180 min, the adsorption rate slowly increased, the adsorption reaching equilibrium after 3h. This may be due to the dynamic adsorption equilibrium between adsorption and desorption as two reversible processes. With the increase of initial phenol concentration, the adsorption rate decreased, probably because of the steric effect between the concentration of phenol molecules, resulting in greater rate, and lower adsorption of phenol.

Effect of temperature on adsorption efficiency of CDs

0.4 g of CDs was added to100 mL ofa100 mg/L phenol solution at pH=6, stirring time of 60 min, stirring speed of 150 rpm, and adsorption time of 240 min. The effect of different temperatures on the rate of phenol removal and the adsorption is shown in Fig.6.

As you can see from Fig. 6, the removal rate of phenol on CDs with the increase of temperature first increased and then decreased, the removal effect at 40 to 60℃was relatively high, respectively: 42.5%, 45.1% and 43.2%;at temperatures above 60℃ the removal rate significantly decreased because the process of adsorption is exothermic, while desorption is endothermic. The adsorption process is also influenced by other factors such as the impact of the formation of hydrogen bonds and van der Waals force forming and disappearing process. With the temperature increase, the removal of phenol first increased and then decreased. Considering a future industrial popularization and application, the adsorption experiments were performed at 40℃ with an adsorption efficiency of 42.5%.

CONCLUSIONS

CDs treatment of phenol wastewater, with the extension of time, the content of CDs phenol adsorption on the increase, to 300 after min adsorption, adsorption ratio reached 42.5%; the pH value has influence on the adsorption efficiency, with the increase of alkaline solution, CDs on phenol adsorption efficiency decreased, removal rate of pH is the highest at 7 37.2%, in the process of adsorption of phenol wastewater by pH can be adjusted to between 5 and 7; with the increase of amount of CDs, phenol adsorption rate increases, determine the quantity of CDs of 4 g/L; the adsorption efficiency of CDs decreased with the increase of initial concentration of phenol; CDs on phenol removal rate with temperature rise first increased and then decreased, the temperature above 60˚C after the removal rate decreased significantly, considering the promotion and application of industrialization, adsorption temperature can be set as 40˚C.

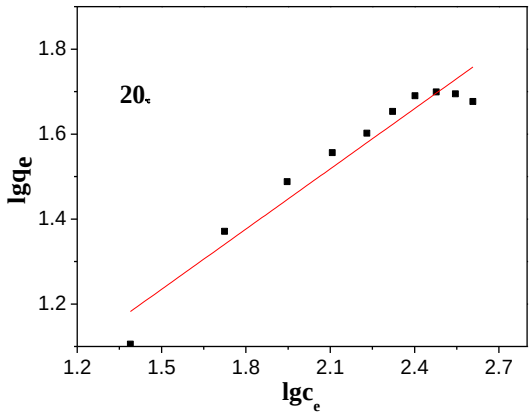

Fig. 7. Effect of temperature on the adsorption efficiency of CDs.

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ИЗСЛЕДВАНЕ НА АДСОРБЦИЯТА НА ФЕНОЛИ ОТ ОТПАДЪЧНИ ВОДИ ЧРЕЗ ЦИКЛОДЕКСТРИНИ

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(Резюме)

Изследвани са оптималните условия за третиране на фенол-съдържащи отпадъчни води с циклодекстрини (CDs). Времето за адсорбция е 240 мин., pH-стойностите са между 5 и 7, концентрацията на CD е 4 g/L. Опитите са проведени при начална концентрация на фенол от 100 mg/L при 40℃. Максималната ефективност на адсорбция е 42.5%. При 30℃ адсорбцията на фенола с CDs се описва от изотермата на Freundlich.