Adsorption of nitrobenzene from aqueous solution on activated sludge modified by cetyltrimethylammonium bromide

Jiangjiang Pan, Baohong Guan*

Department of Environmental Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

A novel method was conducted to modify activated sludge with cetyltrimethylammonium bromide (CB) to obtain an adsorbent to remove aqueous nitrobenzene. The adsorption characteristics of nitrobenzene onto modified activated sludge (MAS) were investigated, by contrast with those of unmodified activated sludge (UMAS). Nitrobenzene adsorption onto MAS is more favorable than that of UMAS at initial nitrobenzene concentrations below 150 mg/L, above which they have an equivalent adsorption capacity. pH value has a significant influence on the adsorption capacity, especially from 10.0 to 12.6 for MAS and from 9.0 to 11.0 for UMAS. The modification changes the steady even surface of activated sludge into uneven one, which is better for adsorption. The hydroxyl of activated sludge and hydrophobic group of CB adsorb nitrobenzene molecules, and CB increases the adsorption sites. The nitrobenzene adsorption onto MAS follows Langmuir isotherm, implying the adsorption occurrence tends to be on a homogeneous surface by monolayer adsorption other than multi-layer adsorption which accounts for the adsorption onto UMAS. The maximum adsorption capacity of MAS is 40.6, 25.0 and 25.6 mg/g at 6.0, 25.0 and 40.0 °C, respectively. MAS presents to be a good adsorbent to remove nitrobenzene from water, and CB is a successful modifier.

1. Introduction

Nitrobenzene is an important raw material as well as a product of industry. It is widely used in chemical plant, lubricating oils refinement, and soaps or shoe polishes production. The large-scale use of nitrobenzene has led to the widespread contamination of groundwater and air, because of its ecotoxicology and harm to animals and humankind [1]. Environmental Protection Agencies of many nations have classified nitrobenzene as main concerned pollutant and growing concern has been focused on its environmental behaviors. Meanwhile, a variety of possible treatment technologies, such as adsorption [2], photochemical reduction [3], oxidation by O_3/UV processes [4], ozonation [5], have been adopted to remove aqueous nitrobenzene. Particularly, granular activated carbon (GAC) has been proved to be one of the most efficient adsorption treatment materials for separating nitrobenzene from water [6]. However, GAC is relatively expensive. Some other promising adsorbents derived from microorganism [7] or seaweed biomass [8] with low cost have been explored. It is reported that a low cost adsorbent based on excess activated sludge has been applied to adsorb pollutants from wastewater [9,10], which is also considered to be one effective way to resolve the problem of excess activated sludge.

Excess activated sludge, which emerges as solid waste during wastewater biological treatment operation, has an increasing huge quantity along with the development of wastewater treatment industry. It can cause secondary pollution if there is no proper treatment and disposal. However, disposal of excess activated sludge is an increasingly expensive and environmentally sensitive problem throughout the world. Various methods have been proposed, such as landfill, application to farmland, incineration, sea dumping, and reclamation. Preparation of adsorbent from sewage sludge offers an attractive re-use alternative to the traditional disposal routes [11]. In recent years, the pyrolytic carbonization of the sewage sludge has been developed to obtain useful adsorbents [12]. It is regarded as a more efficacious and safer alternative for activated sludge utilization. However, this method needs plenty of energy. From the viewpoint of cost, chemical modification perhaps provides a flexible choice. Some surfactants have been proved efficient in modifying organobentonite [13], Chitosan beads [14], and kaolinite [15]. But little research has been conducted on the modification of activated sludge by surfactant or the other chemicals, while such chemical may enhance the adsorption capability of adsorbent due to the characteristics of radicals in chemicals. In fact, the interactions between activated sludge and chemical modifier are not well known.

* Corresponding author. Tel.: +86 571 88273650.
  E-mail address: guanbaohong@zju.edu.cn (B. Guan).

To achieve the goal of effective utilization of the excess activated sludge as adsorbent, we have begun to illustrate the adsorption characteristics of activated sludge modified by cetyltrimethy-lammonium bromide (CB) for aqueous nitrobenzene, and to discriminate the adsorption mechanism between modified activated sludge (MAS) and unmodified activated sludge (UMAS).

2. Materials and methods

2.1. Nitrobenzene solutions and modification of activated sludge

The 20.0 mL of ethanol, 0.2 mL of nitrobenzene and deionized water were introduced into a 1000 mL flask, to obtain a solution containing about 240 mg/L nitrobenzene. Then the exact concentration of nitrobenzene was determined. The dilute solution of nitrobenzene was obtained from it by adding deionized water.

Raw material (the excess activated sludge) was obtained from a large municipal sewerage treatment plant in Hangzhou, China. It was rinsed several times until harmonious without any suspended residue and solid impurities on the bottom. Then it was dried in an oven at 60.0 °C for 24 h and ground to a size smaller than 65-mesh.

The 6.0 g of CB of analytical grade was dissolved in 200.0 mL of deionized water. Then 30.0 g of dried activated sludge powder was added to the solution and homogenized for 2 h in a homogenizer with a magnetic stirrer at 250 rpm. The solid phase by filtration was dried in an oven at 60.0 °C for 24 h, and then rinsed with deionized water till no foam could be found. After being dried again, the solid was ground to a particle size smaller than 65-mesh and kept in an oven for use.

2.2. Experimental procedures

The powder of MAS or UMAS was added into nitrobenzene aqueous solution, which was magnetically stirred at a speed of 250 rpm in a 250 mL conical flask tightly capped with a glass stopper. The 2.0 mL of the mixture was taken periodically from the conical flask for analysis. Sample was filtered using a syringe to separate the sludge. The concentration of nitrobenzene was tested by spectrophotometer (Livibond ET99731 COD/TOC Multi-parameter Instrument, Germany) at 545 nm using 10 mm colorimetric plate.

The effect of pH on the adsorption capacity of MAS and UMAS was evaluated at 25.0 °C. 1.0 g MAS or UMAS and 200 mL aqueous nitrobenzene (the initial concentration is 50.0 mg/L) were introduced into a 250 mL conical flask. The remaining concentration of nitrobenzene was measured after 120 min. The adsorption efficiency was determined in a range of pH (2.0–14.0). Similarly, the equilibrium time of adsorption was determined at 6.0, 25.0 and 40.0 °C, respectively. The adsorption isotherms were conducted at pH 12.6 with other conditions the same as those of determining equilibrium time experiments. Simultaneously, a control experiment without MAS or UMAS was carried out to determine the amount of nitrobenzene adsorbed on glassware and volatilization loss.

The sample of the dried sludge was coated with gold and subjected to a scanning electron microscope (Tabletop Microscope TM-1000, HITACHI, Japan) for a SEM image. The FT-IR spectra were obtained from KBr pellets with a Nicolet NEXUS (TM) 670 FT-IR E.S.P spectrophotometer used in transmission mode with a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}.

3. Results and discussion

3.1. Optimization of adsorption parameters

3.1.1. Impact of pH on adsorption capacity

pH is usually one of the critical parameters in adsorption [16]. The impact of pH on the adsorption capacity of MAS and UMAS is
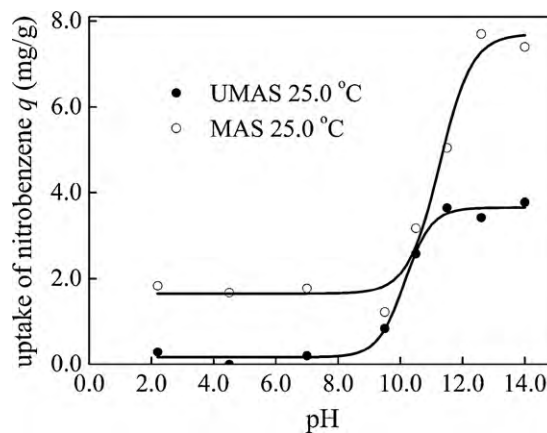

Fig. 1. Effect of pH on the nitrobenzene adsorption capacity of MAS and UMAS: temperature 25.0 °C, adsorption time 120 min, dosage of adsorbent 5.0 g/L, initial concentration of nitrobenzene 50 mg/L.

shown in Fig. 1. A sharp increase of nitrobenzene uptake is observed from pH 9.0 to 11.0 for UMAS while from pH 10.0 to 12.6 for MAS, indicating the adsorption capacity of sludge strongly depends on the pH of the aqueous solution. Only a small amount of nitrobenzene (adsorption capacity 0.2 mg/g) can be removed from aqueous solution by UMAS at pH below 9.0. Even if the pH is above 11.0, its adsorption capacity is no more than 3.5 mg/g. The adsorption capacity of MAS makes a remarkable increase by contrast with that of UMAS. It maintains about 1.7 mg/g at pH below 10.0, but increases greatly to 7.5 mg/g at pH 12.6 and varies little in the range of pH (12.6–14.0). It can be deduced that the optimal pH for the adsorption of nitrobenzene on MAS is from 12.6 to 14.0. The removal efficiencies of nitrobenzene are about 75% in this range of pH. Alkali may cause partly ionization of adsorbate, resulting in alterations in the adsorbent surface and the interface property of solid–liquid with primarily electrostatic forces and complex formation [16]. With the increase in pH, alkali becomes the main fact to dominate the charges distribution on the surface of MAS, which induces the surface to be attractive for nitrobenzene, followed by a great adsorption capacity. The sharp increase of nitrobenzene adsorption onto MAS was 5.8 mg/g, which is much greater than that onto UMAS (3.3 mg/g). This difference implies that pH influences not only the molecular of nitrobenzene and the surface property of sludge, but also the molecular of surfactant modifying the sludge.

3.1.2. Adsorption equilibration time

The uptakes of nitrobenzene by UMAS and MAS varying with adsorption time at 6.0, 25.0 and 40.0 °C are illustrated in Fig. 2. The adsorption equilibration times are all less than 120 min. There is a dramatic increase in uptake of nitrobenzene within the first 50 min but no significant further adsorption can be observed afterwards with a final uptake of 3.5 mg/g within 240 min. The adsorption of nitrobenzene onto MAS at 25.0 °C reaches equilibration within 80 min, which is longer than that of UMAS. More than 90% of the nitrobenzene adsorption amount is obtained within the first 14 min for MAS, which is shorter than that for UMAS (27 min). The adsorption capacity shows a negative correlation with temperature, i.e., a higher temperature will shorten the equilibrium time. At temperatures of 6.0, 25.0 and 40.0 °C, one gram of MAS adsorbs 8.9, 7.5, and 6.8 mg nitrobenzene, respectively, while the corresponding adsorption equilibrium time is 120, 80 and 11 min. The uptakes of nitrobenzene by UMAS are much smaller than those by MAS under the same conditions. It is proved that CB modification provides an effective way to improve the adsorption capacity of activated sludge.
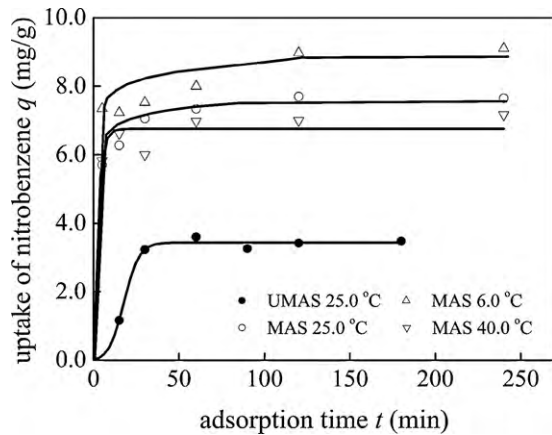
Fig. 2. Adsorption equilibration time of nitrobenzene on MAS and UMAS: temperature (6.0, 25.0 and 40.0 °C), initial pH value 12.6, dosage of adsorbent 5.0 g/L, initial concentration of nitrobenzene 50 mg/L.

3.1.3. Effect of initial concentration of nitrobenzene on the adsorption

The influence of initial concentration of nitrobenzene on the adsorption was investigated for both UMAS and MAS at pH 12.6. The results are shown in Fig. 3. MAS appears more effective than UMAS at the initial concentration of nitrobenzene below 150 mg/L at 25.0 °C. With the increase in initial concentration of nitrobenzene, the uptakes of both MAS and UMAS reach the same level of 17.6 mg/g.

The nitrobenzene uptake by MAS varies linearly with the nitrobenzene concentration and seems to be independent on temperature when the initial concentration is below 60 mg/L. However, differences occur when the initial concentration of nitrobenzene is above 60 mg/L. The maximum uptake of nitrobenzene by MAS is achieved to be 24.8 mg/g at temperature of 6.0 °C and initial concentration of 180 mg/L. Under the conditions of 25.0 °C and initial concentration of 120 mg/L, MAS obtains its maximum uptake of nitrobenzene 17.6 mg/g. However, the maximum uptake declines to 12.1 mg/g when temperature increases to 40.0 °C. The adsorption capacity of MAS decreases with the increase in temperature when the initial concentration of nitrobenzene is above 60 mg/L.

3.2. Mechanism of adsorption

The adsorption capacity of sludge mainly depends on its surface property, especially on the characters of extracellular polymeric
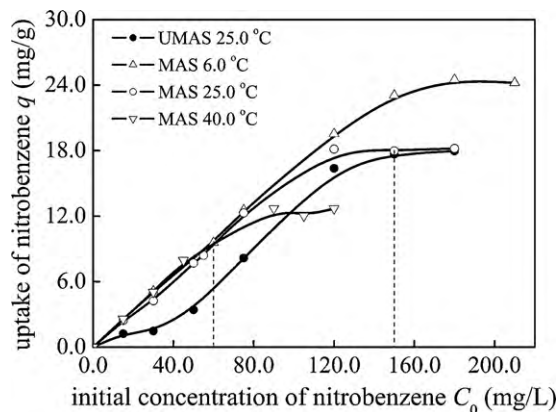

Fig. 3. Effect of initial concentration of nitrobenzene on the uptake of nitrobenzene: temperature (6.0, 25.0 and 40.0 °C), initial pH value 12.6, adsorption time 120 min, dosage of adsorbent 5.0 g/L.
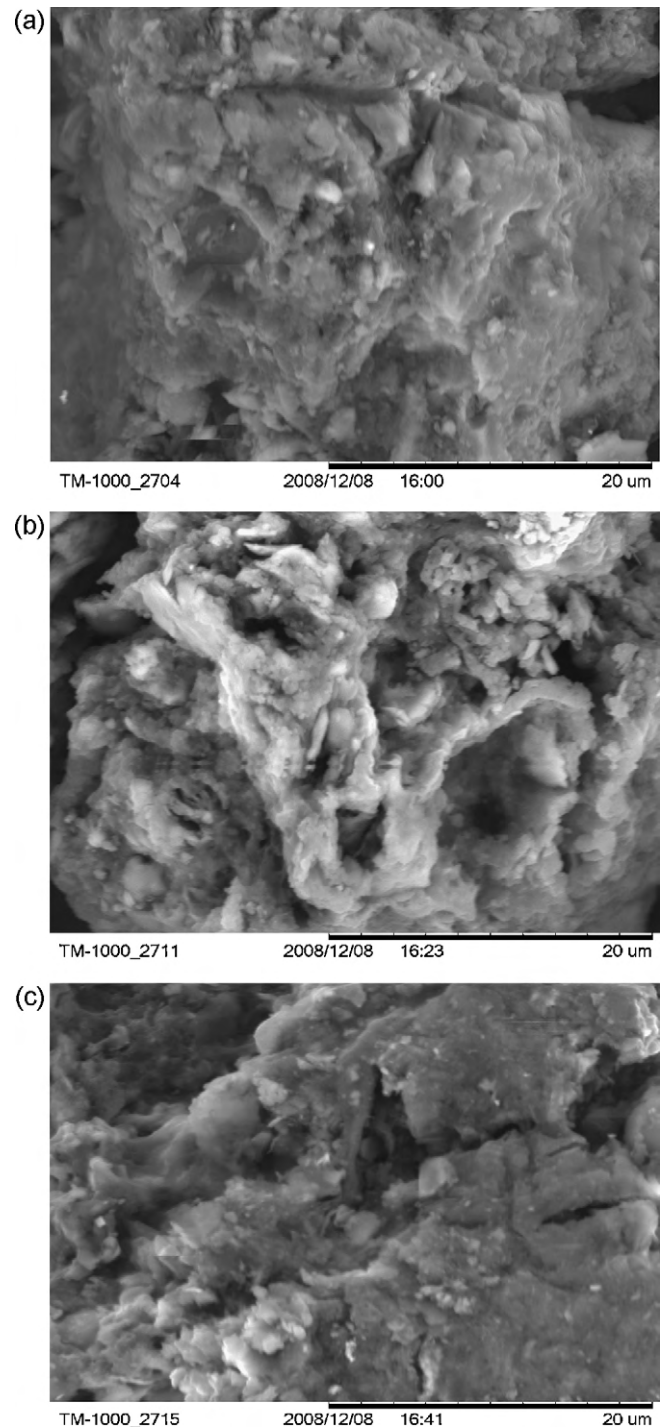

Fig. 4. Scanning electron micrographs of UMAS (a), MAS (b), and MAS on which nitrobenzene was adsorbed (at 25.0 °C, initial pH value 12.6, dosage of adsorbent 5.0 g/L, initial concentration of nitrobenzene 50 mg/L) (c).

substances (EPS), which plays an important role in the formation of sludge floc [17]. Carbohydrates and proteins are major constituents of EPS, the other organic substances, such as humic substances, uronic acids and nucleic acids, are in smaller quantities [18,19]. The surface of EPS is negative charged and thus easily adsorbed by positive or partly positive charged molecules, such as surfactant (e.g., CB), and polarized nitrobenzene. The hydrophilic group of surfactant (e.g., the charged part of CB) will combine with EPS when the activated sludge is modified. It is more likely to adsorb nitrobenzene from water by the hydrophobic group of surfactant
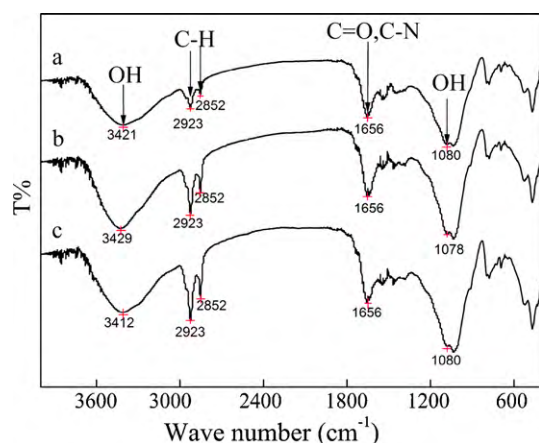
Fig. 5. FT-IR spectra of UMAS (a), MAS (b) and MAS on which nitrobenzene was adsorbed (at 25.0 °C, initial pH value 12.6, dosage of adsorbent 5.0 g/L, initial concentration of nitrobenzene 50 mg/L) (c).
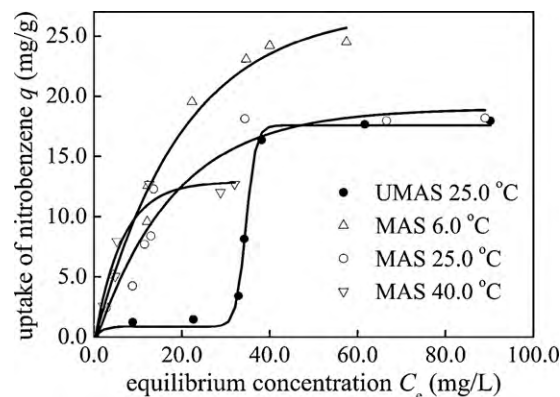

Fig. 6. Adsorption isotherm of nitrobenzene on UMAS and MAS: temperature (6.0, 25.0 and 40.0 °C), adsorption time 120 min, dosage of adsorbent 5.0 g/L, initial pH value 12.6.

(e.g., the carbon chain part of CB) when MAS is used as an adsorbent. On the other hand, nitrobenzene can be directly adsorbed by sludge because of the electrostatic interaction between polarized nitrobenzene and EPS.

SEMs of UMAS, MAS and MAS with nitrobenzene absorbed on are shown in Fig. 4. There is an explicit change in surface morphology between UMAS and MAS (see Fig. 4a and b). The former looks very steady and has a multi-angular but relatively even surface, while the later looks like a rough and uneven surface with many obvious "soft channels", which have blunt edges. The modification provides activated sludge with an undulating surface, which may lead to a greater specific surface and thus, increase the number of adsorption sites for nitrobenzene. As a result, MAS has a larger adsorption capacity. Fig. 4c shows that MAS has a relatively smooth surface covered with colloid-like floc after the adsorption of nitrobenzene. In other words, nitrobenzene can be captured by the surface of MAS to form some colloid-like compounds, which could reshape the surface of sludge.

The FT-IR spectra (Fig. 5) reveal a highly complex composition of the sludge. Some characteristic peaks can be assigned according to Table 1. The broad peak at 3421 cm^{-1} for UMAS is attributed to OH stretching vibrations, and the peaks at 2923 and 2852 cm^{-1} are due to C–H stretching vibrations of CH, CH$_2$ and CH$_3$ groups. The peak at 1656 cm^{-1} is attributed to C=O or C–N. It is clear that UMAS contains –COOH and –CONH–, which indicate protein and other organic substances. The stronger peaks at 2923 and 2852 cm^{-1} illustrate that CB has been effectively settled on acti-

vated sludge. CB should be bonded with OH or C=O, since there are some changes for OH peak from 3421 to 3429 cm^{-1} and C=O peak around 1600 cm^{-1}. Unfortunately, no characteristic peaks for nitrobenzene can be observed in Fig. 5c, indicating no obvious evidence from IR to support that nitrobenzene was adsorbed by MAS. In fact, nitrobenzene adsorbed by MAS was desorbed during the analysis process, since nitrobenzene is highly volatile under the conditions of sample grinding and drying for FT-IR test. However, there is less transmittance around 1400 cm^{-1}, which could be explained that –C–NO$_2$ in nitrobenzene adsorbs IR in that range. Nitrobenzene can be adsorbed by or react with hydrophobic group of modifier as well as OH group of the sludge, judging from the stronger peaks in Fig. 5c than that in Fig. 5b at 2923 and 2852 cm^{-1} and changes on the peak of OH (from 3429 to 3412 cm^{-1}). In a word, CB creates more adsorption sites for nitrobenzene and improves the adsorption capacity of MAS. The hydrophobic group of CB (–CH$_3$) is more preferable for nitrobenzene adsorption, which accelerates the adsorption process.

4. Adsorption isotherms

The equations of Langmuir and Freundlich isotherms were used to describe the adsorption of nitrobenzene onto MAS and UMAS. The adsorption isotherms at pH 12.6 and adsorbent dosage 5.0 g/L are plotted in Fig. 6.

Langmuir isotherm equation is as follows.

$$q = \frac{q_m \cdot C_e}{(K + C_e)} \tag{1}$$

Table 1
Main functional groups on UMAS and MAS observed by FT-IR.

| Wave number (cm^{-1})	Vibration type	Functional type
3200–3400	Stretching vibration of OH	OH into polymeric compounds
2936–2916	Asymmetric stretching vibration of CH$_2$	
2843–2863	Symmetric stretching vibration of CH$_2$	
1700–1725	Stretching Variation of C=O (shoulder)	Carboxylic acids
1650–1670	Stretching variation of C=O	Carboxylic acids
1640–1660	Stretching variation of C=O and C–N (amide I)	Proteins (Peptidic bond)
1615–1540	Asymmetric stretching vibration of NO$_2$	
1550–1560	Stretching variation of C–N and deformation vibration of N–H (amide II)	Proteins (Peptidic bond)
1445–1485	Deformation vibration of CH$_2$	
1400–1410	Stretching vibration of C=O	Carboxylates
	Deformation vibration of OH	Alcohols
1390–1320	Symmetric stretching vibration of NO$_2$	
1240	Deformation vibration of C=O	Carboxylic acids
1040–1070	Stretching vibration of OH	
<1000	Fingerprint zone	
	Several bands visible	Phosphate or sulphur functional groups, or –(CH$_2$)$_n$–, $n > 4$
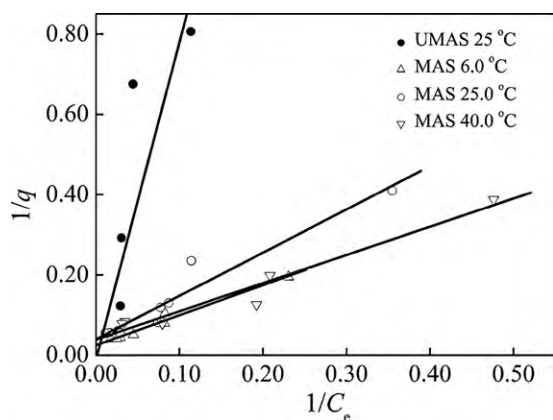
Fig. 7. Langmuir isotherm of nitrobenzene on MAS and UMAS: temperature (6.0, 25.0 and 40.0 °C), adsorption time 120 min, dosage of adsorbent 5.0 g/L, initial pH value 12.6.

Table 2
Parameters of Langmuir isotherms for nitrobenzene adsorption by UMAS and MAS: temperature (6.0, 25.0 and 40.0 °C), adsorption time 120 min, dosage of adsorbent 5.0 g/L, initial pH value 12.6.

adsorbent	T (°C)	q_m (mg/g)	K (mg/L)	R
MAS	6.0	40.6	30.4	0.988
MAS	25.0	25.0	26.9	0.966
MAS	40.0	25.6	18.0	0.975
UMAS	25.0	−100.0	–	0.862

where q is equilibrium concentration of adsorbate on adsorbent (mg/g), q_m is the maximum adsorption capacity (mg/g), C_e is the liquid phase equilibrium concentration of adsorbate (mg/L), K is the saturation constant (mg/L).

A linear equation is derived as follows to calculate K and q_m.

$$\frac{1}{q} = \frac{1}{q_m} + \frac{K}{(q_m \cdot C_e)} \qquad (2)$$

The equilibrium concentrations of nitrobenzene on MAS, UMAS and in liquid phases are presented in Fig. 7. The adsorption parameters are shown in Table 2.

From the Langmuir isotherm equation, the q_m of MAS reaches 40.6 mg/g at 6.0 °C and exhibits little change as temperature increases from 25.0 °C to 40.0 °C. The q_m is much greater than that obtained from experiment, indicating that the adsorption sites of MAS is far away from completely being occupied by nitrobenzene molecules. The q_m of MAS at 25.0 °C is 25.0 mg/g, which is almost 90% of the maximum uptake of nitrobenzene by nanotubes, 27.8 mg/g at 293 K [20] and can be of the average uptake by activated carbon, ranging from 20 to 40 mg/g (1.7–3.3 mmol/g [21]). Consequently, MAS has a great adsorption capacity for nitrobenzene removal from aqueous solution. Whereas, the q_m of UMAS is negative, which implies the adsorption can not be described by Langmuir isotherm equation. This may be due to the multi-layer other than single-layer adsorption of nitrobenzene onto UMAS. Also, the Langmuir isotherm equation is much more suitable for the description for nitrobenzene adsorption onto MAS judging from the parameter R. So we can deduce that the modification with CB gives the activated sludge a different adsorption character.

Based on the Langmuir isotherm equation, the adsorption intensity (R_L) is expressed as follows [22]:

$$R_L = \frac{1}{(1 + C_0/K)} \qquad (3)$$

where C_0 is initial concentration of adsorbate (mg/L). R_L is often used as a parameter to determine whether the adsorption is a favorable one. A favorable adsorption has R_L values between 0 and 1 at

Table 3
Adsorption intensity (R_L) for nitrobenzene adsorption on MAS: temperature (6.0, 25.0 and 40.0 °C), adsorption time 120 min, dosage of adsorbent 5.0 g/L, initial pH value 12.6.

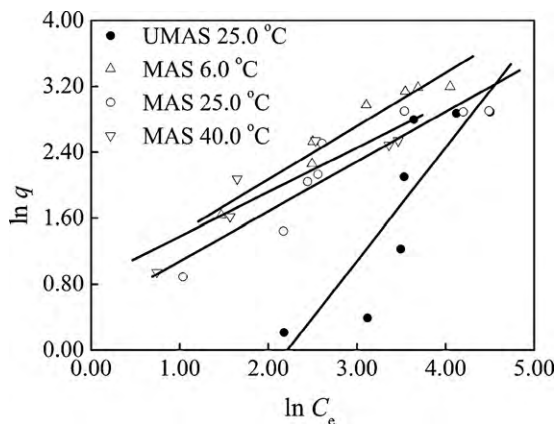| 6.0 °C		25.0 °C		40.0 °C	
C_0 (mg/L)	R_L	C_0 (mg/L)	R_L	C_0 (mg/L)	R_L
0	1.00	0	1.00	0	1.00
30	0.50	15	0.64	15	0.55
60	0.34	30	0.47	30	0.38
75	0.29	50	0.35	45	0.29
120	0.20	55	0.33	90	0.17
150	0.17	75	0.26	105	0.15
180	0.14	120	0.18	120	0.13
210	0.13	150	0.15	–	–
–	–	180	0.13	–	–

Fig. 8. Freundlich adsorption isotherm of nitrobenzene on MAS and UMAS: temperature (6.0, 25.0 and 40.0 °C), adsorption time 120 min, dosage of adsorbent 5.0 g/L, initial pH value 12.6.

different initial concentrations of adsorbate. In these experiments R_L varies from 0.13 to 1.00 (Table 3), implying that MAS is a kind of favorable adsorbent for nitrobenzene.

The Freundlich isotherm describes a monolayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.

$$q = \kappa C_e^{1/n} \qquad (4)$$

where κ stands for adsorption capacity (mg/g) and n for adsorption intensity. The logarithmic form of Eq. (4) is:

$$\ln q = \ln \kappa + \frac{1}{n} \cdot \ln C_e \qquad (5)$$

where κ and n are calculated from Fig. 8 and shown in Table 4.

The κ is much greater at 6.0 °C than that at 25.0 °C, indicating both UMAS and MAS tend to adsorb more nitrobenzene at lower temperature. However, the κ at 40.0 °C is greater than that at 25.0 °C. To compromise these two opposite trends, the adsorption preference may vary with the temperature. The adsorption intensity (n) shows the similar trend. The κ of UMAS is only 0.048 mg/g,

Table 4
Parameters of Freundlich isotherms for nitrobenzene adsorption by UMAS and MAS: temperature (6.0, 25.0 and 40.0 °C), adsorption time 120 min, dosage of adsorbent 5.0 g/L, initial pH value 12.6.

Adsorbent	T (°C)	κ (mg/g)	n	R
MAS	6.0	2.171	1.546	0.970
MAS	25.0	1.608	1.658	0.923
MAS	40.0	2.323	1.862	0.905
UMAS	25.0	0.048	0.727	0.871

much less than that of MAS (1.608 mg/g), which demonstrates that UMAS is undesirable for nitrobenzene adsorption.

In the light of the correlation coefficients (R), it is found that the Langmuir isotherm is more accurate than the Freundlich isotherm to depict the adsorption of nitrobenzene onto MAS. This suggests that the adsorption occurrence tends to be on a homogeneous surface by monolayer adsorption to some extent.

5. Conclusions

The activated sludge was modified by CB to prepare adsorbent to remove nitrobenzene from aqueous solution. The pH is a critical factor for adsorption process and temperature has a negative correlation with adsorption capacity. MAS can absorb nitrobenzene much more effectively than UMAS.

It seems the hydrophobic group of modifier (CB) as well as OH group of the activated sludge provides the adsorption sites for MAS. The modification by CB enhances the adsorption capacity of activated sludge for nitrobenzene from water.

Langmuir isotherm other than Freundlich isotherm is more appropriate to depict the nitrobenzene adsorption on MAS, which suggests the adsorption occurrence tends to be on a homogeneous surface by monolayer adsorption.

The maximum adsorption capacity of 24.8 mg/g was achieved by MAS. The application of MAS to remove nitrobenzene from water is potentially feasible, and CB is a reasonable modifier for activated sludge.

Acknowledgments

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