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Intensive removal of organic matter from a real hypersaline wastewater containing organic and inorganic salts

Jiameng Wang, Limin Yang*, Fan Jiang, Wenlong Cui*

Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou City 213164, China, Tel.: +8613813693879; email: lyang@cczu.edu.cn (L. Yang), Tel.: +8618306111220; emails: cuiwl@cczu.edu.cn (W. Cui), 1187851528@qq.com (J. Wang), 1043061198@qq.com (F. Jiang)

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ABSTRACT

The existence of organic salts in hypersaline wastewater enlarges the difficulty of wastewater treatment. In this study, a real hypersaline wastewater containing both organic and inorganic salts from the bifenthrin alcohol production processes was firstly neutralized to convert and release the organic salt to organic compound and inorganic salt, and then adsorbed by macroporous resins. The optimal operating conditions and adsorption mechanisms were investigated and analyzed through the wastewater treatment. The experimental results show that after the wastewater is neutralized with the naturally accompanied evaporation of resulted organic compound, removals of chemical oxygen demand (COD) and ammonia nitrogen (AN) can reach up to 22.7% and 36%, respectively. Thereafter the wastewater was adsorbed by macroporous resins, the highest total COD removal can only reach up to 65.9% for the single resin adsorption case, which is not enough for the inorganic salt recovery with a high purity. Whereas the removal of organic matter can be remarkably promoted by the sequentially coupled macroporous resin adsorption case. The highest total COD and AN removals can reach up to 93% and 100%, respectively, when the neutralized wastewater is adsorbed firstly by resin NKA-II and then by resin XAD-4. The adsorption isotherms of sequentially coupled resins of NKA-II and XAD-4 are both better fitted by Freundlich's model and the adsorption processes can be well fitted by pseudo-second-order kinetic model.

Keywords: Adsorption; Hypersaline wastewater; Organic salt conversion; Coupled resins; Neutralization; Wastewater treatment

1. Introduction

Hypersaline wastewater can be considered as liquid waste effluent containing >3.5% wt salts and organic matter [1]. It comes from a variety of industries, such as, chemical synthesis, food production, textile process, pulp/paper production, coal chemical conversion. It contains very complex composition of organic matter with a high chemical oxygen demand (COD) value. It was estimated such wastewater in China exceeds 300,000,000 m^3 annually and once used to be a severe threat to the water resources [2]. In the recent two decades, numerous researchers have made tremendous efforts to treat such wastewater by using various methods [3]. In addition, the investment of treatment facilities functioned as the industrial infrastructure has being increased rapidly, resulting in a sharp reduction of its discharge to the water bodies. Extensive reviews on this subject have been published [1–6]. Traditional methods, such as, biological methods [7,8], membrane methods [9,10], and distillation methods [11,12] have been widely used for effective treatment to specific wastewater of this kind.

Among the hypersaline wastewater, there is a special wastewater, which contains not only inorganic but also organic salts. Such wastewater often comes from the

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* Corresponding authors.

production processes, such as pharmaceutical, pesticide, dyes, and food industries [2,5]. Because it contains high contents of both organic and inorganic salts in addition to various other organic impurities, it is very difficult to be treated efficiently and completely by the traditional methods mentioned above. For example, treated by distillation methods, organic salts remain in the bottom products, leading to contamination of inorganic salt crystals after crystallization and/or a low quality of recovered salts [13].

At present, two methods, that is, incineration technology [14,15] and advanced oxidation methods [6,16] are usually suggested to treat such wastewater in practice. For the incineration method, all the organic matter are oxidized by high-temperature combustion in a special incinerator. The disadvantages of this technique include high energy consumption and carbon emission. Furthermore, such a process would involve high investment, ready corrosion of equipment and easy blockage of pipes by salts. The advanced oxidation method uses Fenton oxidation, photocatalytic oxidation, electrochemical oxidation, sonochemical oxidation and other oxidation techniques to degrade the organic matter in the wastewater. Since most organic matter in the wastewater contains elements of N, P, and/or S, they are easy to generate NO_x, PO_x and/or SO_x as the possible secondary pollution for these two methods [15]. Therefore, effective treatment of the hypersaline wastewater containing organic and inorganic salts still remains as an unsolved issue, resulting in a huge threat to the environments.

The hypersaline wastewater contains not only various toxic, harmful and complex organic substances, but also recyclable inorganic salts. To treat such hypersaline organic wastewater, the priority objective is to recover salts whilst remove or recycle all organic matter. The solution that has been found involves a hybrid solution, that is, the combination of two processes, neither of which alone would suffice [1,10,17]. The treatment of such wastewater can be considered as two operations: extraction/removal of organic compounds and recovery of salts. The latter operation is a combined process of evaporation and crystallization, which is used widely in the process industry [18]. The premise of obtaining high-quality inorganic salts in this process only exists when the contents of organic and other impurities are low enough. One of the most effective, complete, and economical techniques which extract organic matter from the wastewater is adsorption [19,20]. There are various adsorbents available [21–28]. Among them, macroporous resins are widely used in adsorption treatment of various wastewater in recent years because of their stable physical and chemical properties, which are not affected by the presence of low molecular compounds and inorganic salts, and can effectively adsorb medium and small molecular organic substances, with a long renewable and recycling service [29,30].

For adsorption of organic matter from hypersaline wastewater, several researchers noticed that the pH of the wastewater did affect the adsorption outcomes [29,31]. For example, increasing pH was beneficial for adsorption of cationic dyes in the wastewater, while decreasing pH was helpful for adsorption of anionic dyes [31]. Actually, most of these ionic dyes may exist as organic salts in the wastewater, but the variation of adsorption outcome with the wastewater pH is rarely attributed to the adsorption change of these organic chemicals combined as organic salts due to the conversion of these organic salts. Therefore, the treatment difficulty of such wastewater has not been attributed to the treatment of organic salts contained.

In this study, a real hypersaline organic wastewater containing both organic and inorganic salts from bifenthrin alcohol production processes was treated to remove its organic matter according to its characteristics of organic salt and organic chemicals. pH of the wastewater was adjusted to convert organic salt into organic chemical and inorganic salt, and then single macroporous resin and coupled macroporous resins were experimentally examined for adsorbing the organic matter from the wastewater. Adsorption thermodynamics and kinetics of the selected adsorbents were investigated experimentally to explore their adsorption mechanisms.

2. Material and methods

2.1. Materials

Macroporous resins which are available in the market of the world were screened for the adsorption abilities to the wastewater. The typical resins used in the present study are listed in Table 1. Among these resins, the Tulsimer ADS-600

Table 1
Parameters of macroporous resins used

Resin	Polarity	Structure	Particle size (mm)	Specific surface area (m^2/g)	Pore size (nm)
H103	Non-polar	SDVB	0.3–1.25	1,000–1,100	8.5–9.5
XAD-4	Non-polar	SDVB	0.3–1.25	750	5.0
X-5	Non-polar	CLPS	0.3–1.25	500–600	29–30
D3520	Non-polar	CLPS	0.3–1.25	480–520	8.5–10
XAD-2	Non-polar	SDVB	0.3–1.25	330	9.0
ADS-600	Non-polar	CLPS	0.3–1.0	550	20–40
AB-8	Weak-polar	CLPS	0.3–1.25	480–520	13–14
CAD-40	Weak-polar	CLPS	0.3–1.25	450–500	7–8
NKA-II	Middle-polar	CLPS	0.3–1.25	160–200	14.5–15.5
S-8	Strong-polar	CLPS	0.3–1.25	100–120	28–30

CLPS: Cross-linking polystyrene; SDVB: Styrene-divinylbenzene.

was purchased from Cohesion (Beijing) Co., Ltd., H103, S-8, CAD-40, D3520, X-5, AB-8, NKA-II were purchased from Hecheng New Material Technology Co., Ltd., (Zhengzhou, China), and the Amberlite XAD-2 and XAD-4 were purchased from Sunlight Technology Co., Ltd., (Tianjin, China). All chemicals are of analytical grade purchased from Sinopharm Chemical Reagent Co., Ltd., China and used as received.

The wastewater was supplied by a chemical plant in Jiangsu Province, China. It is a hypersaline wastewater with a color of bright yellow and a slight odor. It mainly contains organic salt of 8.3% wt dimethylamine hydrochloride, inorganic salts of 10.1% wt $MgCl_2$, and 0.5% wt NaCl, as well as organic impurities, such as arene chloride, aromatics, and coupling aromatics, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), etc. The COD and ammonia nitrogen (AN) of this wastewater are 22,000 and 287.7 mg/L, respectively. The density of the wastewater is 1,260 kg/m^3 and pH 3.

2.2. Adjustment of wastewater pH

Through analyzing the production processes and chemical measurement, dimethylamine hydrochloride is found as an organic salt presence in the wastewater with a concentration of 8.3% wt. This organic salt is relatively difficult to be treated at inorganic salt recovery operation, but it can be converted to dimethylamine and sodium chloride by adding NaOH as the following reaction [32]:

$$\left(CH_3\right)_2 NH \cdot H^+ + OH^- \rightleftharpoons \left(CH_3\right)_2 NH \uparrow + H_2O \tag{1}$$

Note that this is a reversible reaction and as the solution pH increases the conversion of organic salt increases until all the salt has been converted. In addition, dimethylamine has a boiling point of 6.1°C under atmospheric pressure and it is easy to evaporate into air. Therefore, the pH adjustments were carried out in a three necked flask with an agitator. 40% wt NaOH solution was gradually added to 250 mL original wastewater in the flask under agitation and the gasified vapour was connected to a reflux condenser and a downstream washing bottle containing hydrochloric acid to absorb the evaporated dimethylamine.

The pH of the wastewater was adjusted from 3 to 4, 5, 6, and 7, by adding 40% wt NaOH aqueous solution into the wastewater with a volume ratio of NaOH solution/wastewater at 0, 0.375%, 0.625%, 0.875%, and 1.125%, respectively. As pH of the wastewater increases, more dimethylamine molecules escape from the wastewater and its COD and AN decrease accordingly. The removals of COD and AN can be calculated by Eq. (2):

$$R_i = \frac{\left(V_0 C_0 - V_E C_E\right)}{V_0 C_0} \tag{2}$$

where C_0 (mg/L) and C_E (mg/L) are the original and final COD or AN of the wastewater (measured by using 6B-80 water quality analyzer, Jiangsu Shengaohua Environmental Protection Technology Co., Ltd., China), respectively. V_0 (mL) and V_E (mL) are the original and final volumes of the wastewater, respectively. Generally, V_0 and V_E are approximately equal.

2.3. Adsorption equilibrium experiments

All macroporous resins were firstly pretreated according their manufacturers' instructions before they were used. For adsorption equilibrium experiments, a fixed amount of one macroporous resin and 250 mL of the neutralized wastewater were added into a 500 mL conical flask. The flask was maintained at a constant adsorption temperature, which was controlled by a thermostated water bath with an intelligent magnetic stirrer (ZNCL-GS, Changzhou Yawang Experimental Equipment Co., Ltd., China) that controlled the temperature within ±0.1°C. The resin and the wastewater were mixed uniformly at a stirring speed of 260 rpm. The COD of the solution can be detected as time goes by. The adsorption equilibrium can be determined as the COD of the solution was no longer changed with the contact time. After the adsorption equilibrium was attained, equilibrium COD and AN of the residual solution can be measured and compared with its original ones, the COD and AN removals can then be calculated by Eq. (2).

The adsorption equilibrium quantity on resin q_e (mg/g) can be calculated by Eq. (3):

$$q_e = \frac{\left(V_0 C_0 - V_E C_E\right)}{m} \tag{3}$$

where m (g) is the mass quantity of the resin.

For batch adsorption isotherm experiments, a series of 250 mL neutralized wastewater with different initial COD concentrations were individually added to the corresponding 500 mL conical flasks, containing a fixed amount of resin each. After the adsorption equilibrium attained, the solution was sampled, its COD and AN were measured, and the equilibrium adsorption amount q_e was calculated by using Eq. (3).

2.4. Adsorption kinetics experiments

For adsorption kinetics measurement, 30.0 g resin was added to 250 mL wastewater in a 500 mL conical flask and the system was stirred at 260 rpm and maintained at a constant temperature. Samples were taken and their CODs, which can represent total organic matter, were measured at different time intervals.

3. Results and discussion

3.1. Effect of wastewater pH

According to Eq. (1), dimethylamine hydrochloride in the wastewater can be converted to dimethylamine and NaCl by adding NaOH or adjusting its pH. The contents of COD and AN decrease as the wastewater pH increases by adding 40% wt NaOH due to naturally accompanied evaporation of dimethylamine. The results are shown in Table 2.

It can be seen that when the wastewater pH is adjusted from 3 to 7, the AN decrease from 278.7 to 178.3 mg/L, and the COD decreases from 22,000 to 17,000 mg/L. In this case, the removals of AN and COD are 36.0% and 22.7%, respectively. Obviously, the removal of AN is significantly higher than that of COD. The reason is that the content of AN in the wastewater mainly comes from two constituents, that

Table 2
Relationship between the contents of COD and AN and the wastewater pH

pH	3	4	5	6	7
AN (mg/L)	278.7	246.5	210.3	192.4	178.3
R_{AN} (%)	0	11.6	24.5	31.0	36.0
COD (mg/L)	22,000	19,600	18,200	17,900	17,000
R_{COD} (%)	0	10.9	17.3	18.6	22.7

is, the unreacted raw material DMF and the by-product dimethylamine hydrochloride, whereas COD is contributed by all organic impurities, including organic salts and all other organic compounds. Therefore, dimethylamine hydrochloride only accounts for a small fraction of the organic matter, but accounts for a much larger part of AN. As the reaction takes place during the pH adjustment by adding NaOH, gasification and escape of dimethylamine from the wastewater happen, leading to a higher removal of AN than that of COD. Note that a higher pH value of the wastewater than 7 might result in forming $Mg(OH)_2$, which is detrimental to the further treatment of the wastewater, especially salt recovery.

3.2. Adsorption treatment of the neutralized wastewater by single resin

When the neutralized wastewater is adsorbed by a single macroporous resin to its equilibrium state with a ratio of resin 30 g to wastewater 250 mL at 298 K, the removals of COD and AN measured are tabulated in Table 3. These 10 macroporous resins can represent typical adsorption resins with different polarities, specific surface areas, and pore sizes. It can be seen from the COD removal data R_{COD} in the table that all resins can adsorb a certain amount of organic matter with the highest COD removal of 55.9% for resin XAD-4. Whilst, from the AN removal data R_{AN}, it can be seen that the AN removals can vary from 0 to 85.6%, depending on nature of the resins. Note that resins S-8 and ADS-600 have no AN adsorption effect, while NKA-II has the highest AN removal.

These phenomena can be explained by the adsorption theory. Most adsorption processes of organic chemicals on macroporous resins are physical processes, where adsorbates bind to the adsorbent surface due to weak forces, such as, van der Waals force, hydrogen bonds, polarity, dipole–dipole, and π–π interactions [19,20]. Accordingly, all these 10 macroporous resins can adsorb a part of organic impurities in the wastewater due to the weak force existence between the resin surface and the organic compounds. However, since S-8 macroporous resin is a hydrophobic adsorbent with surface structure of cross-linked polystyrene, its adsorption capacity for small hydrophilic molecules, such as, DMF, and other small polar molecules is very small. Similarly, ADS-600 is a special macroporous adsorption resin without any modified functional groups at its surface, it can adsorb derivatives of benzene ring by mechanisms of van der Waals force and π–π interaction, but cannot adsorb small polar molecules, such as DMF. NKA-II resin has a special modified functional group on its surface and it can remarkably adsorb small polar molecules like DMF with a higher capacity [33].

Table 3
Removals of COD and AN by adsorption using different macroporous resins

Resin	R_{COD}, %	R_{AN}, %
S-8	23.0	0
D3520	26.5	3.6
H103	27.8	7.7
AB-8	34.7	14.3
XAD-2	36.3	21.6
X-5	38.5	16.7
CAD-40	43.0	18.8
ADS-600	50.0	0
NKA-II	52.4	85.6
XAD-4	55.9	14.1

By comparing the removals between COD and AN, it can be seen that different resins can adsorb different combinations of chemical species in the wastewater and their adsorption capabilities mainly depend upon their own nature of attracting the chemicals in the wastewater. Therefore, the better way to improve the removals of COD and AN in this case is to use two or three different macroporous resins in series.

3.3. Adsorption by sequentially coupled resins

Table 3 indicates that NKA-II has the highest AN removal and a relatively higher COD removal. Therefore, NKA-II is a necessary composition when using a multi-resin adsorption scheme. For a coupled resin adsorption scheme, another composition can be chosen from other four resins in the table with higher COD removals and a certain AN removals, that is, XAD-4, CAD-40, X-5 and XAD-2. These four resins are sequentially combined with NKA-II to adsorb the organic matter in the neutralized wastewater with a ratio of 30 g resin to 250 mL wastewater at 298 K. The removals of COD and AN by the coupled resin adsorption and their total removals of COD and AN obtained experimentally are tabulated in Table 4.

It can be seen from Table 4 that the treatment results with the coupled resins are obviously better than that of any single resin alone. The best adsorption results appear at the last group in the table with the COD removals of 90.9% and the AN of 100%, in which the sequentially coupled resins are consisted of a combination adsorption firstly by NKA-II and then by XAD-4. After treated by neutralization and coupled resin adsorption, the total removals of COD and AN in the wastewater for this case can reach 93% and 100%, respectively, and its color changes from bright yellow to colorless. In addition, it can be seen from the last two groups of data in Table 4 that if the sequence of adsorption operation by two resins is reversed, the removals of COD and AN are changed. The reason is that the adsorption of organic substances by adsorbents can be promoted or

Table 4
Removals of COD and AN by adsorption using sequentially coupled resins

Sequentially coupled resins	COD removal (%)	Total COD removal (%)	AN removal (%)	Total AN removal (%)
NKA-II+X-5	64.5	72.6	89.8	93.5
NKA-II+XAD-2	84.9	88.3	96.6	97.8
NKA-II+CAD-40	68.7	75.8	91.9	94.8
XAD-4+NKA-II	83.4	87.2	96.2	97.6
NKA-II+XAD-4	90.9	93.0	100	100

inhibited in the presence of other organic substances [29]. When the wastewater is successively adsorbed by two resins in series, the preferential adsorption capability of the upstream adsorbent will inevitably affect the adsorption outcome of the downstream adsorbent, thus affecting the overall treatment results.

The original wastewater was directly adsorbed by the last two groups of sequential resin combinations in Table 4 to check the adsorption effect under the presence of the organic salt of dimethylamine hydrochloride. The experimental results show that the COD removals can reach only 74.7% and 81.3%, respectively, with much lower AN removals of 53.5% and 61.6%, respectively. It implies that the unconverted organic salt is a component that is more difficult to be adsorbed by the macroporous resins. Therefore, converting the organic salt into inorganic salt and organic matter is beneficial to the effective removing of organic matter in the wastewater.

3.4. Effect of resin dosage for sequentially coupled resin adsorption

In order to decide the optimal conditions for the ratios of coupled resins to the neutralized wastewater, the wastewater was firstly adsorbed by using different dosages of NKA-II, and then the wastewater, in which the solutes have been fully adsorbed by NKA-II, was adsorbed by using different dosages of XAD-4. The results for the COD removals are shown in Fig. 1.

In Fig. 1, the COD removal increases with the resin dosage until adsorption equilibrium is attained where the COD removal remains almost unchanged. At this equilibrium, all the adsorbable solutes in the solution have been fully adsorbed by the resin and achieved the maximum removal of organic impurities for the operating conditions. It can be seen from Fig. 1 that the corresponding dosages of NKA-II/wastewater ratio and XAD-4/wastewater ratio are 80 and 40 g/L, respectively, for the equilibrium. After adsorbed by NKA-II, COD of the wastewater decreases from 17,000 to 8,100 mg/L with a COD removal of 52.4%. Further adsorbed by XAD-4, its COD decreases to 1,500 mg/L with a COD removal of 81.5%. Compared with the COD removal of 55.9% for XAD-4 in Table 3 for the single resin adsorption case, the COD removal here is much higher. This indicates that the adsorption capacity of XAD-4 to organic matter in the neutralized wastewater is greatly improved after firstly removing some organic constituents by using NKA-II adsorption. This also verifies that the existence of other organic chemicals in the wastewater may affect the adsorption results to the targeted organic compounds and the order of the coupled resin adsorption is crucial to the treatment outcomes.

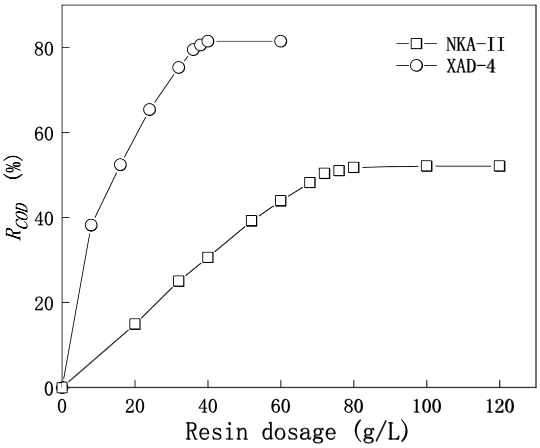

Fig. 1. Effect of resin dosages on the chemical oxygen demand removals for sequential coupled resin adsorption.

3.5. Adsorption isotherm for sequentially coupled resins

Although there are many research reports on adsorption thermodynamics and kinetics for wastewater treatment in the literature [19,29], due to the complex organic components in the wastewater, it is still necessary to investigate the thermodynamics and kinetics of adsorption by the coupled resins.

The neutralized wastewater was diluted to fixed proportions and adsorbed by NKA-II to isothermal equilibrium at 298, 308, and 318 K, respectively, to investigate the relationship between its adsorption equilibrium quantities and equilibrium concentrations, Fig. 2a. Then the wastewater, in which the solutes have been fully adsorbed by NKA-II, was diluted to fixed proportions and adsorbed to isothermal equilibrium by XAD-4 at 298, 308, and 318 K, respectively, to examine the relationship between the adsorption equilibrium quantities of the second resin and the equilibrium concentrations Fig. 2b.

As can be seen from Fig. 2, the adsorption equilibrium quantities of the resins NKA-II and XAD-4 increase with the organic concentrations, but decrease with the adsorption temperature. At 298 K, the adsorption equilibrium quantities of NKA-II and XAD-4 are 110.82 and 165.08 mg/g, respectively.

Once adsorption isothermal equilibrium was attained at a fixed temperature, adsorbates adsorbed on resin particles were in equilibrium with their counterparts dissolved in solution. There are multiple models to describe such adsorption isotherm. Two typical models for adsorption processes in liquid/solid systems are Langmuir's and Freundlich's models [34]. Langmuir's model which represents monolayer adsorption of adsorbates on solid surface can be expressed by Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

where q_e (mg/g) is adsorption equilibrium quantity, q_m (mg/g) is the maximum adsorption quantity, K_L (L/mg) is Langmuir's adsorption constant, and C_e (mg/L) is equilibrium concentration in solution. Whereas Freundlich's model can be expressed by Eq. (5):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

where K_F (mg/g) is Freundlich's adsorption constant and n is a constant related to the attractive force between adsorbates and adsorbent.

The adsorption isothermal data obtained from the experiments were fitted with Langmuir's and Freundlich's models, respectively, and the relevant parameters obtained are tabulated in Table 5.

It can be seen from the correlation coefficient R^2 in Table 5 that the Freundlich's model is better fitted with the measured data both for NKA-II and XAD-4. Because the wastewater contains a variety of organic components and the macroporous resins have multilayer surfaces which also exhibit a spectrum of different binding energies, the adsorptions of adsorbates on the resins in the wastewater are multilayer adsorption, which was similarly reported in the literature [35]. The model parameter $n > 1$ means that more adsorbate presence can enhance the free energies of further adsorption, leading to a slower adsorption quantity increase with further increasing the adsorbate concentration. Here, n for XAD-4 is smaller than n for NKA-II, which indicates that the free energy increase is smaller and further adsorption process happens more easily for XAD-4 than for NKA-II.

3.6. Adsorption kinetics for sequentially coupled resins

30 g NKA-II and 250 mL neutralized wastewater were firstly used to measure the NKA-II adsorption kinetic data at 298 K, and then the wastewater, filtered out the NKA-II resin particles, was used to measure XAD-4 adsorption kinetic data at 298 K. Their experimental results are shown in Fig. 3.

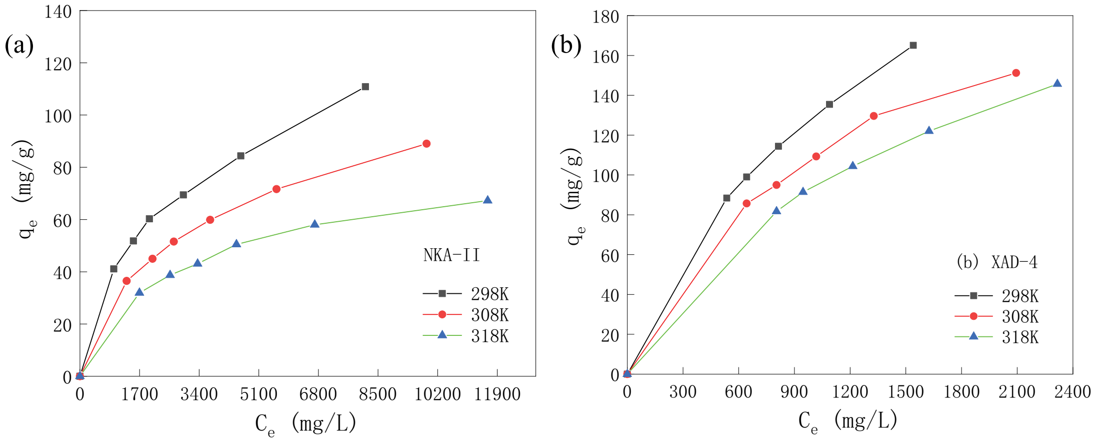

Fig. 2. Relationship between the equilibrium concentration and the adsorption quantity for sequentially coupled resins. (a) NKA-II and (b) XAD-4.

Table 5
Langmuir and Freundlich parameters for sequentially coupled resins

Resin	Temperature T (K)	Langmuir			Freundlich		
		K_L	q_m	R^2	K_F	n	R^2
NKA-II	298	5.0×10^{-4}	123.5	0.9788	1.69	2.20	0.9993
	308	3.9×10^{-4}	104.2	0.9830	1.64	2.23	0.9960
	318	3.8×10^{-4}	80.0	0.9885	1.53	2.26	0.9938
XAD-4	298	8.8×10^{-4}	263.2	0.9973	2.17	1.71	0.9996
	308	8.6×10^{-4}	238.1	0.9892	2.14	1.76	0.9967
	318	6.9×10^{-4}	227.3	0.9840	1.98	1.77	0.9990

Table 6
Fitted parameters of three kinetic models for sequential coupled resin adsorption

Resin	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	q_e	k_1	R^2	q_e	k_2	R^2	b	k_3	R^2
NKA-II	40.46	0.0202	0.946	112.1	1.27×10^{-3}	0.9979	73.48	2.67	0.9178
XAD-4	70.51	0.0435	0.954	166.7	1.57×10^{-4}	0.9965	99.07	7.33	0.9151

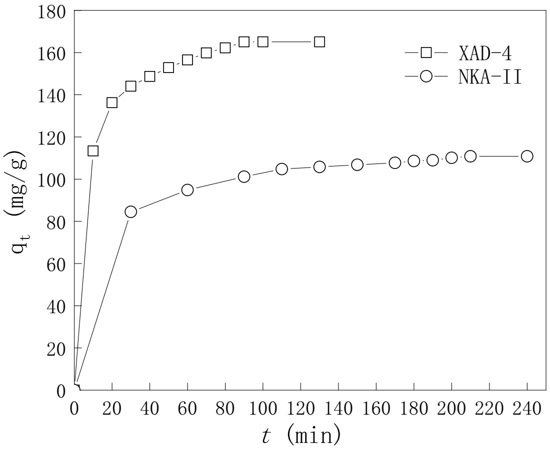

Fig. 3. Effect of contact time on adsorption quantity for sequentially coupled resins, firstly by NKA-II and then by XAD-4.

It can be seen from Fig. 3 that the adsorption quantity on both resins increases with the contact time before the adsorption equilibrium. The adsorption rates are faster in the first 30 min, and then slow down with the contact time. When the adsorption process for NKA-II passes 210 min, the adsorption quantity tends to be almost unchanged. Whereas for XAD-4, the adsorption quantity tends to be stable at the contact time of 90 min.

The adsorption kinetics is crucial to design and optimize operating parameters for application of adsorption processes in full-scale apparatus. Numerous models have been proposed for this purpose. However, the most feasible and applicable models are pseudo-first-order, pseudo-second-order kinetic, and intraparticle diffusion models [36–38]:

Pseudo-first-order kinetic model: $\ln(q_e - q_t) = \ln q_e - k_1 t$ (6)

Pseudo-second-order kinetic model: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ (7)

Intraparticle diffusion model: $q_t = k_3 t^{0.5} + b$ (8)

where, k_1 (min^{-1}), k_2 (g/mg·min), and k_3 (mg/g·min$^{0.5}$) are rate constants for 3 models, respectively, t (min) is contact time, and b (mg/g) is a constant, which is related to the thickness of mass transfer boundary layer.

These 3 models are used to fit the experimental data of NKA-II and XAD-4 in Fig. 3. The model parameters obtained are tabulated in Table 6.

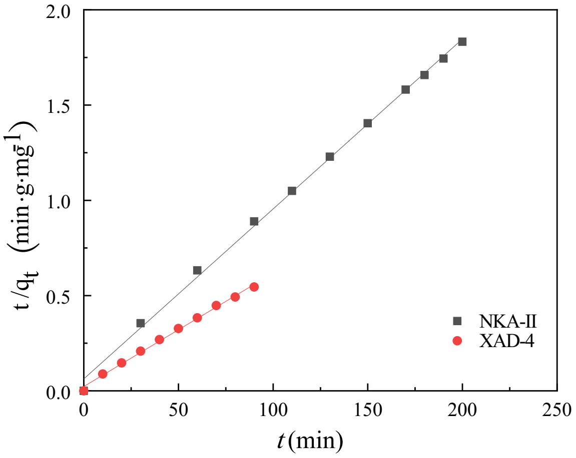

Fig. 4. Correlation of pseudo-second-order kinetic model with the data for sequentially coupled resins.

It can be seen from the correlation coefficients in Table 6 that the adsorption dynamic data of both NKA-II and XAD-4 are better fitted by pseudo-second-order kinetic model as shown in Fig. 4. In addition, their correlation coefficients R^2 for the intraparticle diffusion model show that the intraparticle diffusion is weak in the process of organic matter adsorption by resins NKA-II and XAD-4, and the main factor affecting the adsorption rate is the rate of liquid film diffusion.

4. Conclusions

A real hypersaline organic wastewater containing organic and inorganic salts from bifenthrin alcohol production processes was treated by neutralization with organic salt conversion and adsorption processes. The following main conclusions can be made.

(1) By adding neutralizing agent to the wastewater, the organic salt inside can be converted to organic chemical and inorganic salt, which is beneficial to the effective removing of organic matter in the later adsorption process.
(2) Adsorption treatment of the neutralized wastewater by sequentially coupled resins of NKA-II and XAD-4 can greatly improve the removal of organic matter from the wastewater.
(3) The isothermal curves of sequentially coupled resin adsorption firstly by NKA-II and then by XAD-4 are better fitted by Freundlich's model.

(4) The dynamic processes of sequentially coupled resin adsorption firstly by NKA-II and then by XAD-4 can be well fitted by pseudo-second-order kinetic model.

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