ATLANTIS PRESS

Advances in Engineering Research, volume 184

2nd International Conference on Sustainable Energy, Environment and Information Engineering (SEEIE 2019)

Study on the Adsorption Properties of Modified Attapulgite for Petroleum Hydrocarbon Contaminants in the Petroleum Hydrocarbon Contaminated Wastewater

Ning Sun, Chengzhen Du and Zhiyong Han
College of Petroleum, Lan Zhou University of Technology, Lanzhou, China, 730050

***Abstract*—In view of the current increasingly serious problem of petroleum hydrocarbon pollution in water bodies and the lack of effective pollution control technology, the attapulgite is used as the adsorption medium in this study.**

Firstly, a series of laboratory experiments (roasting, Acidic, and organic modification) are designed to investigate the performance difference to adsorb the petroleum hydrocarbon pollutants on the basis of its purification, then modified b, the optimal modification and adsorption conditions and kinetic characteristics were studied in order to provide a certain new for the effective removal of petroleum hydrocarbon pollutants in water. Materials, new methods and development of new pollution control technologies.

The experimental results of adsorption performance of adsorption media show that the adsorption performance of attapulgite original soil on petroleum hydrocarbon pollutants in water is better than that of common water, such as activated carbon, artificial zeolite, iron powder, corn stover and chitosan.

Then, on the basis of the purification of the attapulgite original soil, the purified attapulgite was subjected to hydrochloric acid acidification modification, octadecyltrimethylammonium chloride organic modification experiment and its petroleum hydrocarbon pollutants before and after modification. A comprehensive study of the changes in adsorption performance and microscopic pore changes.

Finally, the optimal modification method of modified attapulgite was determined and the microscopic mechanism and optimal adsorption conditions and adsorption kinetics of the modified petroleum hydrocarbon pollutants were studied.

Research indicates:

(1) The attapulgite modified by acidification of hydrochloric acid and octadecyltrimethylammonium chloride has a significant improvement on the adsorption performance of petroleum hydrocarbon pollutants.

(2) Batch and orthogonal experiments show that the optimal adsorption conditions of modified attapulgite for petroleum hydrocarbon pollutants are: treatment time 80min, attapulgite dosage 0.3g/100mL, pH 7. Reaction temperature 40 ° C

(3) Acidification of hydrochloric acid and organic modification of octadecyltrimethylammonium chloride The attapulgite adsorption behavior of petroleum hydrocarbons in wastewater is subject to quasi-secondary kinetics.

Keywords—attapulgite; petroleum hydrocarbon contaminated groundwater; adsorption; modification

I. INTRODUCTION

Petroleum is a complex mixture of hydrocarbons and small amounts of other organic matter. A potential chemical containing a variety of "three-way" (carcinogenic, teratogenic and mutagenic). According to the data, about 3 billion tons of oil are mined every year in the world, and about 100 million tons of them are re-entered into the environment through various channels, which have serious potential harm to the environment. Once the petroleum hydrocarbons enter the human body, they can dissolve the cell membrane and interfere with the enzyme system, causing severe lesions of the liver and kidneys [1]. Domestic and foreign investigation reports show that once the groundwater source is polluted by petroleum hydrocarbons, even if control measures are taken on the pollution sources, it is generally difficult to restore the water quality in the natural state in the next few decades [2]. Therefore, how The economic, rapid and effective removal of petroleum hydrocarbon pollutants from groundwater has become a hot spot for environmental scholars and hydrogeologists in various countries.

In view of the treatment of petroleum hydrocarbon-contaminated groundwater, this study proposes the idea of using attapulgite to adsorb and remove it, and the effect of adsorbing petroleum hydrocarbon pollutants on attapulgite and improving adsorption performance and optimal adsorption conditions and adsorption kinetics. In-depth research was carried out to explore a good groundwater petroleum hydrocarbon pollution remediation technology.

The research firstly treated the groundwater contaminated with petroleum hydrocarbons by acidification of hydrochloric acid and octadecyltrimethylammonium chloride organically modified attapulgite to determine the optimal reaction conditions, and then carried out orthogonal batch experiments on this basis. Determine the optimal adsorption process parameters, determine the optimal dosage of attapulgite, optimal treatment time, optimum temperature conditions and optimum pH value, adsorption kinetics experiment and two modification methods to improve the adsorption performance of attapulgite The microscopic mechanism was deeply analyzed.

II. MATERIALS AND METHODS

A. Materials

Test drugs: sulfuric acid, sodium chloride hydrochloride, anhydrous sodium sulfate, petroleum ether, silver nitrate, sodium hydroxide, octadecyltrimethylammonium chloride, sodium pyrophosphate, all of which are analytically pure, attapulgite original soil (Gansu Linze), 0# diesel.

0# Diesel and deionized water are thoroughly mixed. The water sample after phacoemulsification replaces petroleum hydrocarbons to pollute groundwater.

B. Method

1) Detection method

(1) Standard curve method

Different petroleum hydrocarbons have characteristic absorption zones in the ultraviolet region. The aromatic compound with a benzene ring mainly absorbs at a wavelength of 250 to 260 nm, and the two absorption peak wavelengths of a general crude oil are 225 and 256 nm, respectively. The compound with a conjugated double bond mainly absorbs at a wavelength of 215 to 230 nm, and the absorption wavelength of other petroleum hydrocarbons is similar to that of crude oil.

The content of total petroleum hydrocarbons was determined by ultraviolet spectrophotometry, and the measurement results are shown in Fig.1.

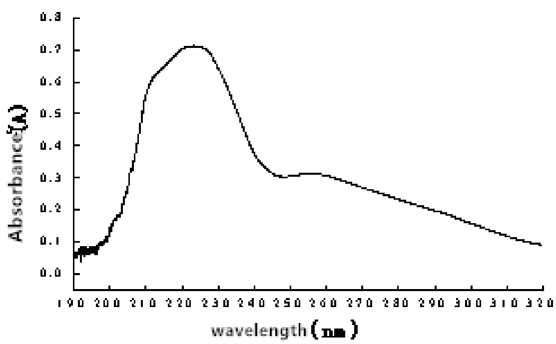


FIGURE I. THE ULTRAVIOLET ABSORPTION SPECTRUM OF THE OIL

It can be seen from Fig. 1 that the measured petroleum hydrocarbons have obvious absorption peaks at wavelengths of 225 nm and 256 nm. Based on the principle of "maximum absorption and minimal interference", 225 nm was selected as the measurement wavelength of petroleum hydrocarbons.

(2) Marking line drawing

0# diesel was selected as the standard petroleum hydrocarbon, and the standard solution was accurately prepared, and the absorbance was measured at a wavelength of 225 nm. The measurement results are shown in Fig. 2.

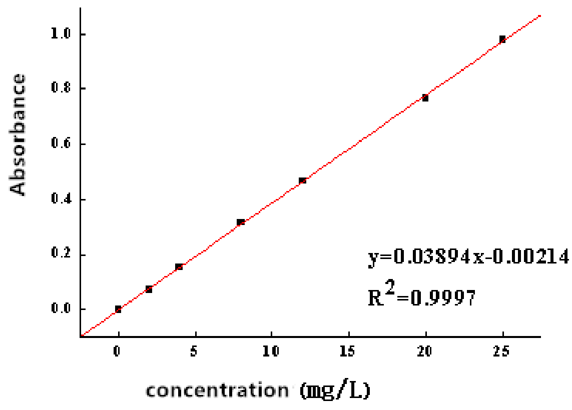


FIGURE II. THE STANDARD CURVE OF PETROLEUM HYDROCARBONS

As can be seen from Fig. 2, the regression equation of the standard curve is y=0.03894x-0.00214, R2=0.9997, X represents the concentration of petroleum hydrocarbons, and Y represents the absorbance.

(4) Calculation of petroleum hydrocarbon concentration:

$$C(mg/L) = \frac{m}{V} \times 1000 \quad (1)$$

In the formula:

M—the content of petroleum hydrocarbons found by the standard curve, mg;

V—water sample volume, mL;

(5) Calculation formula for the removal rate of petroleum hydrocarbons:

$$\text{Removal rate}(\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (2)$$

In the formula:

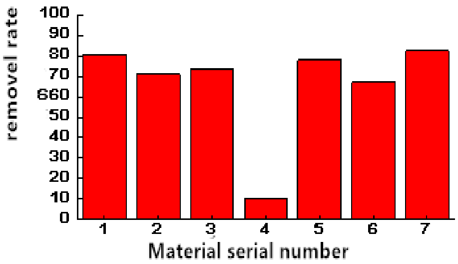
C_0 - simulating the concentration of petroleum hydrocarbons in wastewater, mg/L;

C - concentration of petroleum hydrocarbons in treated wastewater, mg/L

III. EXPERIMENT

A. Comparison of Media Adsorption Performance

Seven kinds of materials including 0.5mm activated carbon, 0.25mm activated carbon, artificial zeolite, iron powder (50 mesh), corn stover, chitosan and attapulgite (original soil) were selected for the screening of PRB reaction medium and its properties. Take 2 grams of each of the above 7 reaction media, add them to a volumetric flask with a volume of 250 mL, and add 100 mL of groundwater contaminated with petroleum hydrocarbons with an initial concentration of 40 mg/L, and set a blank control. , oscillate at 15 ° C, 120 r / min in a gas bath constant temperature incubator for 1 h. The total petroleum hydrocarbons were tested and analyzed after extraction with petroleum ether. The results are shown in Figure 3.



(1. Activated carbon (0.5mm); 2. Activated carbon (0.25mm); 3. Artificial zeolite; 4. Iron powder; 5. Straw; 6. Chitosan; 7. Attapulgite original soil)

FIGURE III. REMOVAL RATE OF PETROLEUM POLLUTANTS BY DIFFERENT REACTION MEDIA

B. Attapulgite Original Soil Performance Optimization Experiment

In view of the fact that the original soil is still not ideal for the adsorption performance of petroleum hydrocarbons, this study decided to carry out performance optimization experiments, including original soil purification, acid modification, roasting modification, octadecyltrimethylammonium chloride. The organic modification modification experiment, in which the original soil purification pretreatment is the premise of each modification experiment.

The purification of the attapulgite original soil is to pulverize and dry the attapulgite original soil. Sodium pyrophosphate was dissolved in water under stirring, and stirring was continued after the temperature was raised. Then, under the condition of high-speed stirring, the original soil which has been pulverized and dried is added, stirred for 1 hour, and after standing, the upper suspension is extracted, and an appropriate amount of concentrated hydrochloric acid is added until no bubbles escape. The mixture was centrifuged, washed with water until the supernatant was neutral, and the obtained product was dried at 105 ° C to obtain purified attapulgite, finely ground, passed through a 200 mesh screen, and used.

1) Acid modification: The purified attapulgite is added to the hydrochloric acid solution, shaken at 30 ° C for several minutes at a constant temperature, and then centrifuged several times. The pH is nearly neutral after washing to the night, dried, ground, passed through a 200 mesh sieve, and sealed and stored. That is, acid-modified attapulgite is obtained.

2) Roasting modification: The purified attapulgite is calcined at different temperatures for different time, cooled to room temperature, and ground, and passed through 200 sieves to obtain a calcined modified purified attapulgite. The attapulgite samples treated at different calcination temperatures for different time were added to the groundwater contaminated by petroleum hydrocarbons, and a blank control was set up, and the culture was incubated at a constant temperature. Total petroleum hydrocarbon analysis after extraction with petroleum ether.

The results are shown in Figure 4.

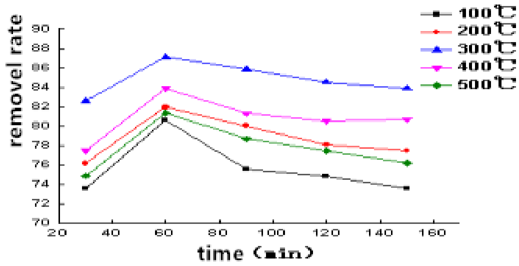


FIGURE IV. THE REMOVAL EFFICIENCY OF DIFFERENT MODIFIED TEMPERATURES ON PETROLEUM

It can be seen from Fig. 4 that the attapulgite modified by calcination at 300 °C has the best effect on the removal of petroleum hydrocarbons in groundwater. This is because the attapulgite contains a large amount of water molecules. When the calcination temperature is lower than 300 ° C, the outer surface adsorption water, the channel adsorption water and the partially crystal water in the attapulgite are first removed as the temperature increases, so that The internal structure becomes loose and porous, and the adsorption capacity is increased, so that the removal rate increases with an increase in temperature; and when the calcination temperature exceeds 300 ° C, the crystal water or even the structure in the attapulgite increases with the increase of the calcination temperature. The water is largely removed from the crystal, causing the attapulgite structure to collapse and the specific surface area to decrease rapidly, so the removal rate decreases significantly with increasing temperature.

a) *Comparison of modification effects of reaction media:* The attapulgite after purification, acid treatment and calcination are respectively added to the groundwater contaminated with petroleum hydrocarbons, and cultured at a constant temperature. After the petroleum ether was extracted, the total petroleum hydrocarbons were tested and analyzed. The results are shown in Fig. 5.

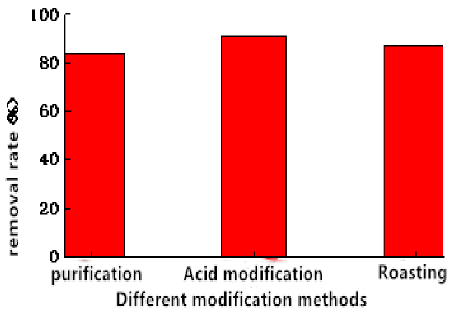


FIGURE V. THE EFFECTS OF DIFFERENT MODIFIED ON PETROLEUM REMOVAL EFFICIENCY OF ATTAPULGITE

It can be seen from Fig. 5 that the removal effects of the different modification methods on the simulated petroleum pollutants are as follows: the purified attapulgite < roasting treatment < acid modification, that is, the acid-modified attapulgite has the best removal effect. This is because the modification of hydrochloric acid can change the structural charge and surface charge of the attapulgite in the aqueous solution, which has a significant effect on the cation exchange capacity and specific surface area which are important in the physicochemical properties of the attapulgite.

In view of the above several modification methods, the performance improvement of attapulgite is still not ideal. In this study, the organic modification of octadecyltrimethylammonium chloride was selected to explore an ideal and practical. The modification of the application value.

3) Organic modification: The organic modification of attapulgite generally uses an organic surfactant or a silane coupling agent as a modifier, and the inorganic cation between the attapulgite is replaced by a long carbon chain organic cation to increase the interlayer spacing. The organic modifier used in this experiment is octadecyltrimethylammonium chloride (OTMAC) (the molecular structure is shown in Figure 6).

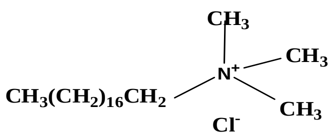


FIGURE VI. OCTADECYL TRIMETHYL AMMONIUM CHLORIDE (OTMAC)

The OTMAC organically modified attapulgite was added to the groundwater contaminated by petroleum hydrocarbons, sonicated for a certain period of time, and used as a blank control. After a certain period of shaking, the petroleum oil was extracted and tested for total petroleum hydrocarbons.

The adsorption properties of attapulgite after acid modification and organic modification are obviously better than those of roasting and purification modified attapulgite. Therefore, the acidification and organic modification of attapulgite are studied in the subsequent research.

C. Experimental Study of Influencing Factors

Aiming at the influencing factors of many adsorption processes, this paper selects the adsorption time, the modified attapulgite dosage, the optimal pH value and the optimal adsorption temperature, and conducts batch experiment research and orthogonal experiments on these factors. The best conditions for the adsorption of petroleum hydrocarbon pollutants by attapulgite.

1) Optimal adsorption time: OTMAC organically modified attapulgite and attapulgite modified by hydrochloric acid were added to the petroleum-contaminated groundwater, and used as a blank control. After constant temperature oscillation for different time, the petroleum oil was extracted and tested for total petroleum hydrocarbons. The result is shown in Figure 5.

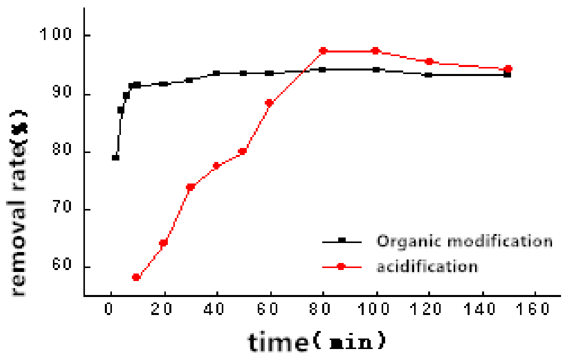


FIGURE VII. THE EFFECT OF THE REACTION TIME ON PETROLEUM HYDROCARBON ADSORPTION

It can be seen from Fig. 7 that when the reaction time is 80 min, the acid-modified attapulgite can reach the highest removal rate of petroleum hydrocarbon pollutants: 97.37%. When the reaction time exceeds 80 min, the removal rate curve tends to be stable, so the optimum reaction time is determined to be 80 min. When organically modified attapulgite is used, the removal rate of petroleum hydrocarbons increases gradually with the increase of treatment time in 0-8 min, and the removal rate reaches 91.28% at 80 min. The adsorption effect was not significantly enhanced, and it was considered that the adsorption equilibrium was reached, and the removal rate slightly decreased after 100 min. It can be seen from the experimental results that the reaction system reaches the adsorption equilibrium at the 80th minute.

The experimental results show that the removal rate of petroleum hydrocarbon wastewater treated by OTMAC organic modification is not only higher than that of acidified attapulgite in the initial stage, but also the time for the reaction to reach equilibrium is significantly shortened. The removal rate is higher. It can be seen from the overall effect that the effect of treating the groundwater contaminated with petroleum hydrocarbons by the organically modified attapulgite is better than that of the attapulgite modified with hydrochloric acid.

This is because the modification of hydrochloric acid can change the structure charge and surface charge of the attapulgite in the aqueous solution, thereby changing the chargeability and adsorption activity of the attapulgite colloid, and thus affecting the physicochemical properties of the attapulgite. In particular, it has a significant effect on the cation exchange capacity and specific surface area.

The advantage of OTMAC organically modified attapulgite is the long carbon chain. In the initial stage of adsorption, petroleum hydrocarbons can be quickly adsorbed on the surface layer of the organic layer, but on the one hand, the adsorption gradually becomes saturated due to the increase of adsorption with time, and the adsorption capacity is limited; on the other hand, due to the weak adsorption, with time On the other hand, the petroleum hydrocarbons adsorbed on the attapulgite are desorbed, resulting in a slight decrease in the removal rate after reaching the maximum, and then the petroleum hydrocarbons gradually diffuse from the surface layer of the organic layer to the inside and gradually stabilize.

However, the treatment of attapulgite modified by hydrochloric acid is inferior, and the time required for adsorption equilibrium is long. Due to slow adsorption, the desorption phenomenon is not significant, so it can be stabilized after reaching equilibrium.

2) Best dosage: Acidification of different quality hydrochloric acid and attapulgite organically modified by OTMAC are respectively added to groundwater contaminated by petroleum hydrocarbons and oscillated at a constant temperature. After the petroleum ether was extracted, the total petroleum hydrocarbons were tested and analyzed. The results are shown in Fig. 6 and Fig. 7, respectively.

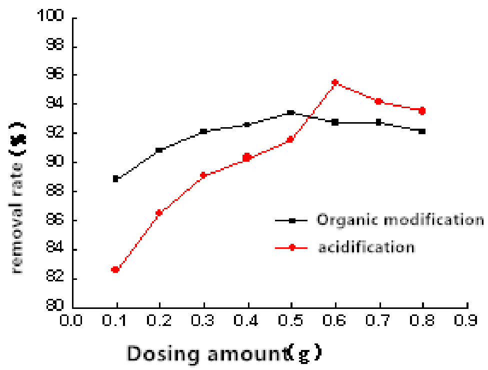


FIGURE VIII. THE EFFECT OF ATTAPULGITE DOSAGE ON PETROLEUM HYDROCARBON ADSORPTION

It is known from Fig. 8 that as the amount of attapulgite increases, the removal rate of petroleum hydrocarbons in the reaction medium is continuously increased. When the attapulgite is added to 0.6 g, the maximum removal rate of groundwater containing petroleum hydrocarbons can be reached 95.44. %, then decreased slightly. With the increase of reaction time, the adsorption amount and the removal rate showed opposite trends. Considering the comprehensive consideration, the dosage of the best attapulgite was determined to be 0.3g.

For the attapulgite modified by OTMAC, although the removal rate of petroleum hydrocarbons in water is gradually increased with the increase of the amount of attapulgite, the unit adsorption amount is reduced. When the amount of adsorbent reached 0.3 g, even if the quality of the attapulgite was continuously increased, the removal rate did not increase significantly, and the unit adsorption amount decreased sharply. Compared with the attapulgite modified by hydrochloric acid, the organically modified attapulgite treatment of groundwater contaminated by petroleum hydrocarbons fluctuates less with the change of the amount of attapulgite, and the maximum value appears at 0.5g. The removal rate was 93.51%. Except that the curve has a significant upward trend when the dosage is 0.1g~0.2g, the curve is slightly decreased, but the whole is relatively flat. As the reaction time increases, the adsorption amount and the removal rate show opposite trends. There is also a problem with the amount and a turning point occurs at 0.3 g. On the one hand, this may be due to the adsorption equilibrium between petroleum hydrocarbons and attapulgite when the amount of attapulgite reaches a certain value; on the other hand, excessive addition of OTMAC quaternary ammonium salt cationic surfactant may cause foaming. At the same time, it will increase the workload of subsequent washing. Considering factors such as removal rate, unit adsorption amount, cost and modification effect, it is determined that 0.3g of OTMAC organically modified attapulgite is added per 100ml of wastewater.

3) Optimal pH: The hydrochloric acid-modified attapulgite and the OTMAC-modified attapulgite were added to the petroleum-contaminated groundwater to adjust different pH values and oscillate at a constant temperature. The petroleum oil was extracted and tested for total petroleum hydrocarbons. The result is shown in Figure 7.

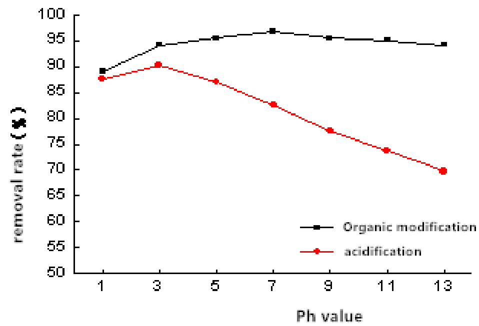


FIGURE IX. THE EFFECT OF THE PH VALUES OF SOLUTION ON PETROLEUM HYDROCARBON ADSORPTION

It can be seen from Fig. 9 that when the pH is increased from 1 to 3, the removal rate of petroleum hydrocarbons increases with the increase of pH; when the pH exceeds 3, the removal rate begins to decrease; when the pH is 3, the adsorption effect is optimal. At a pH of 3, the maximum removal rate of groundwater containing petroleum hydrocarbons contaminated by the acidified attapulgite process can be achieved, ie 90.03%.

It can be seen from Fig. 9 that when the organically modified attapulgite treatment is contaminated with petroleum hydrocarbons, the pH of the reaction system can be adapted to a wide range, and in the above selected pH range, the petroleum hydrocarbon pollutants are The removal rate is greater than 89%. However, when the pH value is 7, the organically modified attapulgite treatment reaches the maximum removal rate by the petroleum-contaminated groundwater. When the pH is neutral, the organically modified attapulgite has the best oil removal effect.

By comparison, the organically modified attapulgite not only has a higher removal rate than the hydrochloric acid-modified attapulgite, but also has a wider pH range. The reason is that, on the one hand, the attapulgite has a structural charge and a surface charge, which are produced by the hydrolysis of the Si-O bond and the Al-O bond at the surface. The hydroxyl group (OH-) on the R-OH produced by the hydrolysis of the bond is amphoteric, both as an acid and as a base, and they can further interact with H+ or OH- in the following form:

$$R\text{-}OH + H^+ \rightarrow R\text{-}OH_2^+$$

$$R\text{-}OH + OH^- \rightarrow R\text{-}O^- + H_2O$$

At relatively low pH conditions, it will have anion exchange capacity; at relatively high pH conditions, it will have cation exchange capacity. On the other hand, under acidic conditions, H+ can neutralize the negative charge layer on the surface of the oil particles, destroying its stability and enhancing the degreasing effect. The net charge of the attapulgite particles is the algebraic sum of the positive and negative charges on the surface. The pH value when the net charge is zero is called the charge zero point or the isoelectric point () (the isoelectric point of the concave soil is around pH 3). When pH<, the clay particles are positively charged, the attapulgite will adsorb anions by ion exchange; when pH>, the clay particles are negatively charged, at which point the cations are mainly adsorbed.

4) Determine the optimal temperature: The hydrochloric acid-modified attapulgite and the OTMAC-modified attapulgite were added to the petroleum-contaminated groundwater, and were placed at different temperatures for constant temperature oscillation adsorption. The petroleum oil was tested and analyzed by extraction with petroleum ether, and the results are shown in Fig.9.

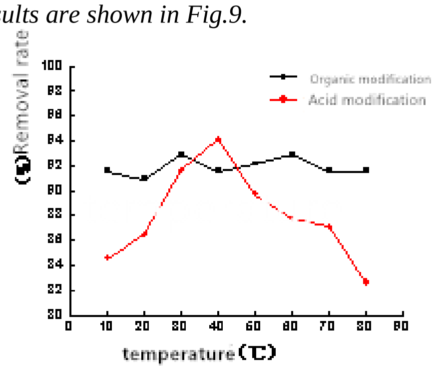


FIGURE X. THE EFFECT OF THE REACTION TEMPERATURE ON PETROLEUM HYDROCARBON ADSORPTION

It can be seen from the figure that at the beginning of adsorption, as the reaction temperature increases, the removal rate of the attapulgite modified by hydrochloric acid is continuously increased, and when the reaction temperature reaches 40 ° C, the maximum removal rate can be achieved. It is 94.15%; when the reaction temperature exceeds 40 ° C, the removal efficiency gradually decreases. Therefore, the optimum temperature is 40 °C. In the range of 10～80 °C, the removal rate of total petroleum hydrocarbons of organic modified attapulgite is higher (more than 90%), but the maximum removal rate can be achieved when the temperature is 30 °C. In the range of 10 to 30 °C, the removal rate increases with the increase of temperature, but after 30 °C, the adsorption effect begins to decrease slightly. It can be considered that the organically modified attapulgite has a wide temperature range as a water treatment agent, and in actual operation, groundwater contaminated with petroleum hydrocarbons can be treated at room temperature.

Low temperature is beneficial to physical adsorption. As shown in the figure, when acid-modified attapulgite is used to treat groundwater contaminated by petroleum hydrocarbons, the removal rate increases from 10 °C to 40 °C, and the removal rate increases to 40 °C. When the reaction temperature is lower than 40 °C, the activation energy required for the chemical adsorption of the acid-modified attapulgite is not achieved. At this time, the physical adsorption is dominant; when the temperature reaches 40 °C, the temperature of the reaction system is continuously increased. The removal rate of petroleum hydrocarbons decreases, which means that when the temperature is sufficient to provide the activation energy required for chemisorption, if the reaction temperature is further increased, the chemical adsorption will not be greatly contributed, and the physical adsorption will be inhibited.

D. *Influencing Factors Orthogonal Experiment*

Some single factors affecting groundwater pollution caused by petroleum hydrocarbons have been discussed above. Considering the actual impact of each factor, four factors including pH value, treatment time, dosage, and temperature are selected for this study. The orthogonal test was performed on the orthogonal table L9 (34). The removal rate of total petroleum hydrocarbons was used as the evaluation index. The orthogonal test factors and level tables are shown in Table 1. The experimental results are shown in Table 2.

TABLE I. FACTORS AND LEVELS OF L9(34) ORTHOGONAL TABLE

Level	factors			
	A pH value	B handling time/ min	C Dosage(g)	D temperature/℃
1	3	60	0.1	20
2	5	80	0.2	40
3	7	100	0.3	60

TABLE II. THE RESULTS OF L9(34) ORTHOGONAL TEST FOR REMEDIATION OF PETROLEUM CONTAMINATED GROUNDWATER

Experimental number	A	B	C	D	Removal rate(%)
1	3	6	0.1	20	69.02
2	3	8	0.2	40	96.08
3	3	10	0.3	60	94.15
4	5	6	0.2	60	83.87
5	5	8	0.3	20	92.87
6	5	10	0.1	40	85.80
7	7	6	0.3	40	89.65
8	7	8	0.1	60	90.94
9	7	10	0.2	20	87.08
10	259.25	242.54	245.76	248.97	
11	262.54	279.89	267.03	271.53	
12	267.67	267.03	276.67	268.96	
13	8.42	37.35	30.91	22.56	

It can be seen from the table that the order of magnitude of the main influencing factors is processing time, dosage, temperature, and pH. When the treatment time is increased from 60min to 100min, the removal rate of petroleum hydrocarbon pollutants first increases and then decreases. When the treatment time is 80min, the removal effect of petroleum hydrocarbons is the best; from the dosage, with organic modification The dosage of attapulgite increases, and the removal rate of petroleum hydrocarbon contaminants increases. When the dosage of attapulgite is 0.3g, the removal effect is best; as the temperature of the reaction system increases from 20 °C to 60 °C, the removal effect first increases and then decreases, the removal effect is best at 40 °C; the pH value of the reaction system increases from 3 to 7, the removal effect of petroleum hydrocarbons increases sequentially, but the increase trend is slow, pH value changes The effect on the removal effect is minimal. Through the above analysis, the best experimental process conditions are A3B2C3D2, namely: treatment time 8 min, dosage 0.3 g/100 ml, temperature 40 ° C, pH 7.

E. Adsorption Kinetics

(1) Kinetic model----Pseudo second-order equation

The differential form of the quasi-secondary adsorption rate equation is:

$$\frac{dq_t}{dt} = \kappa_2 (q_e - q_t)^2 \tag{3.4}$$

The boundary condition of the differential equation is:t=0, qt=0

t=t, qt=qt

Points, rearrangement:

$$\frac{t}{q_t} = \frac{1}{\kappa_2 q_e^{\ 2}} + \frac{t}{q_2} \tag{3.5}$$

Then the initial adsorption rate:

$$h = \left(\frac{dq_t}{dt}\right)_t = 0 = \kappa_2 q_2^{\ 2} \tag{3.6}$$

In the formula:

Qe-balance adsorption amount, mg.g-1;

Qt-the amount of adsorption at any time t, mg.g-1;

K2-quasi-secondary equation adsorption rate constant, g.mg-1.min-1;

H-initial adsorption rate, mg.mg-1.min-1;

(3) Analysis of quasi-secondary dynamics model

The straight line equation for the quasi-second-order kinetic equation for the adsorption of petroleum hydrocarbons by acidified attapulgite at equation 3.7 is expressed as:

t/qt=0.7784 +0.0724t (3.7)

Correlation coefficient R2=0.9944, as shown in Figure 3.20 and Table 3.6

The straight line equation for the quasi-second-order kinetic equation for the adsorption of petroleum hydrocarbons by organic modified attapulgite at equation 3.8 is expressed as:

t/qt=-0.0337 +0.0815 t (3.8)

Correlation coefficient R2=0.9996, as shown in Figure 3.17 and Table 3

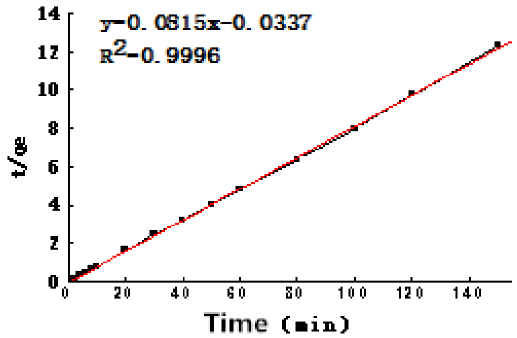


FIGURE XI. PSEUDO-SECOND-ORDER SORPTION KINETIC(AGITATE SPEED: 120R.MIN-1, INITIAL CONCENTRATION: 40MG/L, DOSE: 3 G.L-1) (ORGANICALLY MODIFIED)

TABLE III. FITTING RESULTS OF THE QUASI - SECOND-ORDER KINETIC EQUATION

Modification mode	regression equation	R22	qe,cal/ (mg/g)	k2 (g/mg.min)	qe,exp/ (mg/g)
acid modification	y=0.0724 x+0.7785	0.9 944	13.81	0.0067	12.982
Organic modification	y=0.0815 x-0.0337	0.9 996	12.27	0.1971	12.554

Treatment of petroleum hydrocarbon-contaminated groundwater by acid-modified and octadecyltrimethylammonium chloride (OTMAC) organically modified attapulgite to study the mechanism of adsorption of petroleum hydrocarbons, using quasi-secondary adsorption The kinetic model experimental data is fitted, and the correlation coefficient R of the equation obtained by linearizing each model is used to test the fitting result, as shown in Table 3.3 above:

The qe2 and cal calculated by the quasi-second-order kinetic equation are close to the experimentally obtained qe,exp. The qe2 and cal under two different modification conditions are calculated by the model, which are 13.81 and 12.27, respectively. 12.982 and 12.554 are relatively close, and the correlation coefficient R22 is 0.9944 and 0.9996 respectively. This shows that the quasi-second-order kinetic equation can well describe the adsorption process of petroleum hydrocarbons in groundwater, that is, the adsorption process uses chemisorption as the rate control step. The quasi-secondary kinetics reflect that the adsorption rate is proportional to the square of the concentration of petroleum hydrocarbons.

F. Summary

(1) The attapulgite modified by acidification of hydrochloric acid and octadecyltrimethylammonium chloride has a significant improvement on the adsorption performance of petroleum hydrocarbon pollutants, which is acidified by hydrochloric acid. The mechanism for improving the

adsorption performance is that it can remove impurities distributed in the pores of the attapulgite and make the pores clear; second, because the cations of the attapulgite have exchangeability, the smaller radius of the H+ can replace the attapulgite lattice The cations such as K+, Na+, Ca2+ and Mg2+ in the interlayer further increase the pore volume, while the performance of the attapulgite modified by the organic modification of octadecyltrimethylammonium chloride is due to the surface properties directly by the pro The water-based transition is oleophilic, so its adsorption performance for organic pollutants has been greatly improved.

The optimum adsorption conditions of modified attapulgite for petroleum hydrocarbon pollutants are as follows: treatment time 80min, attapulgite dosage 0.3g ⁄100mL, pH value 7. Reaction temperature 40 ° C

(2) Acidification of hydrochloric acid and octadecyltrimethylammonium chloride organically modified attapulgite adsorption behavior of petroleum hydrocarbons in wastewater all followed the quasi-secondary dynamics

REFERENCES

[1] Chen MQ,Zhou ZS,Wang YS, et al. Effects of attapulgite-supported transition metals catalysts on glycerol steam reforming for hydrogen production[J].International Journal of Hydrogen Energy,2018,43(45):20451-20464

[2] Chen Zhongshan,He Jietao,Chen Lei,et al. Sorption and desorption properties of Eu(III) on attapulgite[J].Journal of Radioanalytical and Nuclear Chemistry,2016,307(2):1093-1104

[3] Zhang Gaoke,Wang He,Guo Sheng,et al.Synthesis of Cu/TiO2/organo-attapulgite fiber nanocomposite and its photocatalytic activity for degradation of acetone in air[J].Applied Surface Science,2016,362:257-264

[4] Nor Aina Mohd,Othman Nadras,Ismail Hanafi.Mechanical & Morphological Properties of Attapulgite/NR Composites: Effect of Mixing Time Variation.Proceedings of the 23rd Scientific Conference of Microscopy Society Malaysia,2015,1669

[5] [5]Lu Lei,Li Xingyang,Liu Xiaoqin,et al.Enhancing the hydrostability and catalytic performance of metal-organic frameworks by hybridizing with attapulgite, a natural clay.Journal of Materials Chemistry.2015,3(13):6998-7005

[6] Lu Zhanhui,Hao Zhiqi,Wang Jian,et al.Efficient removal of europium from aqueous solutions using attapulgite-iron oxide magnetic composites.Journal of Industrial and Engineering Chemistry.2015,34:374-381

[7] Chen Zhanxiang, Chen Chuansheng Chen Weiping,et al.Effect and Mechanism of Attapulgite and Its Modified Materials on Bioavailability of Cadmium in Soil. Huanjing kexue,2018,39(10):4744-4751

[8] Li Jie,Lei Yu,Xu Dingding,et al. Improved mechanical and thermal insulation properties of monolithic attapulgite nanofiber/silica aerogel composites dried at ambient pressure. Journal of Sol-gel Science and Technology.2017,82(3):702-711