



Removal of petroleum sulfonate from aqueous solutions using freshly generated magnesium hydroxide

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ABSTRACT

Freshly generated magnesium hydroxide (FGMH), produced by adding water-soluble magnesium salts to highly alkaline solutions, was used to remove anionic surfactant petroleum sulfonate (PS) from aqueous solutions. Adsorption experiments were carried out to investigate the effects of pH, adsorbent dosage, contact time, PS concentration, and temperature. The results showed that FGMH displayed excellent treatment efficiency for PS in the pH range 12.0–13.0. The maximum PS removal efficiency was reached within 60 s. The best dosage of magnesium chloride was 2.0 g/L. The adsorption capacity of FGMH for PS decreased as the temperature increased from 303 K to 333 K. The adsorption process was exothermic. The removal mechanism of PS by FGMH may be a coagulation–adsorption process involving a combination of flocculation, adsorption, charge neutralization, and netting catch affection. The results of this study showed that FGMH can be effectively used to treat surfactant wastewaters.

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1. Introduction

Surfactant wastewaters are produced in the manufacture and use of surfactants. Anionic petroleum sulfonate (PS) surfactants, which are mixtures of sulfonated alkyl- and aryl-petroleum products and free mineral oils, are widely used in oil exploitation [1]. PS surfactants are used to improve the flooding efficiency of crude oil; however, the water containing PS that is produced in the flooding process may pollute surface water and groundwater if it is not treated effectively. Surfactants in water can foam and reduce the re-oxygenation rate and oxygen levels, resulting in deterioration of water quality. In addition, some toxic pollutants in water can be emulsified, and then the concentrations and the toxicities of these pollutants increase and cause secondary contamination [2]. Residual surfactants in wastewaters should therefore be treated effectively before the water is released into the environment.

Biological treatment can be a cost-effective and environmentally friendly treatment method. However, low biodegradability has a direct influence on the treatment of PS surfactant wastewaters because the active components of PS surfactants are alkyl- and aryl-sulfonates [3–5]. Several types of adsorbents such as activated carbon, silica, and layered double hydroxides display high adsorption capacities for various anionic surfactants [6–8],

but the adsorption process takes a long time. Kowalska et al. [9] reported a large decrease in the retention of sodium dodecyl sulfate after separation using Intersep Nadir ultrafiltration membranes, but the membranes were easily polluted fouled in membrane surface in the separation process, and the cost of using this method to treat industrial wastewaters would be high. Fenton oxidation, ozonation, photocatalytic treatment and electrochemical oxidation, which have also been investigated for treating anionic surfactants, are all relatively costly methods [10–13]. In contrast, precipitation–adsorption methods are considered to be effective and low-cost methods for wastewater treatment; these methods have reduced chemical costs, and sludge disposal is possible [14]. In recent years, a series of laboratory- and pilot-scale experiments have been conducted to investigate the effects of both calcium and magnesium precipitation on the chemical clarification of wastewaters. Dollof et al. [15] used a high-pH lime–magnesium process to treat municipal wastewaters, and total organic carbon (TOC), chemical oxygen demand (COD), and biological oxygen demand (BOD) were each reduced by up to 80%. The high-pH lime–magnesium process also efficiently removed most pollutants from secondary effluents by coagulation–flocculation and sedimentation [16]. Recently, Gao et al. [17] reported that an $\text{MgCl}_2/\text{Ca}(\text{OH})_2$ system could be used to treat dye-containing wastewaters, and a dye removal efficiency of up to 95% was achieved. In our previous studies, leaching solutions of white mud (mainly containing MgCl_2 and CaCl_2) were used to treat anionic dyes, and the dye removal efficiencies were significant

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[18]. These experiments proved that adding water-soluble magnesium salts to alkaline solutions (the Mg-OH method) can be used to remove organic substances in wastewaters; hence this Mg-OH method could be used to treat PS-containing wastewaters. This is an in situ adsorption method and this process proceeds rapidly, is predictable, and can be conveniently controlled by simple techniques. When magnesium is added to alkaline solutions, magnesium hydroxide is precipitated, and freshly generated magnesium hydroxide (FGMH) has a high surface free energy with a large adsorptive surface area and a positive surface charge, which can be used to attract negatively charged colloidal particles [19]. Precipitation-adsorption methods have attracted considerable attention in different areas but there has been little research on removal of surfactants in aqueous solutions by this method.

The purpose of this paper is to evaluate the efficiency of FGMH produced by the Mg-OH method for the removal of PS from aqueous solutions. The optimum operating conditions for the removal of the active PS components were determined. The interaction mechanism between FGMH and PS was investigated.

2. Materials and methods

2.1. Materials

The PS surfactant used in the present work was obtained from the ShengLi oilfield in China. The components of the PS surfactant were analyzed using a solvent-extraction method with solvents of pentane, absolute alcohol, isopropyl alcohol, petroleum ether (boiling range 308–338 K) and component solvent isopropanol/water (50%/50%, vol/vol) [20]. The components were 53.97% PS, 39.69% free mineral oil, and 4.13% inorganic salts, with a recovery rate of 96.8%. The PS, the active components of the PS surfactant, was refined by solvent extraction in preparation for further experiments. Some derivatives were obtained from the PS by reductive derivation with trifluoroacetic anhydride ((CF₃CO)₂O) as Lewis acid, KI as strong nucleophile and N,N-dimethylformamide as non-protonated solvent. The derivatives were analyzed by means of GC-MS [21]. The results were showed in Fig. 1. According to the GC-MS analysis, it can be deduced that there are five kinds of isomeric hendecyl benzene sulfonate, four kinds of isomeric dodecyl benzene sulfonate and four kinds of isomeric tridecyl

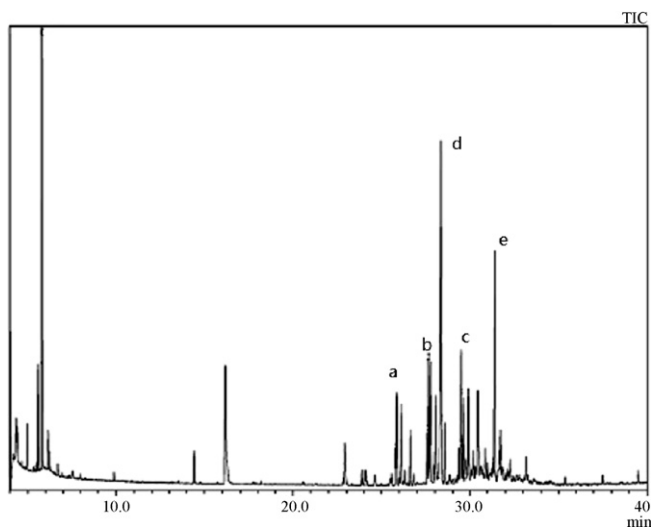


Fig. 1. Total ion chromatogram of PS derivatives from GC-MS analysis (a: thioundecyl phenyl trifluoroacetate; b: thiododecyl phenyl trifluoroacetate; c: thiotridecyl phenyl trifluoroacetate; d: cyclic octaatomic sulfur; e: thiotridecyl phenyl trifluoroacetate).

benzene sulfonate in the PS. The water-soluble magnesium salt used was MgCl₂, and NaOH/HCl was used to adjust the pH of the PS solutions.

All chemical reagents used were analytical reagent (AR) grade.

2.2. Adsorption methods

Adsorption experiments for PS were carried out using a batch equilibrium technique. Initially, PS stock solutions of 5000 mg/L were prepared in deionized water, followed by successive dilution to obtain the necessary concentrations. The pH values of the solutions were adjusted to the required values using 2.0 mol/L HCl and 2.0 mol/L NaOH solutions. The PS adsorption was performed by adding a given amount of MgCl₂ solution (200 g/L) to a 250-mL beaker containing 100 mL of PS solution of the desired concentration and pH. The mixture was then stirred continuously at 400 rpm with a Jintan JJ-1 motor stirrer for a given contact time to achieve adsorption. In this process, the MgCl₂ solution was added dropwise to the PS solution with a dripping speed of about 0.1 mL/s. During the kinetic experiments, the MgCl₂ solution was all added dropwise to the PS solution in 10 s (0.1 mL/s) and then stirred for the given time. After the stirring was finished, the mixture was allowed to settle under static conditions for 20–30 min. Then a centrifuger (LG10-2.4A, Beijing Medical Centrifuge Factory, China) was used at 8000 rpm for 20 min to separate the unsettled small particles from the upper solution after settling. The characteristic PS wavelength was determined using a spectrophotometer (TU-1810, Shanghai Spectrum Instruments Co., Shanghai, China). The PS concentrations in the supernatant were determined from the maximum absorbance wavelength ($\lambda_{\max} = 223$ nm). The effects on PS removal of contact time, initial pH (10.5–13.0) of the solution, and MgCl₂ dosage were investigated.

The PS removal efficiency η (%) can be calculated from the PS concentration before (C_0) and after adsorption (C_a):

$$\eta (\%) = \frac{C_0 - C_a}{C_0} \times 100 \quad (1)$$

The adsorption capacity q was determined using the following equation:

$$q = \frac{(C_0 - C_a)V}{W} \quad (2)$$

where W is the mass of adsorbent (g), and V is the volume of solution (L).

Analog computation using Visual MINTEQ was used to analyze the amounts of FGMH produced by the Mg-OH method and the percentage distribution of magnesium in the NaOH solutions.

2.3. Characterization of PS-Mg(OH)₂

Fourier-transform infrared (FT-IR) spectra of the FGMH before and after adsorption of PS were obtained using an FT-IR spectrometer (Avatar 370, Thermo Nicolet, Waltham, MA, USA).

After adsorption, the solids were filtered and mixed with 100 mL of distilled water, and then acidified to neutral pH to dissolve them. UV-visible spectral analyses of the original, after adsorption, and desorbed solutions were performed using a UV-vis spectrophotometer (SP-2012, Shanghai Spectrum Instruments Co., Shanghai, China).

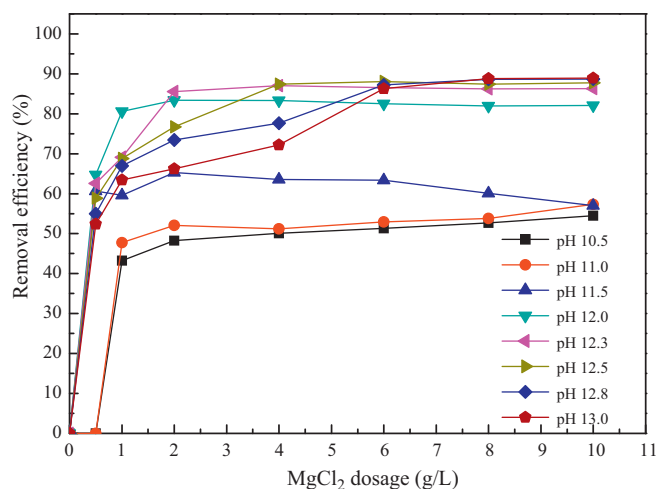


Fig. 2. Effects of MgCl₂ dosage on PS removal (pH 10.5–13.0, $T=303\text{ K}$, $t=60\text{ s}$, $C_{(ps)}=200\text{ mg/L}$).

3. Results and discussion

3.1. Effects of adsorbent dosage on PS removal

In the batch study, for a given initial concentration, it was necessary to find the optimum dosage of the adsorbent, and also the contact time and pH for maximum adsorbate removal.

The effects of MgCl₂ dosage at different initial pH values are shown in Fig. 2. When the initial pH was constant, the PS removal efficiency increased significantly with increasing MgCl₂ dosage at the beginning; however, with further increases in MgCl₂ dosage, the removal efficiency improved only slightly. This is probably because the amount of FGMH increased with increasing MgCl₂ dosage during the adsorption process until the amount of FGMH became constant. To prove this conjecture, the amount of FGMH produced by the Mg-OH method was obtained by analog calculations using Visual MINTEQ. Fig. 3 shows the FGMH amounts as the MgCl₂ dosage changes for different initial pH values. It can be seen that, at the beginning, the amount of FGMH increased with increasing MgCl₂ dosage; once the Mg²⁺ or OH⁻ had all been converted to Mg(OH)₂, the amount of FGMH became constant. The variations in the amounts of FGMH showed the same trend as those for the

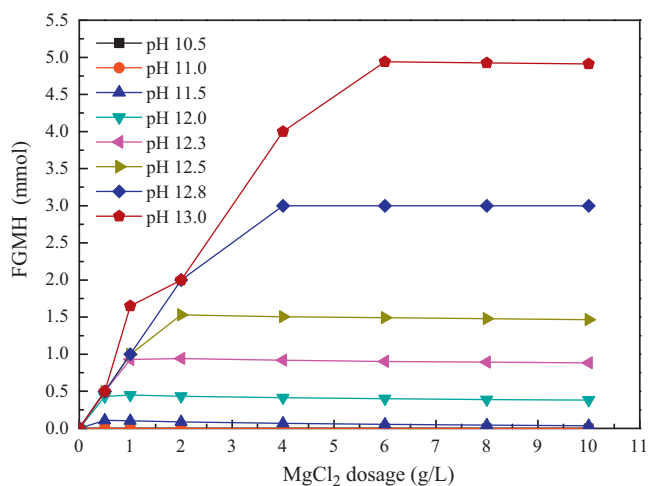


Fig. 3. Effects of MgCl₂ dosage on FGMH amounts (pH 10.5–13.0, $T=303\text{ K}$, $t=60\text{ s}$, $C_{(ps)}=200\text{ mg/L}$).

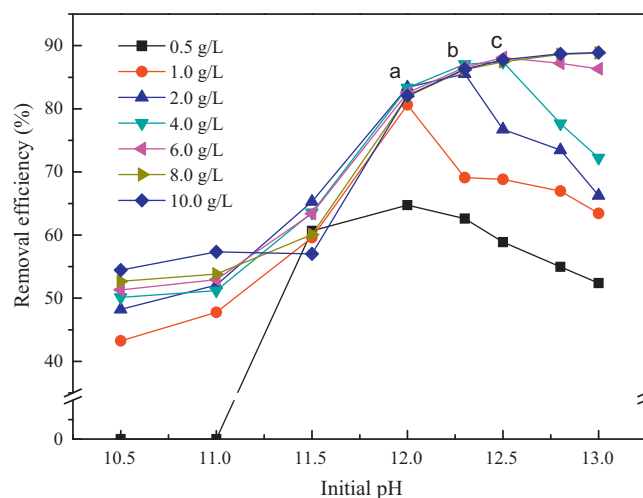


Fig. 4. Effects of pH on PS removal for different MgCl₂ dosage (pH=10.5–13.0, $T=303\text{ K}$, $t=60\text{ s}$, $C_{(ps)}=200\text{ mg/L}$).

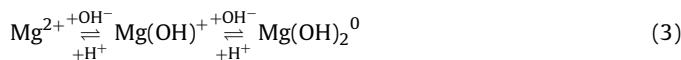
removal efficiency. The PS removal efficiency was therefore closely related to the amount of FGMH.

At higher pH values (>12.0), when the MgCl₂ dosage was 2.0 g/L, the PS removal efficiency was 85%. But for higher MgCl₂ dosages, there was little further increase in the removal efficiency. So, an MgCl₂ dosage of 2.0 g/L was chosen for subsequent batch adsorption experiments.

3.2. Effects of pH on PS removal

Solution pH is one of the most important variables affecting adsorption characteristics. In this study, the effects of pH on PS removal were investigated in the pH range 10.5–13.0 for different MgCl₂ dosages. Fig. 4 shows the effects of pH on PS removal for different MgCl₂ dosages. The figure shows that pH has a significant effect on PS adsorption on FGMH. For the dosage less than 6 g/L, the PS removal efficiency increased with increasing pH, but then decreased with further pH increases. When the pH was higher than 12.8, the removal efficiency increased slightly.

The points a, b, and c in Fig. 4 are the three turning points for the removal efficiency. At these three points, the concentrations of Mg²⁺ and OH⁻ were 0.01 mol/L and 0.01 mol/L, 0.02 mol/L and 0.02 mol/L, and 0.03 mol/L and 0.0316 mol/L, respectively. To investigate why the removal efficiencies were best at these three points, the percentage distribution of magnesium in the aqueous solutions for point b was obtained by analog calculations using Visual MINTEQ. Fig. 5 shows the percentage distribution of magnesium in the solutions. Fig. 6 shows the PS removal efficiency and the actual final pH as the pH changed from 10.5 to 13.0 when the MgCl₂ dosage was 2.0 g/L. The process of Mg²⁺ conversion to Mg(OH)₂ is as follows:



At lower pH (<11.5), the magnesium was almost all present in the solutions as Mg²⁺. When there is a lot of Mg²⁺ in the solution, the PS can form PS flocs. Although there was no Mg(OH)₂ precipitation, some of the PS was removed from the solution.

Figs. 4 and 5 show that, almost no Mg(OH)₂ was generated when the pH was lower than 11.0. However, when the MgCl₂ dosage was more than 1.0 g/L, approximately 50% PS was removed. This is probably because Mg²⁺ can act as a coagulant [19]. When the PS

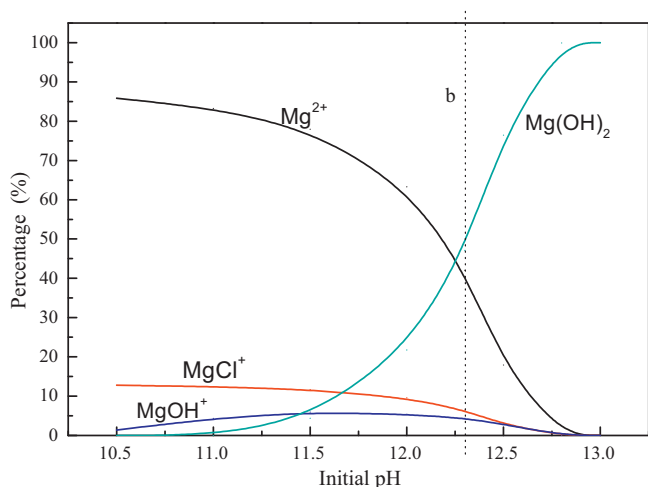


Fig. 5. Effects of pH on the percentage distribution of magnesium (pH = 10.5–13.0, $T = 303$ K, $MgCl_2$ dosage 2.0 g/L).

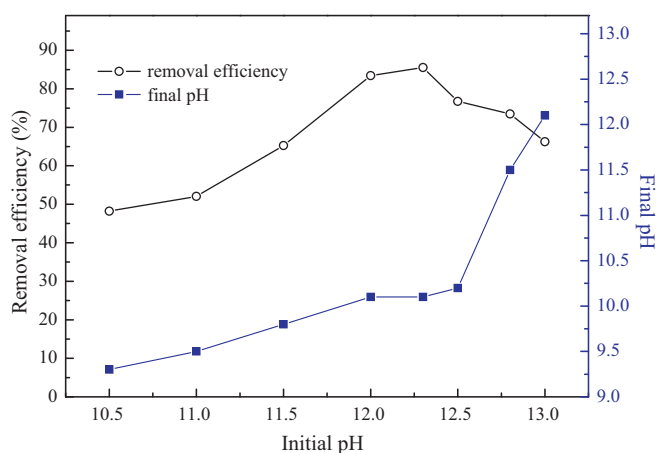


Fig. 6. Effects of pH on the PS removal and final pH (pH = 10.5–13.0, $T = 303$ K, $t = 60$ s, $C_{(ps)} = 200$ mg/L, $MgCl_2$ dosage 2.0 g/L).

solutions contained plenty of Mg^{2+} , the PS molecules flocculated, forming large amounts of flocs and reducing the amount of PS in the solutions.

At pH 11.5–12.8, the magnesium in the solution was mainly Mg^{2+} and $Mg(OH)_2$. The maximum removal efficiency was achieved at pH 12.3, where the $Mg^{2+}/Mg(OH)_2$ ratio was nearly 1:1. Then, as the pH increased further, the amount of $Mg(OH)_2$ increased, but the removal efficiency decreased. It has been reported that FGMH is a gelatinous precipitate, and it has been found to serve as an efficient coagulant and flocculation aid [22]. FGMH has a high surface free energy with a large adsorptive surface area and a positive surface charge [19]; this charge attracts negatively charged colloidal particles, including PS flocs, thus inducing adsorption and agglomeration. When the pH was increased to 12.3, the amounts of Mg^{2+} and PS flocs decreased, and the PS removal efficiency decreased. At pH 13.0 and an $MgCl_2$ dosage of 10.0 g/L, the amount of $Mg(OH)_2$ precipitated was about 5.0 mmol, five times the amount of $Mg(OH)_2$ precipitated at pH 12.3 and an $MgCl_2$ dosage of 2.0 g/L. However, the removal efficiencies under these two sets of conditions were 89.5% and 85.5%, respectively, a difference of only 4%. Fig. 3 shows that the amount of FGMH was almost the same when the dosages of $MgCl_2$ were 1.0 g/L and 2.0 g/L at pH 12.3. However, the removal efficiencies under these two sets of conditions were 69.1% and 85.5%, respectively, a large difference of 16.4%. In addition, when

the $MgCl_2$ dosage and the pH changed at a specific rate at the same time, the turning points a and c also changed. This proved that the presence of Mg^{2+} in the solution was favorable for PS removal when the pH was lower than 12.8.

Intermediate products, i.e., $MgOH^+$ and $MgCl^+$, can also form during the formation of $Mg(OH)_2$ crystals [23,24]; this increased the positive electrostatic surface charge and enhanced the adsorption of anionic PS by charge neutralization.

At higher pH (>12.8), the magnesium was all converted to $Mg(OH)_2$ precipitates. As the pH increased, the PS removal efficiency decreased when the $MgCl_2$ dosage was lower than 8.0 g/L, probably because more negatively charged sites formed at the $Mg(OH)_2$ surfaces as a result of the adsorption of OH^- from solution, and because FGMH nucleation was easier and faster at higher pH values [23]. Fig. 5 shows that the final pH was much higher when the initial pH was higher than 12.8, that is, there was much more OH^- left in the solution when the initial pH was higher than 12.8 than there was in the other cases. As a result, the production of positively charged $Mg(OH)^+$ and $MgCl^+$ decreased and free OH^- adsorbed on the FGMH surfaces, resulting in electrostatic repulsion between the FGMH surfaces and PS anions. Moreover, too fast a crystallization rate reduced the interaction time between FGMH and PS. These were the reasons for the decreasing removal efficiency. An initial pH of 12.3 was therefore chosen for the subsequent batch adsorption experiments.

Steps, ledges, and kinks on the surface of a matching substrate are also particularly effective in nucleation because they allow more of the substrate surface to be in contact with the nucleus [25]. PS might therefore be inserted in the $Mg(OH)_2$ lattice or be adsorbed and bundled continuously. Furthermore, FGMH can aggregate to form a three-dimensional network structure [18,26]. In environmental studies, this action is called netting catch affection.

3.3. Effects of contact time and initial concentration on PS removal

The effects of contact time and initial concentration on PS removal are shown in Fig. 7. The figure shows that for four solutions with different initial PS concentrations in the range 50–500 mg/L, the PS solutions approached equilibrium adsorption within 60 s. The initial PS concentration had no significant effect on the equilibration time. In order to ensure complete adsorption equilibrium, 60 s was chosen as the contact time in each batch equilibrium

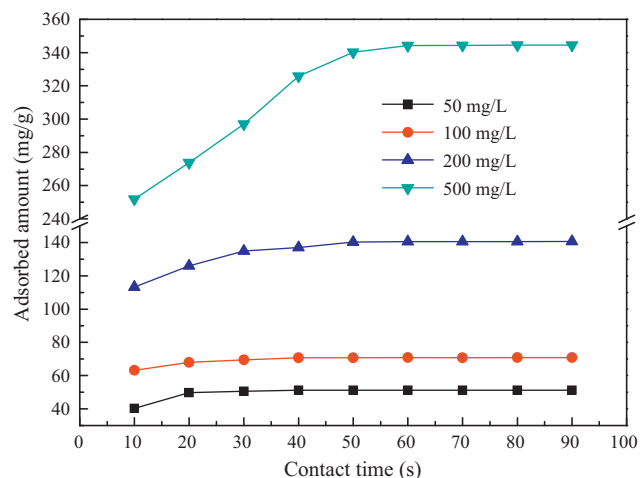


Fig. 7. Effects of contact time and initial concentration on PS removal (pH = 12.3, $T = 303$ K, $MgCl_2$ dosage 2.0 g/L, $V_{(ps)} = 100$ mL).

Table 1
The characteristics and the treatment results of the PS solutions.

Sample	Parameter	Effluent	Treated	Removal (%)
500 mg/L	pH	7.2	10.2	–
	Conductivity ($\mu\text{S}/\text{cm}$)	181.3	4180	–
	Turbidity (NTU)	14.1	0.8	94.3
200 mg/L	pH	7.2	10.1	–
	Conductivity ($\mu\text{S}/\text{cm}$)	85.7	4060	–
	Turbidity (NTU)	6.8	0.6	91.2

adsorption experiment. The relatively low reaction time may be because the adsorption of PS on freshly generated hydroxides is a coagulation–adsorption process. During this process, PS flocs formed and adsorbed on the particles layer by layer, and were finally removed with the $\text{Mg}(\text{OH})_2$ particles.

To investigate the characteristics and the treatment results of the PS solutions, some tests were carried out for 500 mg/L and 200 mg/L PS solutions with pH 12.3 and MgCl_2 dosage 2.0 g/L at 303 K to stir 60 s. Table 1 shows the characteristics and the treatment results of the PS solutions. The removal efficiencies of the two PS solutions for turbidity were all over 90%, and FGMH displayed excellent efficiency for treatment of the PS solutions.

3.4. Adsorption isotherms

In order to analyze the adsorption behavior of PS, two well-known models, i.e., Langmuir and Freundlich isotherms were evaluated using a least-squares method based on an optimization algorithm. The two models are represented mathematically as follows [27,28]:

$$\text{Langmuir equation: } q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$\text{Freundlich equation: } q_e = K_F C_e^{1/n} \quad (5)$$

where q_e is the amount of PS adsorbed by FGMH, C_e is the concentration of the PS solution, q_m is the saturated adsorption capacity of PS by FGMH, and K_L is a constant of the Langmuir isotherm; K_F and n are parameters of the Freundlich isotherm. The adsorption isotherms for PS onto FGMH at different temperatures are presented in Fig. 8.

The parameters of the Langmuir and Freundlich isotherms are presented in Table 2.

The data show that the adsorption isotherms better fitted the Freundlich model. The Freundlich isotherm is applicable to heterogeneous systems and reversible adsorption; the n value in this

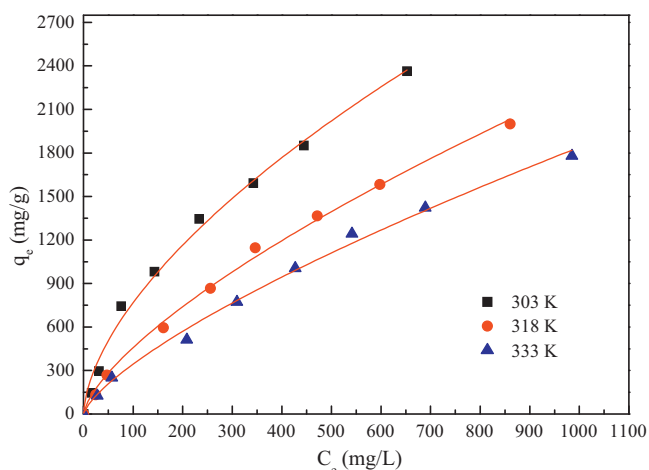


Fig. 8. Adsorption isotherm of PS on FGMH (pH = 12.3, $t = 60$ s, MgCl_2 dosage 2.0 g/L).

Table 2
Parameters of Freundlich and Langmuir isotherms for adsorption of PS on FGMH.

T (K)	Freundlich isotherm			Langmuir isotherm		
	K_F	n	R^2	K_L	q_m (mg/g)	R^2
303	48.05	1.66	0.9922	0.0026	3575	0.9405
318	18.87	1.44	0.9971	0.0019	3134	0.9759
333	12.03	1.37	0.9952	0.0012	2877	0.9838

equation suggests deviation from linearity [29]. In this work, the best-fit Freundlich parameters n at different temperatures are all over 1, which indicates that the adsorption of PS by FGMH is a favorable adsorption process. The maximum saturated adsorption capacity (q_m) for PS onto FGMH was obtained using the Langmuir model; q_m was 3575 mg/g at 303 K in this study. Compared with other adsorbents [7,30,31], FGMH displayed superior adsorption capacities. This is because the removal mechanism of PS by FGMH is a coagulation–adsorption process involving a combination of flocculation, adsorption, charge neutralization, and netting catch affection.

The results in Fig. 8 also indicate that the adsorption efficiency decreased significantly with increasing temperature, indicating that the adsorption reaction was exothermic in nature, and that the solution temperature has a significant effect on PS adsorption.

3.5. FT-IR spectral analysis

FT-IR is a widely used technique for the identification of the surface groups responsible for adsorption of organic substances. The IR spectra of FGMH after PS adsorption are shown in Fig. 9. In the IR spectrum of the unloaded hydroxide precipitates, the peak at 3698 cm^{-1} was assigned to the free O–H stretching vibration mode of the hydroxyl functional groups, and the peak at 3447 cm^{-1} was related to HO–OH₂ and H₂O–OH₂ vibrations. The two peaks of the upper line between 1650 cm^{-1} and 1400 cm^{-1} were attributed to the bending vibration of Mg–OH and –OH bond in crystal structure, respectively [32].

The peaks in the $1450\text{--}1600 \text{ cm}^{-1}$ region were ascribed to the stretching vibration of C=C in the benzene ring. The peaks at 2850 cm^{-1} and 2960 cm^{-1} were attributed to the stretching vibrations of C–H on the –CH₂– and –CH₃ groups. The stretching vibration of S=O on the –SO₄[–] group led to the appearance of the

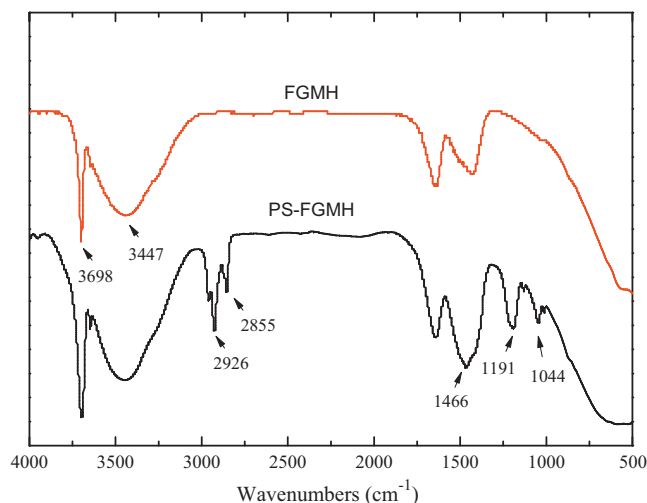


Fig. 9. FT-IR spectra of FGMH before and after PS adsorption (pH = 12.3, $T = 303$ K, $C_{(\text{PS})} = 200$ mg/L, MgCl_2 dosage 2.0 g/L).

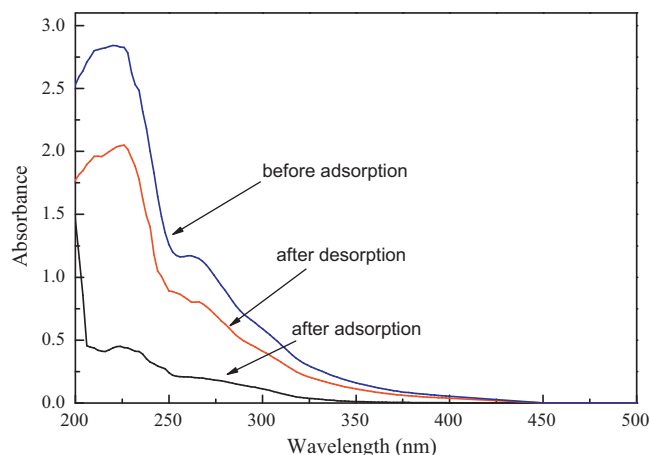


Fig. 10. UV–visible spectra of PS solutions at different stages of adsorption process (pH = 12.3, $T = 303\text{ K}$, $C_{(\text{PS})} = 200\text{ mg/L}$, MgCl_2 dosage 2.0 g/L).

peak at 1192 cm^{-1} . These results confirm that the PS was adsorbed on the FGMH surface.

3.6. UV–visible spectral analysis

Fig. 10 shows the UV–vis spectra of the PS solutions at different stages, i.e., the standard 100 mg/L PS solution, the supernatant after adsorption, and the solution after desorption. It can be seen that there were no new characteristic peaks in the wavelength range $200\text{--}500\text{ nm}$, indicating that no byproducts were formed in the adsorption process. The middle line shows that the PS– $\text{Mg}(\text{OH})_2$ sediments dissolved when the solution was acidified to neutral pH. The shape of the UV–vis spectrum after desorption is similar to that of the original PS solution. This indicated that there were no structural changes of the PS molecules in the coagulation–adsorption process. The differences in absorbance may be partly caused by PS flocculation by the Mg^{2+} in the solution, as well as by the difference between the PS concentration in the original and desorbed solutions. The adsorbed PS can therefore be reused after desorption.

4. Conclusion

FGMH can remove PS from PS-containing aqueous solutions. It showed significant PS removal efficiency. The optimum conditions for PS removal by FGMH are 2.0 g/L MgCl_2 , 60 s contact time, and pH 12.3. With increasing solution pH, the removal efficiency increased significantly, and then decreased at pH values above 12.3. The removal mechanism was a coagulation–adsorption process involving a combination of flocculation, adsorption, charge neutralization, and netting catch affection. The experimental equilibrium data can be interpreted well by the Freundlich equation. The adsorption processes are exothermic in nature, so a lower temperature is favorable. The maximum adsorptive capacity of FGMH for PS is 3575 mg/g , so the Mg–OH method can be used to treat surfactant wastewaters effectively. Meanwhile, the adsorbed PS can desorb after treated and it could be reused after desorption. It can reduce the waste of surfactant to use this method, which is a green technology, to treat surfactant containing wastewaters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.03.059>.

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