



J. Serb. Chem. Soc. 80 (4) 563–574 (2015)
JSCS–4738

Microwave and acid-modified talc for the adsorption of Methylene Blue in aqueous solution

SI-FAN LI, SHUANG-CHUN YANG*, SHAN-LIN ZHAO, PING LI and JIN-HUI ZHANG

College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, FuShun 113001, China

(Received 18 July, revised 19 November, accepted 21 November 2014)

Abstract: Batch adsorption experiments for the removal of Methylene Blue from aqueous solutions onto talcum powder were investigated using microwave-assisted and acetic acid-modified talcum powder. In batch adsorption experiments for the removal of Methylene Blue by the new sorbents, the influences of particle size of the talcum powder, the acid concentration, acidification time and temperature, and radiation time and power were investigated. The results showed that the efficiency for the removal of Methylene Blue was up to 83.03 % under the optimum conditions, namely, talcum powder of 10 μm treated with 1.0 M acetic acid at 313 K for 9 h under 600 W microwave radiation for 5 min. The modified talcum powder was characterized by Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy. The adsorptive capability of the adsorbent was greatly enhanced because of the active groups OH^- and broken Si-O^- and the cracks produced in the face of talcum powder on modification.

Keywords: talcum powder; microwave; acidification; adsorption; Methylene Blue.

INTRODUCTION

Talc, $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$, is a major hydrous magnesium silicate with the chemical composition MgO 31.72, SiO_2 63.52 and H_2O 4.76 %. The crystal structure of talc is a monoclinic system consisting of layers of brucite octahedral, sandwiched between silica tetrahedron sheets.¹ Such successive layers of talc, resulting in the breaking of sheets during grinding, are bonded together by weak van der Waals forces and have no other cation is present. A successive network of silica tetrahedron is formed through bridging oxygen atoms and the reactive oxygens are all toward one side in the crystalline lattice, as shown in Fig. 1. The difference in the surface energy between face surfaces and edge surfaces is relatively large in talc. In addition, some intrinsic properties of talc, such as

* Corresponding author. E-mail: yangchun_bj@126.com
doi: 10.2298/JSC140718116L

chemical inertness, high thermal stability, good lubricity, low electrical conductivity, unique pore structure, high specific surface area, low cost and abundant resources, are beneficial for some applications.

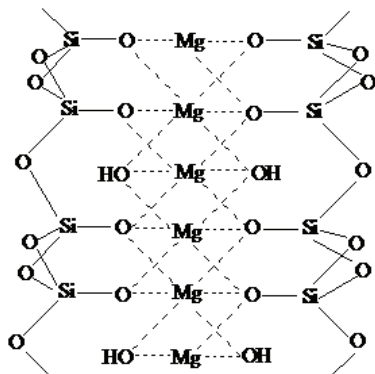


Fig. 1. Schematic diagram of the crystal structure of talc.

The proven talc reserves in China are 250 million tons, which are the second largest in the world. China is the largest exporter of talc in the world, with an estimated annual output accounting for 40 % of the total World exports.² Talc is used extensively in industry, such as, in the automotive, ceramics and coating industries.³ It is also used as an adsorbent in sewage treatment. In addition, talcum powder was employed as a filter aid for the treatment of papermaking wastewater in a membrane bioreactor. The results showed that there was a decrease both in membrane resistance and filter cake resistance when 1.2 g L^{-1} of talcum powder was added to the membrane bioreactor.⁴ In other studies, talcum powder was used as a coagulant aid in the treatment of papermaking wastewater, and the effects were remarkable.⁵⁻⁷ In addition, the adsorption of heavy metal ions was studied, and it was found that talcum powder showed fairly good adsorption for lead ions and the data conformed to the Langmuir model.⁸ Moreover, benzene and toluene removal from aromatic organic wastewater was reported to be much better using talcum powder than when mesoporous silica materials were employed.⁹ Furthermore, the adsorption of a cationic dye using talcum powder was also studied and favorable adsorption of the dye on the adsorbent was evidenced.^{10,11} In conclusion, talc is a promising adsorbent for wastewater treatment, but with some shortcomings. For example, the scope and adsorption amounts of pollutants on talc are limited. In addition, the selectivity of talc for pollutants is low. Therefore, it seemed especially important to study methods of talc modification to improve further its performance in wastewater treatment.

Hitherto, very little work has been performed on the modification of talc using the microwave radiation technology. Modification by microwave heating is more rapid and more uniform, and thus could greatly reduce the heating time and

energy consumption, and the heating quality could also be improved.¹² Meanwhile, minerals treated by acid are more pure. Research showed that associated minerals in talc were dissolved away by monocarboxylic organic acids, with the result that the talc was more pure and particle size of the talc was smaller.¹³ Simultaneously, it was found that the adsorptive ability of talcum powder modified by nitric acid was increased compared to that of unmodified talcum powder, and that the acid could dissolve inorganic salts, which open the internal pores of the talcum powder.¹⁰ Taken together, acid treatments could improve the adsorptive ability of minerals. Furthermore, the adsorption capacity of diatomite treated with vitriol and microwave irradiation was greatly increased, the removal efficiency of sulfide was up to 87 %.¹⁴

Talc has a structure similar to diatomite and they are both porous materials. Therefore, the work presented herein represents a first attempt to modify talcum powder with microwave and acetic acid. The modified adsorbents were applied to Methylene Blue in aqueous solution. The optimum conditions are determined for batch adsorption and a modified mechanism determined by characterization of unmodified and modified talcum powder is discussed.

EXPERIMENTAL

Material

Talcum powder (1250 mesh) samples from Liaoning Haicheng Talcum Powder Company (Haicheng, China), acetic acid 99.5 % purity and Methylene Blue (MB, C.I: 52015, chemical formula: $C_{16}H_{18}ClN_3S \cdot 3H_2O$, molecular weight: 373.90 g mol⁻¹, maximum absorption: 664 nm) from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were used in this study.

Modification methods

Pretreatment of talcum powder. The talcum powder samples were treated before use in the experiments as follows. Different mesh sizes of talcum powder were mixed with 300 mL distilled water, and the mixtures were stirred for 1 h. After stirring, all mixtures were stood for 1 h and the small impurities suspended in the supernatant were removed with a pipette. This process was repeated until the supernatant was clear. The resulting products were then dried at 105 °C.

Acid modified. Talcum powder (10 g) of different mesh sizes was mixed with different concentrations of acetic acid solutions 100 mL at different temperatures for different times. The mixtures were then filtered, washed with distilled water to neutral, and dried at 105 °C.

Microwave-assisted acid modified. The acid modified talcum powder suspensions were placed in flasks and then transferred to the MAS-I microwave synthesis system (Shanghai Sineo Microwave Chemical Technology Co., Ltd.) for different times at 40 °C. The treated products were then dried at 120 °C. The samples were designated M-A-T.

Batch adsorption experiments

To 50 mL of MB solution (20 mg L⁻¹), 0.25 g of unmodified or modified talcum powder were added. The suspension was placed in a water bath shaker at 293 K for 1 h. After the adsorption of MB, the mixtures were centrifuged, and the absorbance of the supernatant was

measured at a wavelength of 664 nm using a 752-B UV–visible spectrophotometer. The efficiency of MB removal, q , was calculated using the following formula:

$$q = 100 \frac{A_0 - A_1}{A_0} \quad (1)$$

where A_0 and A_1 are the absorbance of Methylene Blue before and after adsorption.

Characterization

Chemical bonds of in the unmodified and modified talcum powder were determined by Fourier Transform Infrared Spectroscopy (FTIR) using a Perkin Elmer Spectrum Two instrument (USA). The spectra were obtained in the wavenumber range from 400 to 4000 cm^{-1} . X-Ray diffraction (XRD) was used to identify the phase constitution of the original talcum powder and modified talcum powder. The diffraction patterns were obtained in a Rigaku D/max RB diffractometer (Japan) at 40 kV and 30 mA in the 2θ range from 5 to 70°. The particle sizes of the modified and unmodified talcum powders were calculated using the Scherrer Equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where D is the particle size (nm), K is the Scherrer constant ($K = 0.89$), λ is the X-ray wavelength ($\lambda = 0.15418$ nm), β is the half-high width of the diffraction peak and θ is diffraction angle ($2\theta = 5.12^\circ$).

The morphologies of the powders were examined by scanning electron microscopy (SEM) using a VEGA3 instrument (Tescan, Czech Republic).

RESULTS AND DISCUSSION

Effect of the particle size of the talcum powder on adsorption

Talcum powder of different particle sizes (33, 15, 10, 6.5 μm) were modified with 1 mol L^{-1} acetic acid at 313 K for 3 h. The effect on the removal efficiency of MB on the particle size of the talcum powder is shown in Fig. 2, from which it is clear that the efficiency of MB removal increased with increasing particle size of the talcum powder, but then decreased when the particle size exceeded 10 μm . This might be because more surface bonds were exposed in the larger particles size during grinding.¹⁵ Thus the surface structures tended to be more active, and

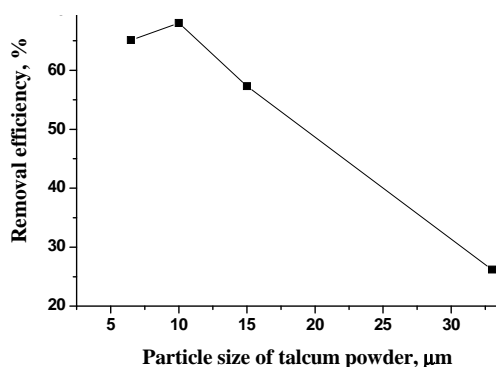


Fig. 2. Effect of the particle size of talcum powder acid-modified with 1 mol L^{-1} acetic acid at 313 K for 3 h on the adsorption of MB.

the surface activity increased. However, the talcum powder with the largest particle size (*i.e.*, 33 μm) removed less MB in the adsorption process, which might be caused by deformation of the lattice and a weakening of the forces between successive layers during grinding. Thus, for remaining adsorption studies, the particle size talcum powder was kept at 10 μm .

Effect of acid concentration on adsorption of talcum powder

In order to study the effect of the acetic acid concentration on the modification of talcum powder, 10 μm powder was modified in 0.1, 1, 2, 3, 4 and 5 mol L⁻¹ acetic acid solutions at 313 K for 3 h. The efficiency of MB removal by the modified talcum powders was found to increase from 64 % to 68 % on increasing the acetic acid concentration employed in the modification from 0.1 to 1 mol L⁻¹. When the acetic acid concentrations were higher than 1 mol L⁻¹, the removal efficiencies of the modified talcum powders decreased; the value decreased by 17.4 % when the acetic acid concentration was increased to 5 mol L⁻¹. Thus, a high acetic acid concentration had no positive effects on the adsorption of MB by the acidified talcum powder. This might be because the acetic acid blocked the active sites and more acetic acid was bonded with the groups on talc surface with increasing acetic acid concentration. On the other hand, the particles of talcum powder modified with 1 mol L⁻¹ acetic acid were more homogeneous in size, which made the adsorption of MB easier. The best adsorptive capability of talcum powder was then shown.

Effect of acidification time on the adsorption of talcum powder

Talcum powder of 10 μm were mixed with 1 mol L⁻¹ acetic acid at 313 K for different times (3, 6, 9, 12, 15 and 18 h). The effect of different acidification time on the adsorption of MB by the modified talcum powder is illustrated in Fig. 3, curve 2. It can be seen that the efficiency of MB removal increased with the acidification time and reached its highest value (73.4 %) at 9 h. Thereafter, it tended to decrease gradually. The above results were probably because the

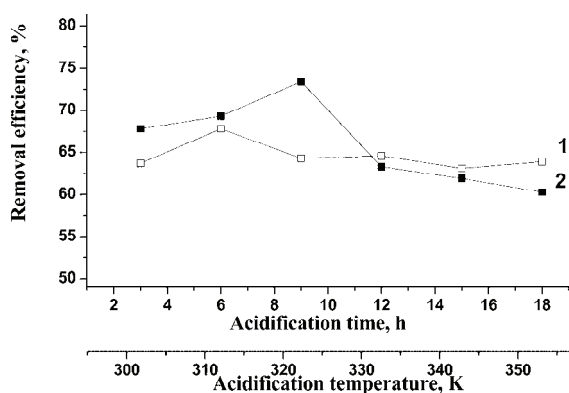


Fig. 3. The effect of the acidification time at 313 K (curve 2) and acidification temperature for 3 h (curve 1) for the modification of talcum powder on the adsorption of MB. The powder size was 10 μm and the acetic acid concentration was 1 mol L⁻¹.

reaction between talcum powder and acetic acid was not sufficient at shorter time for the internal pores to be opened completely. While at longer times, unreacted acetic acid would enter into the holes of the talcum powder, which might reduce the amount of adsorbed MB. Therefore, the best modification time was 9 h.

Effect of acidification temperature on the adsorption by talcum powder

Talcum powder of 10 μm was mixed with 1 mol L⁻¹ acetic acid at the desired temperatures, namely 303, 313, 323, 333, 343 and 353 K, for 3 h. The effect of the modification temperature on the adsorption of MB by the resulting talcum powder is shown in Fig. 3, curve 1. It could be seen that the removal efficiency were all above 63.1 % and differed by only 4.7 % from the highest to the lowest removal efficiency. Thus, it could be considered that there was no apparent effect of acidification temperature on the adsorption efficiencies of the talcum powder over the studied temperature range. The reason might be that more acetic acid would volatilize with increasing temperature and then the talcum powder would become insoluble in the small amounts of remaining acetic acid solution.

Effect of microwave radiation time on the adsorption by talcum powder

Talcum powder of 10 μm and acetic acid (1 mol L⁻¹) were placed in a flask and then transferred to the microwave synthesis system for different times (5, 10, 15, 20, 25 min) at 400 W working power. The effect of M-A-T on the removal of MB for different radiation times is presented in Fig. 4, curve 2. It was observed that as the time of microwave radiation increased, the efficiency of MB removal by the treated talcum powder decreased. The highest MB removal efficiency (80.1 %) was attained at 5 min radiation time, which was about 6.7 % higher than the removal efficiency of MB onto talcum powder modified only by acid. Meanwhile, the two sets of data were equivalent between 10 min and 20min. Thus, microwave radiation for 5 min was the best.

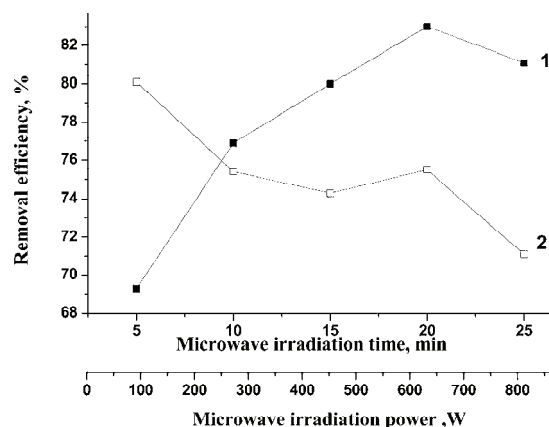


Fig. 4. The effect of microwave radiation time at a power of 400 W (curve 2) and microwave radiation power for 5 min (curve 1) on the adsorption of MB by the modified talcum powders.

Effect of microwave radiation power on the adsorption by talcum powder

Talcum powder of 10 μm and acetic acid (1 mol L⁻¹) were placed in a flask and then transferred to the microwave synthesis system for 5 min at different working powers (100, 200, 400, 600 and 800 W). The effect of M-A-T and microwave radiation of different powers on the adsorption of MB is shown in Fig. 4, curve 1. It was noted that the removal efficiency increased at first but then decreased with increasing power of the microwave radiation. The highest removal efficiency was 83.03 % when the microwave radiation power was 600W. Moreover, the efficiencies of MB removal under microwave irradiation were higher than on the acetic acid modified talcum powder when the power of the microwave radiation exceeded 400 W.

The observations that a suitable power of microwave radiation for a short period was beneficial in improving the adsorption capability of M-A-T might result from two reasons. On the one hand, the unique thermal effect from microwave radiation provided heat from the interior to external in the acidification process, making reactive bonds tend to break into negatively charged groups in the reaction between talcum powder and acetic acid. Then the adsorptive capability of talcum powder was improved. On the other hand, more impurities and water in M-A-T were eliminated by microwave radiation. This led to more pores within the talc. However, as the microwave radiation time and power increased, the structure of M-A-T would be destroyed, then the internal pores would collapse, which would be unfavorable for the adsorption of MB.

Characterization of talcum powder and its mechanism

FTIR spectra. The FTIR spectra of the unmodified and modified talcum powder are presented in Fig. 5. An analysis of the unmodified talcum powder was realized in Fig. 5.^{13,16,17}

The peak areas of Mg–O bonds (463 cm⁻¹) and Si–O–Mg bonds (539 cm⁻¹) were both decreased in the spectrum of M-A-T. This showed that the ordering and bonding effects were influenced in the layer structure of M-A-T, because some of the Mg–O bonds were broken with radiant energy from the microwave synthesis system, making the binding force weaken in the interlayer, then the Si–O⁻ and Mg⁺ were exposed. The active Si–O⁻ and OH⁻ groups that were unchanged after modification from edge surface could adsorb MB cations. Hence, the efficiency of MB removal was improved. Moreover, the absorption peak of carbonate minerals decreased, or even disappeared. This also indicated that the purity of M-A-T samples were increased, which might be because impurities in the pores of talcum powder were removed by acetic acid.¹³

X-Ray diffraction. The results of characterization by XRD of unmodified talcum powder and M-A-T are presented in Fig. 6. The diffraction angles that indicated typical diffraction peaks of the unmodified talcum powder were 9.451°,

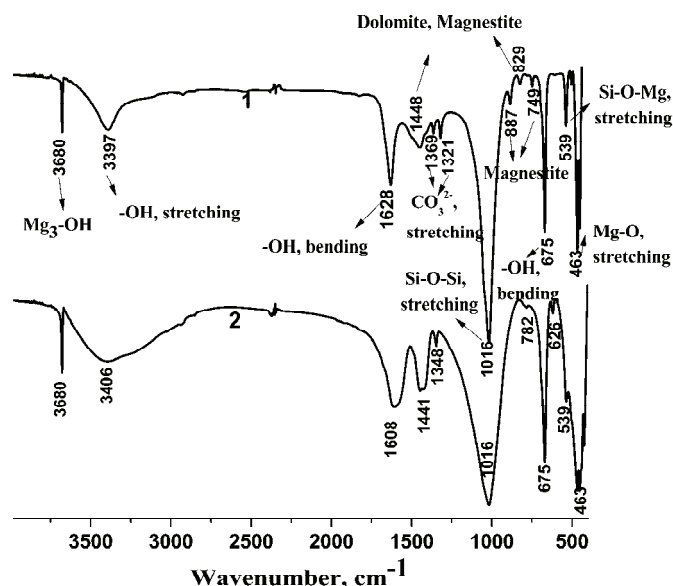


Fig.5. FTIR spectra of the unmodified talcum powder (spectrum 1) and M-A-T (spectrum 2).

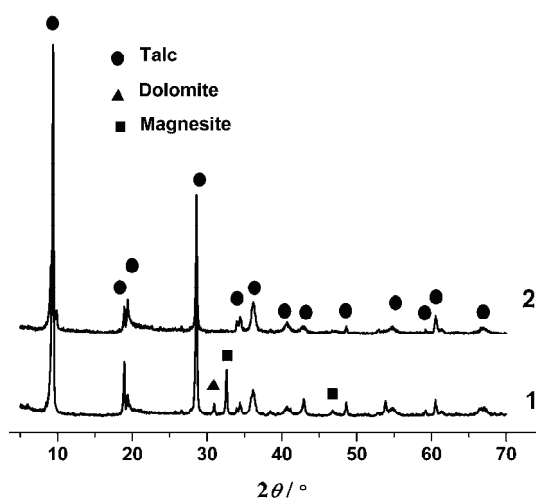


Fig. 6. XRD patterns of unmodified talcum powder (pattern 1) (max. intensity = 16593 counts) and M-A-T (pattern 2) (max. intensity = 7580 counts).

18.988 and 28.586°. The values of the interplane spacing, d , corresponding to $d_{(002)}$, $d_{(004)}$ and $d_{(006)}$, were 9.35, 4.67 and 3.12 Å, respectively. The intensities of the typical M-A-T diffraction peaks were significantly decreased compared with those of the unmodified talcum powder. The interlayer and constituent water were lost and then the layer structure was slightly damaged under the short microwave radiation. Meanwhile, more pores were exposed on the surface of M-A-T. This contributed more MB being adsorbed from the aqueous solution. Accord-

ing to the Scherrer formula, the particle size of talcum powder decreased from 31.5 nm to 22.9 nm after modification. The specific surface area and the activity of the particles could be increased with decreasing particle size. This contributed to the increasing rate of adsorption of MB.

Moreover, as can be seen from Fig. 6, the diffraction peaks for dolomite ($2\theta = 30.962^\circ$) and magnesite ($2\theta = 32.629^\circ$) had both disappeared completely, which corresponded to the results of the FTIR analysis.

SEM micrographs. The SEM micrographs from the unmodified talcum powder and M-A-T at 2000-times magnification are given in Fig. 7a and b, respectively. A large number of attachments, such as fine fragments, could be seen on the unmodified talcum powder surface (Fig. 7a), and these attachments were decreased greatly after microwave radiation and acidification (Fig. 7b). In case of

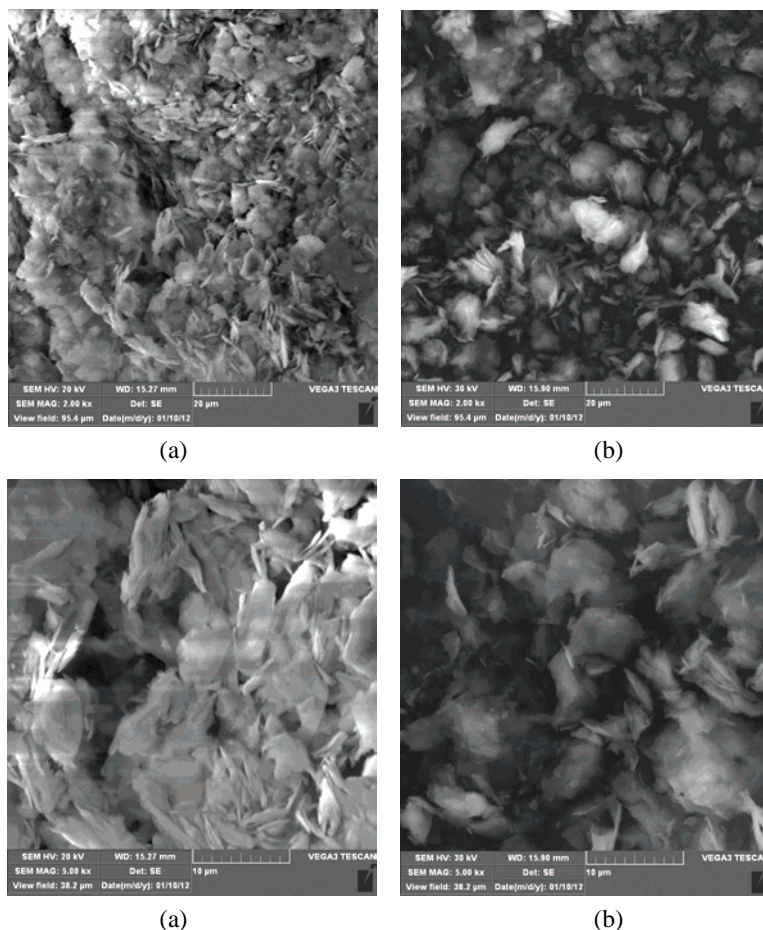


Fig.7. SEM micrographs of: a) unmodified talcum powder and b) M-A-T at 2000 \times magnification; c) unmodified talcum powder and d) M-A-T at 5000 \times magnification.

talc, which has a wetting angle a 64° , a lower roughness of the surface hinders wetting.¹⁸ In Fig. 7b, The surface of M-A-T was more clear and orderly, the roughness was lower and the particles were in loose accumulation. Therefore, the hydrophobic character of M-A-T was enhanced compared to that of the unmodified talcum powder.

The SEM micrographs of the unmodified talcum powder and M-A-T at 5000-times magnification are shown in Fig. 7c and d, respectively. The boundary layers were significant in Fig. 7d. Many cracks occurred in the interparticles on the face surface, which might increase the specific surface area of the pores. Furthermore, these cracks could also produce small fissures, and thus most of the MB adsorption occurred inside the fissures. Overall, the breakage of some of the Mg–O bonds and Si–O–Mg bonds produced cracks on the surface of the M-A-T particles. This corresponded with the results of the FTIR and XRD analyses.

It could be inferred that acetic acid as a polar molecule could absorb the microwave energy strongly.¹⁹ Then a rapid and intensive internal mixing process between acetic acid and the talcum powder occurred in a short period. This enabled the impurities to be removed more completely; hence, the channels of talcum powder could be further enlarged. Likewise, most fine attachments dissolved through the reaction of talcum powder and acetic acid, forming charged states around the interface. These fine attachments then rapidly broke away from the surface of the talcum powder in an instant because of electrostatic repulsion of the interparticles.²⁰ As the fine attachments remaining were removed, most surface groups and pores were exposed. Therefore, the adsorptive capability of M-A-T was greatly enhanced.

CONCLUSIONS

In this work, talcum powder modified by microwave and acetic acid was utilized for the removal of MB from aqueous solution. The chemical bonds, phase constitution and morphology of the unmodified and modified talcum powder were also studied by FTIR, XRD and SEM, respectively. It was found that the particle size of talcum powder, acid concentration, acidification time, and radiation time and radiation power had important influences on the removal process of MB in aqueous solution. The optimum conditions for the microwave-assisted acidification talcum powder were treatment of talcum powder of $10\ \mu\text{m}$ with acetic acid at 313 K for 9 h. The optimal microwave radiation power and time were found to be 600 W and 5 min, respectively. The efficiency of MB removal reached 83.03 % for the microwave-assisted modified and 73.4 % for the acetic acid-modified talcum powder, while the unmodified talcum powder had the lowest removal efficiency of 29.0 %.

The Si–O–Mg bonds from edge surface of talcum powder that were modified by microwave and acid were broken into Si–O⁻ groups, providing more

adsorption sites of higher activity. Moreover, the impurities dolomite and magnesite were completely removed. In addition, the talcum powder surface was more pure. Its roughness was greatly decreased, while many cracks were produced on the face surface by microwave-assisted acidification. Consequently, the adsorption capability of the talcum powder was greatly enhanced. The amount of MB cations adsorbed was increased due to more exposed pores and small cracks and the active Si–O⁻ and OH⁻ groups formed.

Besides, the M-A-T adsorbent shows potential for the treatment of anionic dye wastewater because of the possible adsorption of anionic pollutants between Mg⁺ ions.

Acknowledgement. This work was financially supported by the Liaoning Provincial Industrial Special Resources Protection Office (NO.HSYF-2012-05).

ИЗВОД

ТАЛК МОДИФИКОВАН МИКРОТАЛАСИМА И КИСЕЛИНОМ КАО АДСОРБЕНС
МЕТИЛЕНСКОГ ПЛАВОГ У ВОДЕНОМ РАСТВОРУ

SI-FAN LI, SHUANG-CHUN YANG*, SHAN-LIN ZHAO, PING LI и JIN-HUI ZHANG

*College of Chemistry Chemical Engineering and Environment Engineering, Liaoning Shihua University,
FuShun 113001, China*

Изведени су шаржне експерименти адсорпције за уклањање метиленског плавог из воденог раствора на талку који је био модификован микроталасима или киселином. Испитивани су утицаји величине зрна праха талка, концентрације киселине, времена ацидификације, температуре ацидификације, времена озрачивања и снаге озрачивања. Резултати су показали да је ефикасност уклањања метиленског плавог до 83,03 % у оптималним условима, тј. талк величине зрна од 10 μm је третиран са 1,0 M сирћетном киселином на 313 K током 9 h, а снага и време озрачивања микроталасима били су 600 W и 5 min, редом. Модификовани талк је карактерисан помоћу FTIR, дифракције X-зрака и SEM. Због активних OH⁻ група и раскинутих Si–O⁻ веза, као и пукотина које су произведене на површини зрна талка, значајно је увећана његова адсорпциона моћ.

(Примљено 18. јула, ревидирано 19. новембра, прихваћено 21. новембра 2014)

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