U.P.B. Sci. Bull., Series B, Vol. 81, Iss. 3, 2019 ISSN 1454-2331

EFFECT OF CADMIUM CHEMICAL FORM ON THE ADSORPTIVE PROPERTY OF MAGNESIUM HYDROXIDE MODIFIED DIATOMITE

Zhen LI[1], Qingquan LI[2], Chun BAI[3], Mingyue ZHANG[4], Haodong ZHANG[5]*

Modified by magnesium hydroxide, the diatomite was then characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDX), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) respectively. The results indicate that the magnesium hydroxide modified diatomite (denoted MHD) has better crystal structure with nano-order-scale size, high crystallinity and uneven dispersion than that of natural diatomite (denoted ND). The influence of various factors such as solution pH value, adsorbent content, substrate concentration, temperature and adsorption time on the sorption of Cd(II) were subsequently investigated. Under the optimum conditions (i.e., using 1 g·L-1 MHD for 90 minutes at pH=6 and 25 ℃), the optimal adsorption rates of $Cd(NO_3)_2$, $CdSO_4$ *and* $CdCl_2$ *could reach up to 97.87, 91.33 and 85.4% respectively. And among different chemical forms,* $Cd(NO_3)_2$ *solution is supposed to be a relatively trustworthy simulation wastewater in laboratory research.*

Keywords: magnesium hydroxide, modified diatomite, adsorption, chemical form, cadmium

1. Introduction

With the acceleration of new industrialization process, heavy metal ions have already been the common water pollutant. Since chronic exposure of cadmium could result in kidney dysfunction, it has been classified by U.S. Environmental Protection Agency as a probable human carcinogen, while the high level of exposure could even lead to death [1]. Over the last few decades, adsorption has become an effective purification and separation technique used in wastewater treatment because of its versatility and easy operation [2, 3]. As the filter and adsorbent of medium nice properties and high cost performance,

---

[1] Master, China Gezhouba Group Water Operation Co. Ltd., China, e-mail: 761629863@qq.com

[2] China Gezhouba Group Water Operation Co. Ltd., China, e-mail: 254233989@qq.com

[3] China Gezhouba Group Water Operation Co. Ltd., China, e-mail: 40759817@qq.com

[4] Master, Faculty of Chemical Engineering, Kunming University of Science and Technology, China, e-mail: 1404654177@qq.com

[5] Associate Professor, PhD, Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, China, *corresponding author: e-mail: haodong_zhang1971@163.com

diatomite has been widely employed in heavy metal wastewater treatment and dyeing wastewater disposal [4]. Now, diatomite is restricted to the direct utilization of its porosity and strong adsorption, while its high value-added chemical products couldn’t be yielded through the modification.

The cation species in heavy metal wastewater are multiple, and its competitive behavior may affect the adsorption capacity of diatomite. Besides, the type and quantity of anion and anionic group in solution can also affect the adsorption of heavy metal [5]. The stable valence of cadmium is usually bivalent and positive. Almost all the cadmium compounds are water soluble other than CdS and CdSe, and cadmium discharged into water body could coordinate with inorganic or organic agents to form a variety of dissoluble complexes, such as $CdOH^+$, $Cd(OH)_2$, $HCdO_2^-$, CdO_2^{2-}, etc. For studies on the adsorption of compounded cadmium using diatomite, numerous in-depth researches on $Cd(NO_3)_2$ have been reported [6, 7, 8] and relevant experiments based on the adsorption of $CdCl_2$ are relatively fewer [9, 10], while these experiments have scarcely been conducted on the simulated wastewater containing $CdSO_4$ [11].

Magnesium hydroxide has high surface free energy, large adsorptive surface area, positive surface charge and low solubility, it can continuously release OH^- and precipitate heavy metal ions from wastewater [12]. However, the fine particle size of the magnesium hydroxide makes it very difficult to separate from the water phase, which limits its direct application in wastewater treatment [8]. The diatomaceous silica was partly etched by alkali in the modified process, which caused its surface defects and carried the negative charge. These fresh defects could attract the metal cations to its surface [13]. Magnesium hydroxide successfully entered the pores of diatomite by means of the inorganic modification. The procedure can not only increase the micropore diameter and specific surface area, but also benefit the separation and recycle of adsorption material.

Anaerobic-anoxic-aerobic process obtained a limited biological phosphorus removal effect. When the total phosphorus (TP) concentration of inflow sewage was higher than 3.0 mg/L, this traditional process alone could hardly make the effluent TP conform to the first grade A standards of Urban Sewage Disposal Plant Contamination Integrated Discharge in China ($TP \leq 0.5$ mg/L). Thus, the Ziling municipal sewage treatment plant (affiliated to the China Gezhouba Group Water Operation Co. Ltd.) adopted chemical removing phosphorus technology as one of the assistance measure. We currently add phosphorus removal chemicals (i.e. composite materials of polyaluminium chloride and diatomite) to precipitate the soluble phosphate from sewage, then separate and discharge these sediments from wastewater in forms of excess sludge. As for industrial sewage treatment unit, composite modified diatomite of polyaluminium chloride and magnesium hydroxide would be attempted to remove the superfluous phosphorus and trace heavy metals simultaneously.

2. Experimental

2.1 Materials

All involved chemical reagents are of analytical purity (p.a.). The natural diatomite (denoted ND) from Tianjin Kemiou Chemical Reagent Co., Ltd. was chemically pure. Other chemicals were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., such as $MgCl_2·6H_2O$, $Cd(NO_3)_2·4H_2O$, $3CdSO_4·8H_2O$, $CdCl_2$, NaOH, NaCl, Na_2CO_3, HCl, H_2SO_4, HNO_3, etc. Besides, deionized and doubly distilled water was used in all experiments.

2.2 Preparation of Magnesium Hydroxide Modified Diatomite

The ND was calcined in a muffle furnace at 450 °C for 2 h, cooled, grinded and then passed through a 65-mesh sieve. 3 g of diatomite and 5 mmol $MgCl_2·6H_2O$ were put into a 100 mL bunsen beaker which contained 30 mL of distilled water, and the suspension was stirred for 10 minutes at room temperature. Next, 6.5 mmol NaOH solution was added to the mixture immediately. After the agitation of 5 minutes, sediments were obtained by membrane filtration and dried at 100 °C. Finally, some valve bags are needed to store the adsorbents for further use. The synthesized material is magnesium hydroxide modified diatomite (denoted MHD), and more details about this method have been described elsewhere [14].

2.3 Adsorption Procedure

Under an agitation speed of 150 rpm and temperature 25±1°C for a constant sorption time to attain equilibrium conditions, all batch experiments were carried out in series of 250 mL conical flasks with cover. Mixing various amounts of MHD (0.01–0.5 g) in 100 mL of cadmium-bearing solutions, the adsorption experiments were performed in various concentrations (ranging from 10 to 500 $mg·L^{-1}$) at different pH values, between 2 and 8. Studies based on control variable method were made to determine the optimum pH value, and the maximum Cd(II) adsorption rate could be achieved when using MHD. Using 0.1 g of diatomite (selected through a series of preliminary experiments), relevant tests were conducted at various concentrations of cadmium-bearing solutions (10, 50, 100, 150, 200, 300, 400 and 500 $mg·L^{-1}$) at pH=6. In addition, the changes of absorbance were determined at certain time intervals (5, 10, 30, 60, 90 and 100 min) during the adsorption process. To separate sorbent from the suspension, solutions were then filtered through a 0.45 μm filter paper. The results were eventually analyzed for the residual concentration of cadmium in the filtrate by flame atomic absorption spectrophotometer (Shanghai Spectrum Instruments Co., LTD, SP-3801AA, China) with high sensitivity and low detection limits (10^{-9}). Each experiment was replicated three times and the mean values were used in the analyses. The standard errors were less than 0.01.

The adsorption percentage of Cd(II) (R %) were calculated by the following equation, in which C_0 and C_e represent the solution concentrations of Cd(II) at the initial and equilibrium in mg/L, respectively.

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

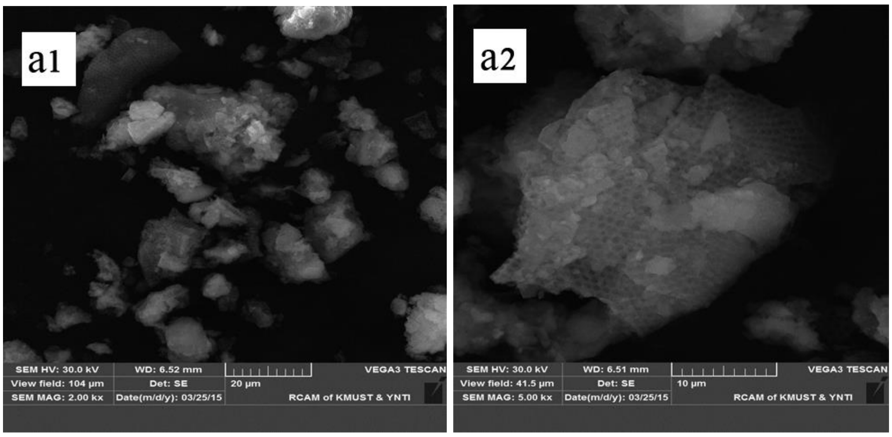
2.4 Characterization Techniques

SEM analysis (Tescan, VEGA-3SBH, Czech Republic) was firstly carried out for ND and MHD to study the specimen morphology, and EDX (HITACHI, S3400N, Japan) associated with SEM are performed to obtained information on chemical compounds and elements. Next, the FT-IR measurements were performed on a specific equipment (Bruker, Tensor27, Germany) in a KBr pellet at room temperature. In addition, the structure and crystalline phases of the diatomite samples were characterized by XRD analysis (Rigaku, D/Max-2200, Japan) with a cobalt tube anode diffractometer (k=0.178901 nm, step size: 0.02 s^{-1}) operated at 36 kV tube voltage and 30 mA tube current in a continuous scan mode by scanning range of 10–100 (2 h). Finally, the N_2 adsorption-desorption isotherms were determined (Tristar, II3020, USA); high speed gas sorption analyzer was used to determine the specific surface area (BET method) and pore volume distribution (BJH method) of the samples.

3. Results and Discussion

3.1 Characterizations of Natural Diatomite and Magnesium Hydroxide Modified Diatomite

SEM analysis. SEM images of both ND and MHD are presented in Fig. 1. Integument is unevenly distributed on the surface of MHD, as well as in the pores, as evidenced in Fig. 1(a).



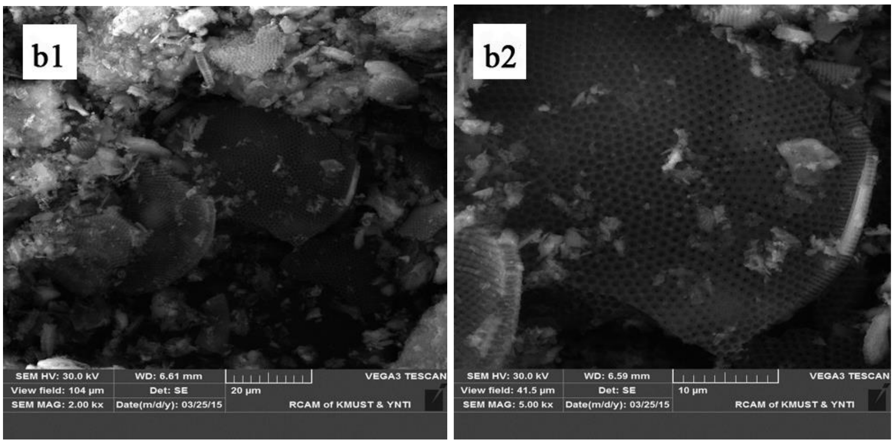
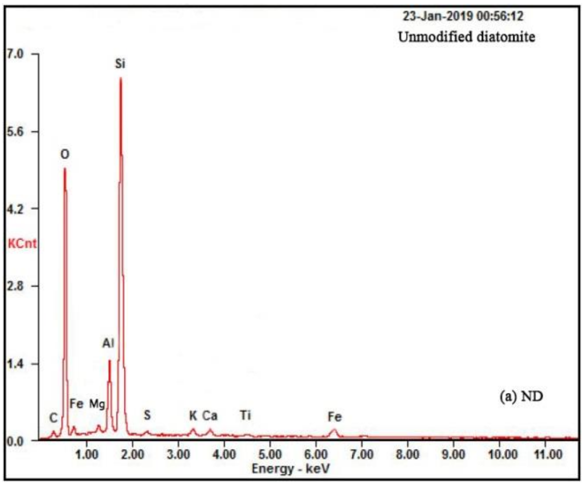


Fig. 1. SEM images of (a) MHD and (b) ND at various magnifications

The ND presents a highly porous structure, as shown in Fig. 2(b), mainly consisting of broken flat discs. In addition, based also on BET and BJH analysis [15], it should be considered that ND possesses a large void volume.

EDX analysis.

Figs. 2(a) and 2(b) are the EDX spectra of ND and MHD respectively, and they qualitatively show that both the two materials mainly contain elements of O, Fe, Mg, Al, Si, etc. According to the quantitative EDX data presented in Table 1, the content of Mg in MHD as At % is close to the theoretical charge ratio. The magnesium atomic fraction increased from 0.52 % to 11.80 % after material modification, and thus EDX associated with the above SEM analysis semi-quantitatively prove the successful material modification.



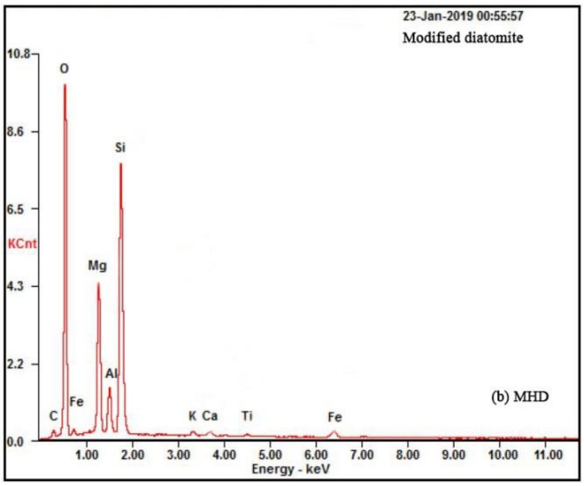


Fig. 2. EDX spectra of (a) ND and (b) MHD

Table 1

The elemental composition (based on EDX spectra) of ND and MHD

Element	ND		MHD	
	Wt %	At %	Wt %	At %
C K	3.31	6.05	3.89	6.75
O K	37.67	51.70	40.64	52.97
Fe K	8.40	3.30	5.74	2.14
Mg K	0.58	0.52	13.76	11.80
Al K	6.55	5.33	4.40	3.40
Si K	39.59	30.95	29.44	21.86
K K	1.22	0.68	0.67	0.36
Ca K	1.49	0.82	0.94	0.49
Ti K	0.77	0.35	0.53	0.23
S K	0.41	0.28	-	-

FT-IR analysis.

To explore the chemical bonds and groups of ND and MHD, FT-IR spectra of the samples were recorded on a Bruker spectrometer in the range of 400–4000 cm^{-1}. In the spectrum of ND (curve ‘a’ in Fig. 3), the peaks at major adsorption bands were observed at 3448.40, 1628.49, 1090.47, 796.40 and 469.27 cm^{-1}. The peak at 3448.4 cm^{-1} is attributed to the free silanol group (Si–O–H) [16], the peak at 1628.49 cm^{-1} represents (H–O–H) bending vibration of water, the peak at 1090.47 cm^{-1} reflects the siloxane (–Si–O–Si–) group stretching, the peak at 796.4 cm^{-1} is put down to Si-O stretching vibration [17, 18], and the absorption peak around 469.27 cm^{-1} corresponds to the antisymmetric bending vibration (O-Si–O). This suggests that the particles in diatomite (amorphous [SiO_4]) are arranged in tetrahedral structure, and adsorbed water molecules were also found attaching to the surface of diatomite. The peaks of the major bands in the spectrum of MHD (mentioned as ‘b’ in Fig. 3) and ND are similar except certain regions. The characteristic peaks of $Mg(OH)_2$ appeared at 3448.42 and 1090.37 cm^{-1} and they are assigned to the stretching vibration of hydroxyl radical and to the flexural vibration of hydroxyl from $Mg(OH)_2$, respectively. These two peaks are considered to be unique when compared with ND, thus suggesting the successful modification. The band at 1633.65 cm^{-1} illustrates the existence of hydroxyl (–OH), while the absorption bands at 797.21 and 468.77 cm^{-1} are attributed to antisymmetric adsorption and antisymmetric bending vibration separately.

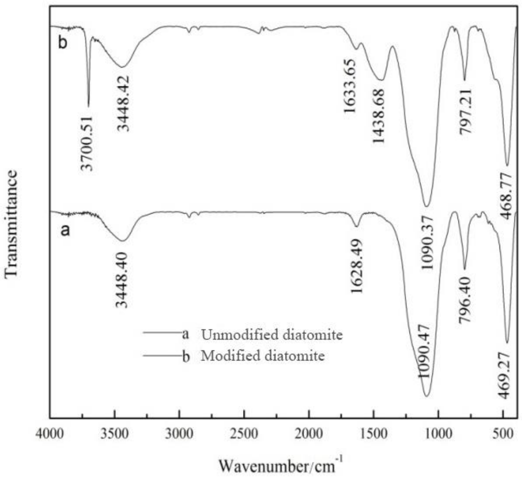


Fig. 3. FTIR spectra of (a) ND and (b) MHD

XRD analysis.

The XRD pattern of ND and MHD was obtained on a X-ray diffractometer equipped with a rotation anode using Cu Kα radiation, and it was integrallty exhibited in Fig. 4. The presence of amorphous SiO_2 (JCPDS 29−0085) was significant at 2 theta degrees (2θ) of 21.80 ° and 26.60 °, but the diffraction intensity herein suffered a slight decrease after modification. On account of low modifier content and weaker peak intensity, the typical diffraction peaks of $Mg(OH)_2$ (JCPDS no.07−0239) were merely observed at 2θ of 38 °, 51 ° and 33.4 ° [14] .

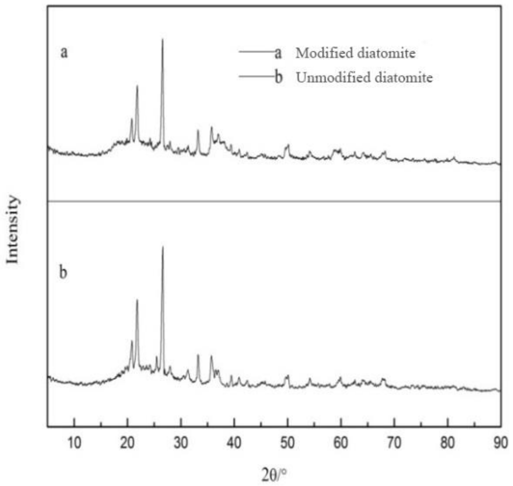
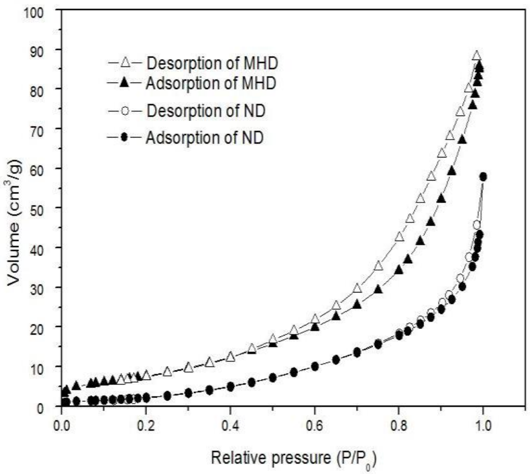


Fig. 4. XRD spectra of (a) MHD and (b) ND

BET and BJH analysis.

Nitrogen adsorption–desorption isotherms were recorded for ND and MHD as shown in Fig. 5, which were identified as the uncommon Type III isotherm. The adsorbent-adsorbate interactions in this type are weaker when compared with the adsorbate–adsorbate interactions. No matter in the high pressure zone or in the low pressure zone, the nitrogen adsorption volume of MHD is higher than that of ND all the time. A hysteresis loop emerged from the bifurcate of adsorption isotherm and desorption isotherm ($P/P_0>0.4$ for MHD and $P/P_0>0.7$ for ND), which could be attributed to equilibrium pressure difference resulting from capillary condensation phenomenon. ND was modified through facile alkali treatment and other simple inorganic operation, which enhanced its electronegativity, and the surface area also increased from 11.6 to 30.9 $m^2 \cdot g^{-1}$ (calculated through BET multi-point method). MHD and ND have similar pore size distributions, since several peaks can be found at the same location in Fig. 6. The wide pore size distribution confirmed the presence of microporosity, mesoporosity and of macroporosity. The average pore size of ND slightly decreased to 10.025 nm from the initial 10.347 nm (calculated through BJH method). In the same range of pore diameter, MHD owns higher adsorption capacity when compared to ND.



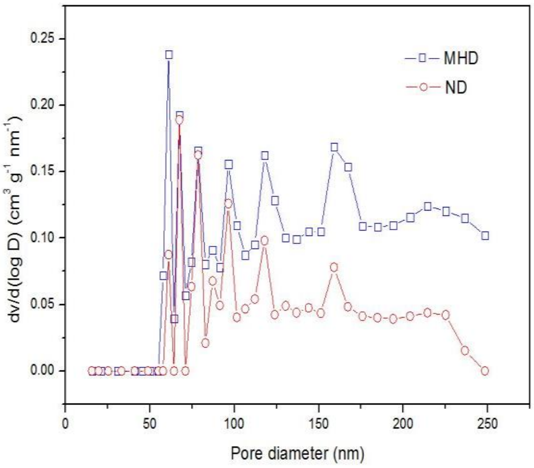


Fig. 5. N_2 adsorption-desorption isotherms at 77K of ND and MHD
Fig. 6. Pore size distribution curves of ND and MHD

3.2 The Influence of Various Factors on Cd(II) Adsorption

The effect of the solution pH value.

The solution pH value has always been regarded as an important factor in adsorption process [19]. To explore the effect of pH value on the Cd(II) adsorption onto diatomite, correlative tests were carried out in batch method (0.1 g of sorbents to 100 mL 100 mg·L^{-1} cadmium-bearing solution under pH=6, at 25 °C for 90 minutes). As presented in Fig. 7, the adsorption of Cd(II) on the MHD strongly depends on the solution pH value. When the pH value increased from 2 to 8, the adsorption rate under different experimental conditions increased from 14 to 81.76% for $Cd(NO_3)_2$, from 21 to 84% for $CdSO_4$ and from 9.5 to 79.25% for $CdCl_2$, respectively. This trend was due to the electrostatic interactions between the metal cations in solution and the negatively charged surface of the diatomite [20]. The adsorption rates of various combined cadmium were low at pH<6, which could be attributed to the fierce competition for sorption sites between the abundant hydronium ions (H_3O^+) and cationic species in aqueous solution. The dissociation of hydroxyl binding from the surface of diatomite suffered the suppression, and thus the electrons carrying negative charge decreased which could also go against the adsorption. Under the condition of slightly alkaline or neutral solution (pH>6), the colloidal formation between Cd(II) and Hydroxyl ions made certain contribution to Cd(II) adsorption. However, this didn't derive from adsorption action. Based on these results, pH=6 was chosen as the optimum pH value for further experiments.

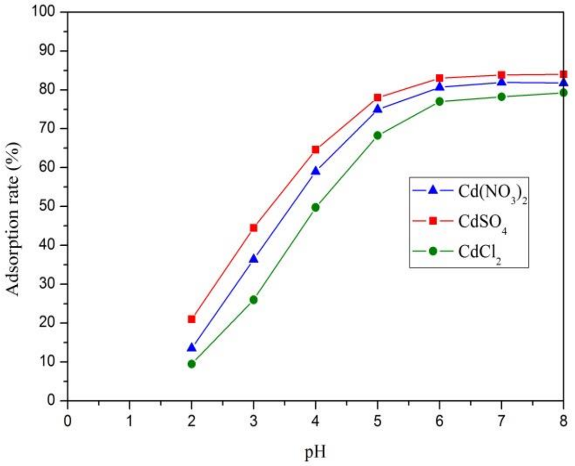


Fig. 7. The effect of the pH value on adsorption experiment. Other experimental parameters are set as: 1 g·L^{-1} adsorbent content; 100 mg·L^{-1} Cd(II); 25 ℃; 90 minutes; 150 rpm

The effect of the adsorbent content.

The effect of the adsorbent content on the Cd(II) adsorption was studied in the range of 0.01–5 g·L^{-1} under desired conditions. In accordance with those three curves in Fig. 8, the Cd(II) adsorption efficiency rapidly increased along with the increase of MHD content at first, which was allegedly due to the increase of available adsorption sites [21]. The maximum adsorption percentage of Cd(II) was obtained at about 1.0 g·L^{-1} of MHD and then stabilized even at higher content. Because the overlapping or aggregation of sorption sites might cause the decrease of the available total surface area for Cd(II) sorption. Hence, 1 g·L^{-1} was reasonably chosen as the optimum content of MHD in consideration of the cost and adsorption effect. Similar behavior was previously investigated by other researchers [22].

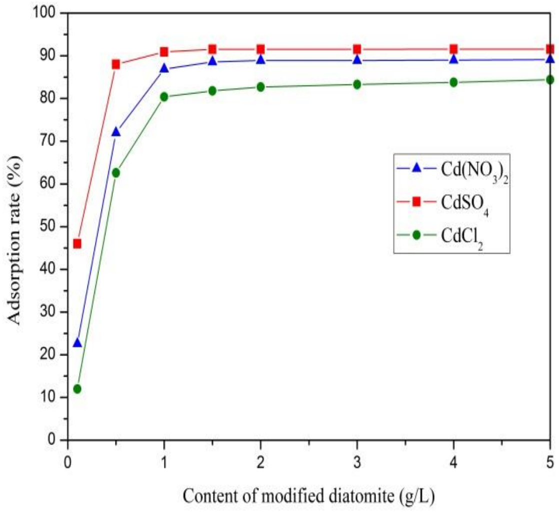


Fig. 8. The effect of the adsorbent content on adsorption experiment. Other experimental parameters are set as: pH=6; 100 mg•L^{-1} Cd(II); 25 °C; 90 minutes; 150 rpm

The effect of the initial concentration of Cd(II) species.

To explore the effect of the initial concentration of Cd(II) species on the adsorption experiment, a concentration range of 10–500 mg·L^{-1}, pH=6, 90 minutes, 25 °C and 1 g·L^{-1} adsorbent content were chosen. In the present work, as depicted in Fig. 9, the adsorption efficiency of $Cd(NO_3)_2$ by MHD decreased throughout the whole research process. Interestingly, the adsorption rate of Cd(II) on MHD reached the maximum prior to 50 mg·L^{-1}, and after which the adsorption capacity for $CdCl_2$ unexpectedly decreased with initial concentration increasing. Because the increased metal ions can enhance the driving force of active sites on the MHD [23] while the suppression effect of anions on active surface groups may weaken the adsorption process. When further increasing the concentration of $CdSO_4$ solution, the uptake rate of Cd(II) demonstrated a slight decrease (from 96.6 to 94.1%). Since the active surface groups on MHD still own strong adsorption activity in high concentration $CdSO_4$ solution, but they are slightly suppressed by the SO_4^{2-} group. As a consequence, 100 mg·L^{-1} was chosen as the optimum initial concentration in batch experiments.

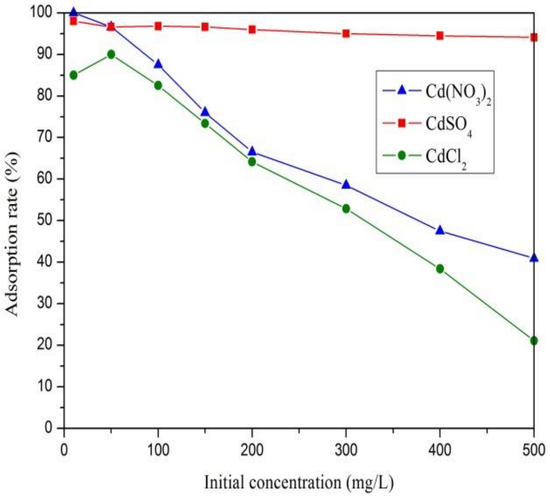


Fig. 9. The effect of the initial concentration of Cd(II) on adsorption experiment. Other experimental parameters are set as: pH=6; 1 g·L^{-1} adsorbent content; 25 ℃; 90 minutes; 150 rpm

Effect of the temperature.

There is no doubt that the temperature has a significant influence on the adsorption of heavy metal ions. Since increasing the temperature can not only change the equilibrium capacity of the adsorbent for a particular adsorbate, but also raise the diffusion rate of ions in the internal pores of the adsorbent [4]. The effect of the temperature on Cd(II) adsorption was determined by investigations at three different temperatures (25, 35 and 45 ℃) in this article. Adsorption isotherms of $Cd(NO_3)_2$, $CdCl_2$ and $CdSO_4$ adsorption onto MHD were separately illustrated in Figs. 10(a), (b) and (c), and the corresponding curves for the solutions with different chemical forms of Cd(II) followed the similar trend at identical temperature. The final adsorption efficiency of the MHD has merely extended from 87.01 to 91% when the temperature increased from 25 to 45 ℃ in Fig. 10(a), although the adsorption of $Cd(NO_3)_2$ is evidently proved to be spontaneous and endothermic [24]. Based on this adsorption method, the remediation process can be performed under the normal temperature for an industrial scale.

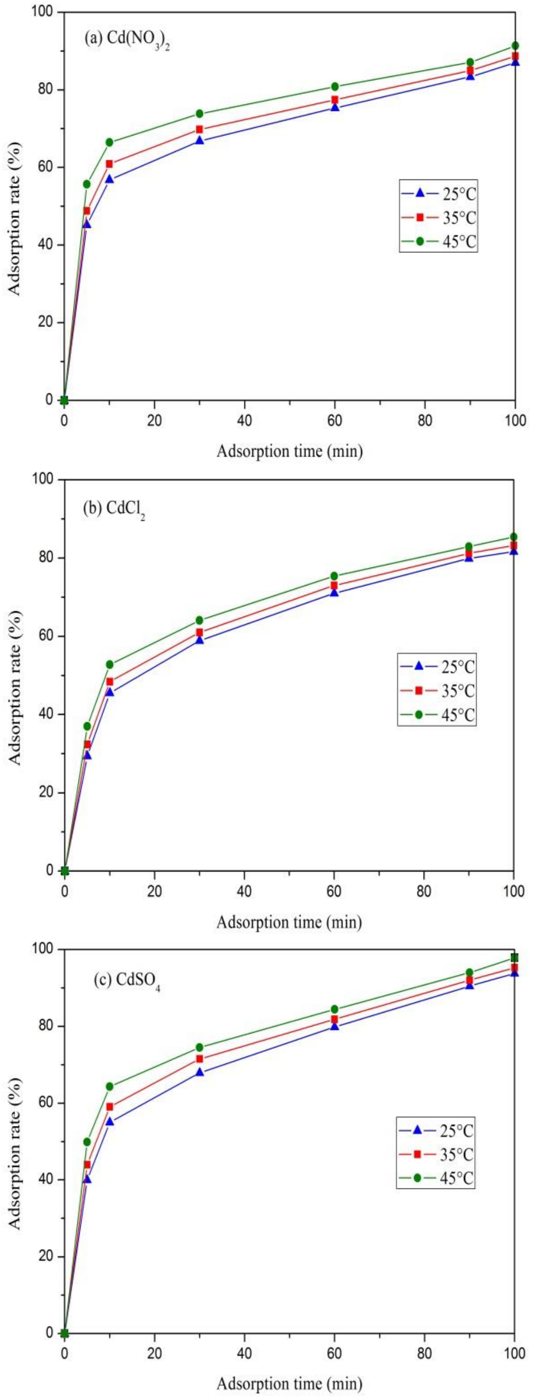


Fig. 10. Effect of the temperature on Cd(II) adsorption for (a) Cd(NO$_3$)$_2$, (b) CdCl$_2$, (c) CdSO$_4$. Other experimental parameters are set as: pH=6; 1 g·L^{-1} adsorbent content; 100 mg·L^{-1} Cd(II); 90 minutes; 150 rpm

Effect of the contact time.

The effect of the contact time on the adsorption process has also been studied. Cd(II) in the aqueous phase was adsorbed by the MHD at specific temperature (25 ℃). As noticed in Fig. 11, the adsorption was fast at early stage of the adsorption process, since the available adsorption sites for massive Cd(II) were abundant [25]. And we found that the adsorption sequence of the solutions with different chemical forms of Cd(II) could be given as $Cd(NO_3)_2 > CdSO_4 > CdCl_2$ in the first twenty minutes. The adsorption velocity slow down thereafter, nevertheless, the $CdSO_4$ adsorption exceeded that of $Cd(NO_3)_2$ within the same contact time. This phenomenon can be explained from the view that different anions may have different suppression effects on active surface groups over adsorption time. And it is obvious from Fig. 11 that the variance of the adsorption capacities between the 90th and the 100th minute were less than the previous ones, which suggested that 90 minutes of adsorption time was a reasonable option. More experiments are necessary to be carried out to prove this investigation.

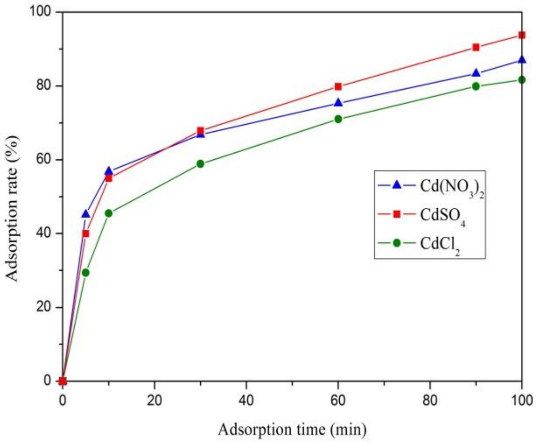


Fig. 11. Effect of the contact time on adsorption experiment. Other experimental parameters are set as: pH=6; 1 $g \cdot L^{-1}$ adsorbent content; 100 $mg \cdot L^{-1}$ Cd(II); 25 ℃; 150 rpm

4. Conclusion

In this work, some modifiers were evenly distributed on the surface of diatomite, and thus the MHD we prepared had nice crystal structures, abundant pores and excellent properties. Based on the analysis of phenomenon and the summary of results, an initial concentration of 100 $mg \cdot L^{-1}$, pH=6, 90 minutes, 25 ℃ and 1 $g \cdot L^{-1}$ adsorbent content was ultimately determined as the appropriate experiment condition. The static adsorption test was considered to be endothermic. To varying degrees, disparate factors affected the adsorption of Cd(II) with different chemical forms. Under the optimum conditions, 85.41% of $CdCl_2$ in aqueous solution were adsorbed by MHD; the maximum adsorption rate of $CdSO_4$ was 91.33%; and the maximum adsorption efficiency of $Cd(NO_3)_2$ could reach up to 97.87%. In the laboratory adsorption studies, it is scientific and reasonable to set $Cd(NO_3)_2$ solution as the simulation effluent among different chemical forms.

Acknowledgements

We gratefully acknowledge the financial help from Kunming University of Science and Technology (14118565) and thank the Analytic & Testing Research Center of Yunnan for its measuring fund support (2016M20152207018).

REFERENCES

[1]. *F. Fu, W. J. Qi,* "Removal of Heavy Metal Ions from Wastewaters: a review", in Environ. Manage., **vol.92**, no.3, 2011, pp. 407-418

[2]. *M. A. Al-Ghouti, M. A. M. Khraisheh and M. Tutuji,* "Flow Injection Potentiometric Stripping Analysis for Study of Adsorption of Heavy Metal Ions onto Modified Diatomite", in Chem. Eng. J., **vol.104**, no.1-3, 2004, pp. 83-91

[3]. *E. Padilla-Ortega, R. Leyva-Ramos and J. V. Flores-Cano,* "Binary Adsorption of Heavy Metals from Aqueous Solution onto Natural Clays", in Chem. Eng. J., **vol.225**, 2013, pp. 535-546

[4]. *R. K. Sheshdeh, M. R. K. Nikou, K. Badii, N. Y. Limaee and G. J. Golkarnarenji,* "Equilibrium and Kinetics Studies for the Adsorption of Basic Red 46 on Nickel Oxide Nanoparticles-modified Diatomite in Aqueous Solutions", in Taiwan Inst. Chem. E., **vol.45**, no.4, 2014, pp. 1792-1802

[5]. *I. H. Chowdhury, A. H. Chowdhury, P. Bose, S. Mandal and M. K. Naskar,* "Effect of Anion Type on the Synthesis of Mesoporous Nanostructured MgO, and its Excellent Adsorption Capacity for the Removal of Toxic Heavy Metal Ions from Water", in RSC Adv., **vol.6**, no.8, 2016, pp. 6038-6047

[6]. *P. Miretzky, C. Munoz and E. Cantoral-Uriza,* "Cd^{2+} Adsorption on Alkaline-pretreated Diatomaceous Earth: Equilibrium and Thermodynamic Studies", in Environ. Chem. Lett., **vol.9**, no.1, 2011, 55-63

[7]. *X. X. Ye, S. H. Kang, H. M. Wang, H. Y. Li, Y. X. Zhang, G. Z. Wang and H. J. Zhao,* "Modified Natural Diatomite and its Enhanced Immobilization of Lead, Copper and Cadmium in Simulated Contaminated Soils", in J. Hazard. Mater., **vol.289**, 2015, pp. 210-218

[8]. *W. H. Zhou, L. Liu, H. P. Li and X. L. Han,* "Investigation of Synergistic Adsorption between Methyl Orange and Cd (II) from Binary Mixtures on Magnesium Hydroxide Modified Clinoptilolite", in Korean J. Chem. Eng., **vol.33**, no.7, 2016, 2073-2083

[9]. *Y. S. Al-Degs, M. F. Tutunju and R. A. Shawabkeh, in Sep. Sci. Technol.,* "The Feasibility of Using Diatomite and Mn-Diatomite for Remediation of Pb^{2+}, Cu^{2+}, and Cd^{2+} from Water", **vol.35**, no.14, 2000, pp. 2299-2310

[10]. *M. A. M. Khraisheh, Y. S. Al-degs and W. A. M. Mcminn,* "Remediation of Wastewater Containing Heavy Metals Using Raw and Modified Diatomite", in Chem. Eng. J., **vol.99**, 2004, pp. 177-184

[11]. *J. Zhu, P. Wang, M. J. Lei and W. L. Zhang,* "Polyhydroxyl-aluminum Pillaring Improved Adsorption Capacities of Pb^{2+} and Cd^{2+} onto Diatomite", in J. Cent. South Univ., **vol.21**, 2014, pp. 2359-2365[12]. *J. L. Cortina, I. Lagreca and J. De Pablo,* "Passive in Situ Remediation of Metal-Polluted Water with Caustic Magnesia: Evidence from Column Experiments", in Environ. Sci. Technol., **vol.37**, no.9, 2003, pp. 1971-1977

[13]. *S. L. Zhan, J. X. Lin, M. H. Fang and X. Q. Qian,* “Adsorption of Anionic Dye by Magnesium Hydroxide-modified Diatomite”, in Rare Metal Mat. Eng., **vol.37**, no.z2, 2008, pp. 644-647

[14]. *F. Z. Xie, F. C. Wu, G. J. Liu, Y. S. Mu, C. L. Feng, H. H. Wang and J. P. Giesy,* “Removal of Phosphate from Eutrophic Lakes through Adsorption by in Situ Formation of Magnesium Hydroxide from Diatomite”, in Environ. Sci. Technol., **vol.48**, no.1, 2014, pp. 582-590

[15]. *S. Nenadovic, L. Kljajevic, S. Markovic, M. Omerasevic, U. Jovanovic, V. Andric and I. Vukanac,* “Natural Diatomite (Rudovci, Serbia) as Adsorbent for Removal Cs from Radioactive Waste Liquids”, in Sci. Sinter., **vol.47**, no.3, 2015, pp. 299-309

[16]. *M. A. M. Khraisheh, M. A. Al-Ghouti, S. J. Allen and M. N. Ahmad,* “Effect of OH and Silanol Groups in the Removal of Dyes from Aqueous Solution Using Diatomite”, in Water Res., **vol.39**, no.5, 2005, pp. 922-932

[17]. *N. Caliskan, E. Sogut, C. Saka, Y. Yardim and Z. Senturk,* “The Natural Diatomite from Caldiran-van (Turkey): Electroanalytical Application to Antimigraine Compound Naratriptan at Modified Carbon Paste Electrode”, in Comb. Chem. High T. Scr., **vol.13**, no.8, 2010, pp. 703-711

[18]. *B. Bahramian, F. D. Ardejani, V. Mirkhani and K. Badii,* “Diatomite-supported Manganese Schiff Base: an Efficient Catalyst for Oxidation of Hydrocarbons”, in Appl. Catal. A-Gen., **vol.345**, no.1, 2008, pp. 97-103

[19]. *M. Bilgin and S. Tulun,* “Use of Diatomite for the Removal of Lead Ions from Water: Thermodynamics and Kinetics”, in Biotechnol. Biotec. Eq., **vol.29**, no.4, 2015, pp. 696-704

[20]. *J. V. Flores-Cano, R. Leyva-Ramos, E. Padilla-Ortega and J. Mendoza-Barron,* “Adsorption of Heavy Metals on Diatomite: Mechanism and Effect of Operating Variables”, in Adsorpt. Sci. Technol., **vol.31**, no.2-3, 2013, pp. 275-292

[21]. *G. Mahajan and D. Sud,* “Application of Ligno-cellulosic Waste Material for Heavy Metal Ions Removal from Aqueous Solution”, in J. Environ. Chemi. Eng., **vol.1**, no.4, 2013, pp. 1020-1027

[22]. *M. M. A. El-Latif, A. M. Ibrahim and M. F. El-Kady,* “Adsorption Equilibrium, Kinetics and Thermodynamics of Methylene Blue from Aqueous Solutions Using Biopolymer Oak Sawdust Composite”, in J. Am. Sci., **vol.6**, no.6, 2010, pp. 267-283

[23]. *M. Q. Jiang, Q. P. Wang, X. Y. Jin and Z. L. Chen,* “Removal of Pb (II) from Aqueous Solution Using Modified and Unmodified Kaolinite Clay”, in J. Hazard. Mater., **vol.170**, no.1, 2009, pp. 332-339

[24]. *Z. H. Yu, Y. F. Zhang, S. R. Zhai, Y. Wang, Y. Z. Pan and C. G. Meng,* “Amino-modified Mesoporous Sorbents for Efficient Cd (II) Adsorption Prepared Using Non-chemical Diatomite as Precursor”, in J. Sol-gel Sci. Techn., **vol.78**, no.1, 2016, pp. 110-119

[25]. *F. Arias and T. K. Sen,* “Removal of Zinc Metal Ion (Zn^{2+}) from its Aqueous Solution by Kaolin Clay Mineral: A Kinetic and Equilibrium Study”, in Colloid. Surface. A, **vol.348**, no.1-3, 2009, pp. 100-108