Vietnam Journal of Science and Technology ***56*** *(6) (2018) 706-713*

DOI: 10.15625/2525-2518/56/6/12749

ADSORPTIVE REMOVAL OF RHODAMINE B USING SODIUM DODECYL SULFATE MODIFIED LATERITE SOIL

Pham Thu Thao, Pham Tien Duc*

Faculty of Chemistry, VNU-University of Science, Vietnam National University, 19 Le Thanh Tong, Hoan Kiem, Ha Noi

*Email: *tienduchphn@gmail.com, tienducpham@hus.edu.vn*

Received: 12 July 2018; Accepted for publication: 7 September 2018

ABSTRACT

Adsorption of the cationic dye Rhodamine B (RhB) onto surfactant modified laterite (SML) was studied in this work. The removal efficiency of RhB using laterite increased significantly after surface modification by pre-adsorption of anionic surfactant sodium dodecyl sulfate (SDS). Some experimental parameters such as pH, adsorbent amount and ionic strength were also investigated. The optimal conditions for RhB removal using SML were found to be pH 4, adsorbent amount 10 mg/mL and ionic strength 0.1 mM NaCl. Under optimum conditions, RhB removal efficiency increased from 25.77 % to 94.85 %, when using unmodified laterite and SML, respectively. After 5 regenerations of SML, the removal efficiency of RhB was still higher than 90 %. Adsorption of RhB onto SML decreased with increasing NaCl concentration from 0.1 to 200 mM, demonstrating that adsorption of RhB onto SML mainly induced by electrostatic attraction. The two-step adsorption model can fit the experimental results of RhB adsorption isotherms onto SML at different NaCl concentrations. Our results indicate that SML is a novel adsorbent to remove ionic dye from aqueous solution.

Keywords: Rhodamine B, adsorption, laterite, surfactant modified laterite.

Classification number: 2.1.3, 3.1.2, 3.2.

1. INTRODUCTION

Dye is one of the major constituents of the wastewaters. Many industries related to textile, paint and varnishes, ink, plastics, pulp and paper, cosmetics, tannery, and dye manufacturers can release dyes [1]. However, numerous dyes are toxic, that can lead to hazardous risks for animals, plants and human's physical health [2]. Rhodamine B (RhB), which is a cationic dye, is widely used in many industrial activities. Nevertheless, RhB is a toxic organic dye when releasing to water environment. Therefore, the removal of RhB from aqueous solution is important in environmental remediation. Many studies investigated the removal of RhB from aqueous solution using different treatment techniques to achieve better water quality [3-7]. Among various techniques to remove RhB, adsorption is one of the most effective and suitable for developing countries when using natural adsorbents.

Laterite is a common soil in Vietn Nam so that it is very cheap. Basically, in acidic or neutral media, laterite has positive charge due to the presence of many metal oxides [8]. Thus, laterite can be used to remove anions directly. For RhB, the surface modification of laterite to enhance the removal efficiency is needed. When the surface of laterite is modified by anionic surfactants, the surface charge of laterite becomes negative so that anionic surfactant modified laterite is a potential material to remove cationic dyes. Sodium dodecyl sulfate (SDS) which is well known anionic surfactant, is an eco-friendly chemical. The surface modification of solid surface by SDS to remove both organic and inorganic contaminants was reported [9]. To our best knowledge, removal of RhB using SDS modified laterite has not been studied.

The present study is the first work which investigates the adsorption of RhB onto SML compared with laterite without surface modification by SDS. Some experimental parameters including pH, adsorbent amount and ionic strength are also investigated. The regeneration experiment is studied to evaluate the potential of the SML adsorbent. The adsorption mechanism is evaluated based on adsorption isotherm.

2. EXPERIMENTAL

2.1. Material

Raw laterite was collected at Thach That, Ha Noi, Viet Nam.

Rhodamine B (RhB) with the spectroscopic reagent, was purchased from Merck (Germany). Other chemicals were obtained from Merck. Ultrapure water system (Labconco, USA) with resistivity 18.2 MΩ cm was used to produce ultrapure water in preparing all aqueous solutions.

NaCl (Merck), HCl and NaOH (Scharlau) were used in the present study.

2.2. Experimental procedure

The laterite was pre-treated with chemicals according to our previously published paper [8]. In the next step, the material was modified with 0.01 M SDS (Scharlau, Spain) in 0.01 M NaCl at pH 5 by thoroughly shaking for 3 h, and then washed with ultrapure water one time. The SDS amount on laterite after washing with ultrapure water is about 10.91 mg/g. The treated-laterite was called as SDS modified laterite (SML).

2.3. Adsorption studies

All adsorption experiments were performed in 15 ml Falcon tubes at 25 ± 2 °C controlled by an air conditioner. A stock solution of 10^{-3}M RhB was prepared by dissolving RhB salt into ultrapure water. The stock would be then diluted appropriately to obtain different concentrations. Ionic strength and pH were adjusted by the addition of NaCl, HCl and NaOH).

For RhB adsorption, a determined amount of laterite and SML was thoroughly mixed with 10 mL RhB at different pH values and NaCl concentrations. The effect of pH, adsorbent amount, ionic strength, and initial concentrations of RhB were investigated. The RhB concentrations before and after adsorption were determined by ultraviolet visible (UV-Vis) spectroscopy at a wavelength of 555 nm using a spectrophotometer (UV-1650 PC, Shimadzu, Japan). The removal of RhB was calculated by equation (1).

$$Removal\ \%R = \frac{C_i - C_e}{C_i} \times 100\ \% \qquad (1)$$

where C_i and C_e are the initial concentration and the equilibrium concentration of RhB, respectively.

The adsorption capacity Γ (mg/g) of RhB onto SML was calculated by equation (2).

$$\Gamma = \frac{C_i - C_e}{m} \times V \qquad (2)$$

where C_i (mg/L) and C_e (mg/L) are the initial concentration and the equilibrium concentration of RhB, respectively. V (L) is volume of solution and m (g) is adsorbent amount.

2.4. General isotherm equation

The obtained isotherms were fitted by general isotherm equation that could be applied to illustrate adsorption isotherms of RhB onto SML. The general isotherm equation (3) is

$$\Gamma = \frac{\Gamma_\infty k_1 Ce\ \frac{1}{n} + k_2 Ce^{n-1}}{1 + k_1 Ce\ 1 + k_2 Ce^{n-1}} \qquad (3)$$

where Γ (mg/g) is adsorption capacity of RhB, Γ_∞ (mg/g) is the maximum adsorption capacity, k_1 (g/mg) and k_2 $(g/mg)^{n-1}$ are equilibrium constants for first layer adsorption and clusters of n molecules.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The pH of the solution plays an important factor on the adsorption because pH strongly affect to surface charge and charging behavior of RhB in the solution. The effect of pH on RhB removal with initial concentration of 10^{-5} M using laterite and SML is studied in the pH range of 3-10 (Figure 1) while other parameters were kept constant, including contact time 120 min, adsorbent amount 10 mg/mL, initial concentration of RhB 10^{-5}M and temperature 25 $^oC \pm 2$ ^oC.

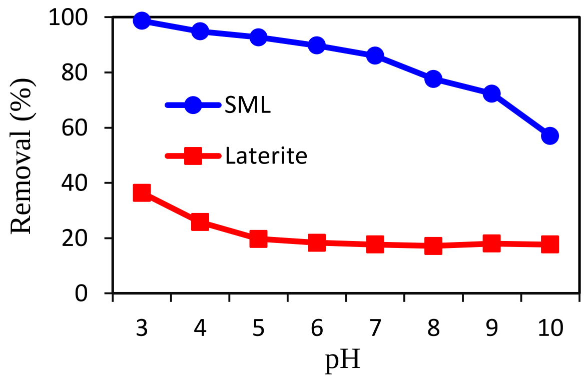

Figure 1. The removal of RhB using laterite and SML at different pH.

In Figure 1, the removal of RhB using SML decreased from 98.69 % to 57.03 % with the increase of pH from 3 to 10. This trend can be explained that the desorption of SDS is increased with increasing pH. When SDS desorption takes place, the surface charge of SML is less negative which leads to the reduction of adsorption of cationic RhB dye onto the surface of SML.

As can be seen in Figure 1, the maximum removal of RhB using laterite is only 36.41% at pH 3, and decreased gradually to 17.67 % with increasing pH from 3 to 10. Figure 1 also indicates that the RhB removal using laterite is much lower than that using SML. At the same initial concentration of 10^{-5} M RhB, removal of RhB using SML is about 3 times greater than that using laterite. At pH lower than 4, the formation of RhB is changed (pKa 3.7), so that pH 4 is selected for future studies.

3.2. Effect of adsorbent amount

The adsorbent amount is important factor because it is proportional to the total surface area of the adsorbent. The effects of adsorbent amounts of laterite and SML on the removal of RhB are shown in Figure 2. Other parameters such as contact time of 120 min, pH of 4, initial concentration of RhB of 10^{-5} M and temperature of 25 °C ± 2 °C were fixed.

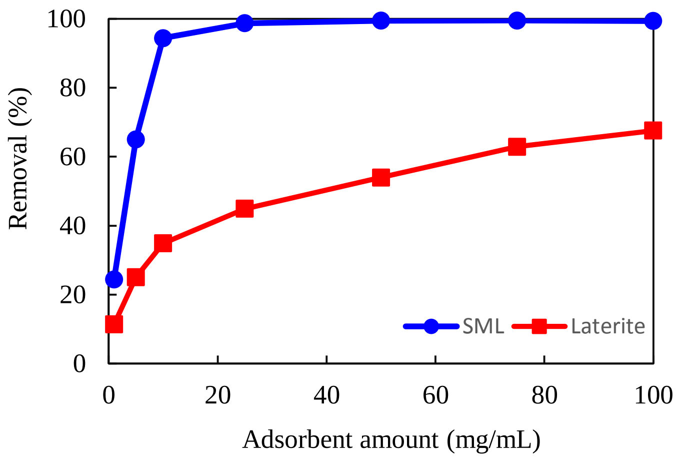

Figure 2. The removal of RhB using laterite and SML at different adsorbent amounts.

Figure 2 and Table 1 show that the removal of RhB using laterite increases from 11.36% to 67.56 % with increasing laterite adsorbent dosages from 1 to 100 mg/mL. This may be due to the increase of coagulation of laterite particles when increasing their amount [12, 13]. For SML, the removal efficiency increases with increasing SML amount and reaches to maximum (100 %) with SML amount of 25 mg/mL. When SML amount is higher than 25 mg/mL, the RhB removal is unchanged. However, increasing adsorbent amount from 10 mg/ leads to the decrease in the adsorption capacity due to the aggregation of laterite particles at high adsorbent dosages [14]. Therefore, the optimum SML amount is of 10 mg/mL g which is kept constant for further experiments.

3.3. Effect of ionic strength

Ionic strength affects the electrostatic attraction between ionic adsorbates and oppositely charged adsorbents, as well as the desorption ability of SDS from the surface of SML adsorbent. In this investigation, salt concentrations were varied from 0 to 200 mM, while the contact time

120 min, pH 4, adsorbent amount 10 mg/mL, initial concentration of RhB 10^{-5} M and temperature 25 ^{0}C ± 2 ^{0}C were kept constant.

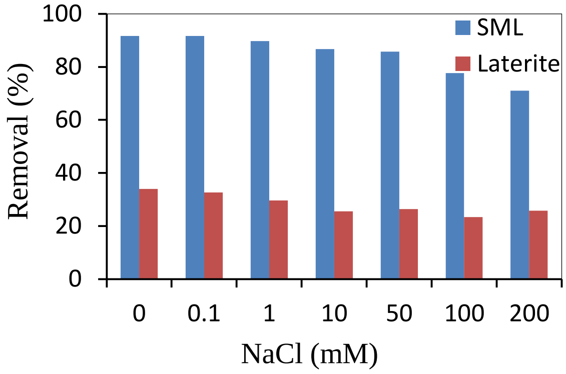

Figure 3. The removal of RhB using laterite and SML at different NaCl concentrations.

Figure 3 shows that the percentages of removal of RhB using SML are all higher than those using unmodified laterite at all investigated salt concentrations. However, these removals decrease when increasing salt concentrations from 0 to 200 mM. In order to demonstrate the effect of ionic strength in more detail and predict the mechanisms, adsorption isotherm is investigated and indicated below.

3.4. Adsorption isotherms

The effect of ionic strength on the adsorption of RhB onto SML was studied at three NaCl concentrations in pH 4 and shown in Figure 4.

Figure 4 shows that the adsorption capacity of RhB decreased with increasing NaCl concentrations from 1 to 100 mM. RhB adsorption capacity achieved the maxima at the lowest salt concentration. When increasing salt, the number of counter Na^+ ions increases and the competitive adsorption between Na^+ and cationic dye RhB onto the SML is enhanced [15]. Furthermore, the electrostatic attraction is also screened by increasing salt [8]. It implies that electrostatic attraction between the cationic RhB molecules and oppositely charged SML surface mainly controlled the adsorption.

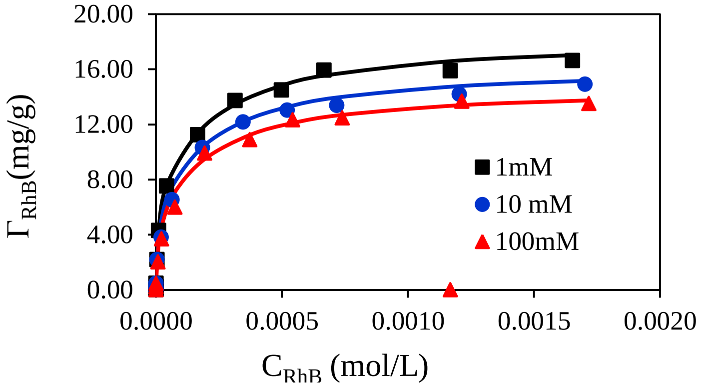

Figure 4. Adsorption isotherms of RhB onto SML at different NaCl concentrations. Points are experimental data, solid lines are fitted by the two-step model.

Figure 4 also indicates that at different NaCl concentrations, the adsorption isotherm of RhB onto SML can be fitted well by general equation Eq. (3). The fitting parameters in Table 1 were optimized to obtain the best fit. At different salt concentrations, adsorption increases with increasing initial RhB concentration and the higher adsorption capacity is obtained at the lower NaCl concentration. The maximum adsorption of 18 mg/g for RhB at 1mM NaCl decreased to 14.5 mg/g at 100 mM NaCl. When concentration of NaCl increases from 1 mM to 100 mM, an increase of k_1 is observed while k_2 and n are not changed. It means that the value of k_2 and n do not depend on salt concentration. These results demonstrate that adsorption of RhB on SML is mainly induced by electrostatic attraction.

Table 1. The fitting parameters for RhB adsorption onto SML.

C_{NaCl} (mM)	$\Gamma_{\infty,RhB}$ (mg/g)	$k_{1,\ RhB}$ (g/mg)	$k_{2,\ RhB}$ $(g/mg)^{n-1}$	*N*
1	18	1.0×10^5	2.0×10^4	2.2
10	16	8.5×10^4	2.0×10^4	2.2
100	14.5	8.0×10^4	2.0×10^4	2.2

1.1. Regeneration of SML

The reuse potential of absorbent is important to estimate ~~novelty~~ the utility of SML. Thus, two parallel experiments were performed to study the reusability of the adsorbent [16]. The regeneration was carried out with five cycles of adsorption/desorption. The adsorbed RhB onto SML was desorbed by using 0.1M NaCl and 0.1 M HCl solutions, the desorbed SML samples were then washed with ultrapure water until the concentration of RhB reached to lower than detection limit of UV-Vis method (10^{-7} M for RhB). The result of reuse SML is indicated in Figure 5.

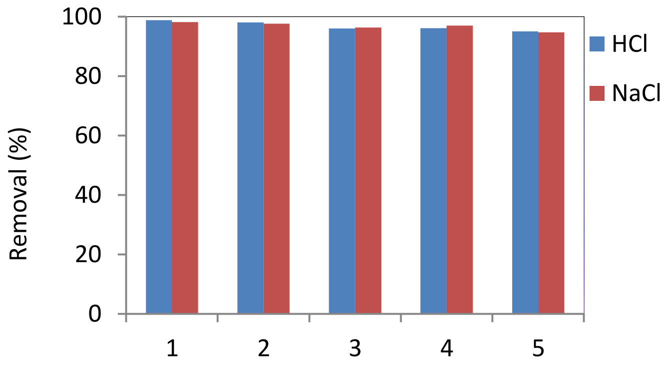

Figure 5. The removal of RhB using regenerated SML within 5 cycles.

As can be seen in Figure 5, the removal of RhB using regenerated SML is only slightly decreased as increasing number of regeneration cycles. However, the removal RhB using SML at 5^{th} cycle of regeneration is still higher 90 %. This result demonstrates that surfactant modified laterite is a novel adsorbent in terms of economic and environmental aspects.

4. CONCLUSIONS

We have studied the removal of Rhodamine B (RhB) using laterite and surfactant modified laterite (SML). The removal efficiency of RhB using SML is all higher than that using unmodified laterite. The optimum conditions for removal of RhB using SML were found to be of pH 4, adsorbent amount 10 mg/mL and ionic strength 0.1 mM NaCl. Adsorption isotherms of RhB onto SML at three NaCl concentrations were fitted well by two-step adsorption model. The adsorption of RhB onto SML decreased with increasing ionic strength due to electrostatic interactions between cationic dye RhB and negatively charged SML surface. Within five cycles of adsorption/regeneration SML, the removal efficiency of RhB was still higher than 90 %, indicating that SML is an economic and novel adsorbent for cationic dye removal.

Acknowledgements. This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.05-2016.17.

REFERENCES

1. Adak A., Bandyopadhyay M., and Pal A. - Removal of crystal violet dye from wastewater by surfactant-modified alumina, Sep. Purif. Technol. **44** (2) (2015) 139–144.
2. Selvam P. P., Preethi S., Basakaralingam P., Thinakaran N., Sivasamy A., and Sivanesan S. - Removal of rhodamine B from aqueous solution by adsorption onto sodium montmorillonite, J. Hazard. Mater. **155** (1–2) (2008) 39–44.
3. Gupta V. K., Suhas, A. I., and Saini V. K. - Removal of Rhodamine B, Fast Green, and Methylene Blue from Wastewater Using Red Mud, an Aluminum Industry Waste, Ind. Eng. Chem. Res. **43** (7) (2004) 1740–1747.
4. Wang M., Fu J., Zhang Y., Chen Z., Wang M., Zhu J., Cui W., Zhang J., and Xu Q. - Removal of Rhodamine B, a Cationic Dye From Aqueous Solution Using Poly(cyclotriphosphazene-co-4,4′ sulfonyldiphenol) Nanotubes, J. Macromol. Sci. Part A **52** (2) (2015) 105–113.
5. Das S. K., Bhowal J., Das A. R., and Guha A. K. - Adsorption Behavior of Rhodamine B on Rhizopus oryzae Biomass, Langmuir **22** (17) (2006) 7265–7272.
6. Damiyine B., Guenbour A., and Boussen R. - Rhodamine B adsorption on natural and modified moroccan clay with cetyltrimethylammonium bromide: Kinetics, equilibrium and thermodynamics, J. Mater. Environ. Sci. **8** (3) (2017) 860-871.
7. Cuiping B. et al. - Removal of rhodamine B by ozone-based advanced oxidation process, Desalination **278** (1–3) (2011) 84–90.
8. Pham T. D., Nguyen H. H., Nguyen N. V., Vu T. T., Pham T. N. M., Doan T. H. Y., Nguyen M. H. and Ngo T. M. V. - Adsorptive removal of copper by using surfactant modified laterite soil. J. Chem. **2017** (2017) 10.
9. Rosen M. J. and Kunjappu J. T. - Surfactants and interfacial phenomena, chapter 2: Adsorption of surface active agents at interface, 53-60, Wiley, 2012.
10. Maiti A., Basu J. K., and De S. - Experimental and kinetic modeling of As(V) and As(III) adsorption on treated laterite using synthetic and contaminated groundwater: Effects of phosphate, silicate and carbonate ions, Chem. Eng. J. **191** (2012) 1–12.
11. John Y., Emery V. D. J., and Mmereki D. - A Comparative Study on Removal of

Hazardous Anions from Water by Adsorption: A Review, Int. J. Chem. Eng. **2018** (2018) 1–21.

12. Mazloomi F. and Jalali M. - Ammonium removal from aqueous solutions by natural Iranian zeolite in the presence of organic acids, cations and anions, J. Environ. Chem. Eng. **4** (2) (2016) 1664–1673.
13. Pham T. D., Do T. T., Ha V. L., Doan T. H. Y., Nguyen T. A. H., Mai T. D., Kobayashi M. and Adachi Y. - Adsorptive removal of ammonium ion from aqueous solution using surfactant-modified alumina, Env. Chem. **14** (2017) 327-337
14. Papić S., Koprivanac N., Lončarić Božić A., Meteš A. - Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process, Dyes and Pigments **62** (2004) 291-298.
15. Pham T. D., Kobayashi M. and Adachi Y. - Adsorption characteristics of anionic azo dye onto large α-alumina beads, Colloid Polym Sci. **293** (2015) 1877-1886.
16. Pham T. D., Bui T. T., Nguyen V. T., Bui T. K. V., Tran T. T., Phan Q. C., Pham T. D. and Hoang T. H. - Adsorption of Polyelectrolyte onto Nanosilica Synthesized from Rice Husk: Characteristics, Mechanisms, and Application for Antibiotic, Polymers **10** (2018) 220.