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BARIUM CHLORIDE MODIFICATION OF DIATOMITE FOR REMOVAL OF METHYLENE BLUE AND LEAD ION FROM AQUEOUS SOLUTION

Le Van Tan* **and Le Thiet Hung**
Department of Chemical Engineering, Industrial University of Ho Chi Minh City-70000, Vietnam
*E-mail: levantan@iuh.edu.vn

ABSTRACT
In this research, the surface of natural diatomite was modified with Barium chloride by hydrothermal method for removal of methylene blue and lead ions. The characterization of natural and modified diatomite was investigated by SEM, FT-IR and XRD. The Brunauer-Emmett-Teller (BET) surface area exhibited that the similar surface areas were obtained between the clean diatomite and modified diatomite. In this study, modified diatomite was attempted to enhance the adsorptive capabilities of diatomite for methylene blue and lead ions. The effect of some operational parameters such as initial concentration and pH on the adsorptive capacity of the diatomite was tested. The sorption rate was affected significantly by the initial concentration of the solution, sorbent amount and pH value of the solution. Batch experiments were conducted to investigate the adsorption effect under different initial concentration (ranging from 50 to 200 mg/L), solution pH (4, 6, 8 and 10), and contact time (0.5 to 12h).
Keywords: diatomite, methylene blue, heavy metal, wastewater

INTRODUCTION

Dyes are widely used in broad industrial sectors such as textile manufacturing, leather tanning, cosmetics, paper, food processing, and pharmaceutical industries. There are many classes of dyes such as azo, anthraquinone, reactive, acidic, basic, neutral, disperse and direct dyes. It is estimated that 5–50 % of unfixed dyes are lost in the effluent during the dyeing process[1]. The growth in the textile dyeing and dyestuff manufacturing industries has resulted in a proportional increase in the volume and complexity of the wastewater discharged to the environment. Chemical pollution caused by these processes has become a concern for many countries which urgently requires environmental measures. These compounds color the water and make penetration of sunlight to the lower layers impossible and hence affecting aquatic life. Many of these are toxic, carcinogenic, mutagenic, or even stable to biological degradation[2]. A wide range of methods have been developed for the removal of textile dyes from the wastewaters such as biological methods, membrane filtration, coagulation–flocculation, electrocoagulation and adsorption[3,4].

Activated carbon is a frequently used method to removal organic pollutants from wastewater but is an expensive material and its use for pollution control applications cannot be justified. The research has been directed towards methods of treatment using natural materials, locally available and effective adsorbents, such as natural diatomite. Diatomite is a material of sedimentary origin consisting mainly of an accumulation of skeletons formed as a protective covering by diatoms. The skeletons are essentially amorphous hydrated or opaline silica but occasionally are partly composed of alumina. Diatomite usually contains other sediments such as clay and fine sand but its deposits sometimes consists of diatom shells only[5]. However, the raw diatomite frequently contains an important rate of impurities that can restrain its efficiency in many applications[6].

In this present research, modification of diatomite surface by barium chloride was reported and its use in adsorption of heavy metal ions and textile dyes in wastewater.

EXPERIMENTAL

Adsorbent Preparation

The diatomite sample was obtained from Hoa Loc, Phu Yen (Viet Nam) and the chemical composition of diatomite obtained by X-ray florescence (XRF) is 82.4% SiO_2, 8.95% Al_2O_3, 6.49% Fe_2O_3, 0.483% MgO, 0.175% K_2O and 0.13% CaO. Firstly, 200 g of diatomite (100 mesh) were immersed in 1000 mL of $BaCl_2$ solution with various concentrations (15-100 g/L), a certain amount of 0.5 mol/L H_2SO_4 was immediately added into the mixture and then shook at room temperature for 3 h under mechanical stirrer. Then, the mixture was exposed to air for 12 h and discard the supernatant and afterwards dried in an oven at 105, 300, 400 and 500 ^oC for 24 h. Finally, the samples were grinded to 100 mesh and stored in the dry box for further study. The prepared samples were named as DA30T105, DA30T300, DA30T400, DA30T500; DA60T105 DA60T300, DA60T400, DA60T500; DA100T105, DA100T300, DA100T400, DA100T500.

Characterizations

The mineral phase of diatomite was characterized by X-ray diffraction (XRD) (Rigaku, Japan). The surface of diatomite and modified-diatomite was observed by using a scanning electron microscope (SEM, JEM-4800). X-ray fluorescence spectrometer (XRF) provided us the element contents.

Adsorption Experiments

Synthetic industrial wastewater was used in the adsorption studies. The solution was prepared by dissolving methylene blue (MB) in deionized water.

Lead (II) stock solution (1000 mg/L) was prepared by dissolving the 1.598 g $Pb(NO_3)_2$ salts in 1000 mL deinoized distilled water. All the solutions for lead removal experiments and analysis were prepared by an appropriate dilution of the stock solution. Adsorption of modified diatomite was performed in a set of Erlenmeyer flasks (250 ml) contained 25 ppm MB solutions (100 mL). The difference types of prepared diatomite (0.05g) was added to MB solutions, and the resulting mixtures were then kept at room temperature. The aqueous samples were taken at determined intervals, and the concentrations of dye were measured at 665 nm, using UV–vis spectrophotometer. The amount of adsorption at time t, q_t (mg/g), is calculated by $q_t = (C_0 - C_t)*V/W$ where C_0 and C_t (mg/L) are the liquid-phase concentrations of MB at initial and any time t, respectively; V is the volume of the solution (L) and W is mass of absorbent (g).

0.5 g of diatomite and 100 mL of $Pb(NO_3)_2$ solution 50 ppm were added in 150 mL conical flask and then were placed in a shaker with a speed of 100 rpm. The concentrations of Pb ions remaining in the supernatant were measured using standard methods recommended for examination of water and wastewater[7].

RESULTS AND DISCUSSION

Preparation and characterization of diatomite

The structure of modified diatomites were characterized by FT-IR, XRD, and SEM. In Figure 1, the general range 3700 – 3440 cm^{-1} may be assigned to asymmetrical and symmetrical O-H stretching vibration modes for water of hydration and the peak at 1632 cm^{-1} belonged to O-H bending vibration modes. The presence of SiO_2 is verified by adsorption bands at 1097 cm^{-1} of asymmetric Si-O-Si stretching vibrations, and Si-O-Si bending vibrations at 468 cm^{-1}. In brief, XRD patterns of 12.20, 20.85, 26365, 34.95, 50.15, 50.90, 62.20^o. The X-ray diffraction spectra displayed that silica was the major component. The cristobalite, quartz and feldspar noteworthy were revealed in the range of $25< 2\theta <33$ in the X-ray diffraction spectra, respectively (Fig.-2).The scanning electron microscope shows that the main pattern of the diatomite was discoid and the surface was porous structure. However, modified diatomite was relatively uneven and a number of pores were filled, it illustrates that the expected barium sulphate formed in the interspaces. Additionally, there was several $BaSO_4$ crystals separated out on diatomite surface and its pores.

Batch Adsorption Studies

In this study, the various amounts of $BaCl_2$ from 15 to 100 g/L were conducted for the removal efficiency of MB on modified diatomite. The results were shown in Figure 4. The removal efficiencies were increased with increasing the concentration of $BaCl_2$ from 0 to about 60 g/L and decreased with rising of $BaCl_2$ concentration to 100 g/L. This may be explained that deposition of $BaSO_4$, which was obtained from the reaction of $BaCl_2$ and H_2SO_4, improved pore structure of the diatomite, the impurities on the diatomite surface were eliminated by rubbing of $BaSO_4$, and the inner-channels in the diatomite were under-propped by $BaSO_4$, this was favorable for adsorption of MB onto the diatomite.

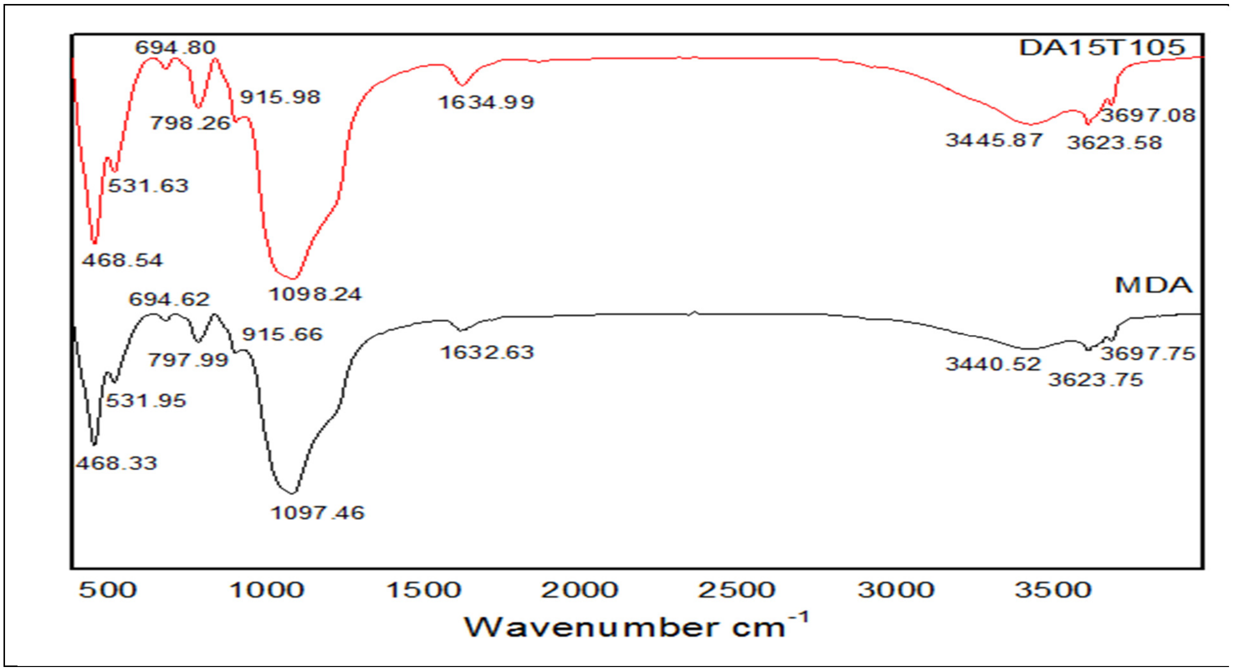


Fig.-1: FTIR spectra of modified diatomite (DA15T105) and natural diatomite (MDA)

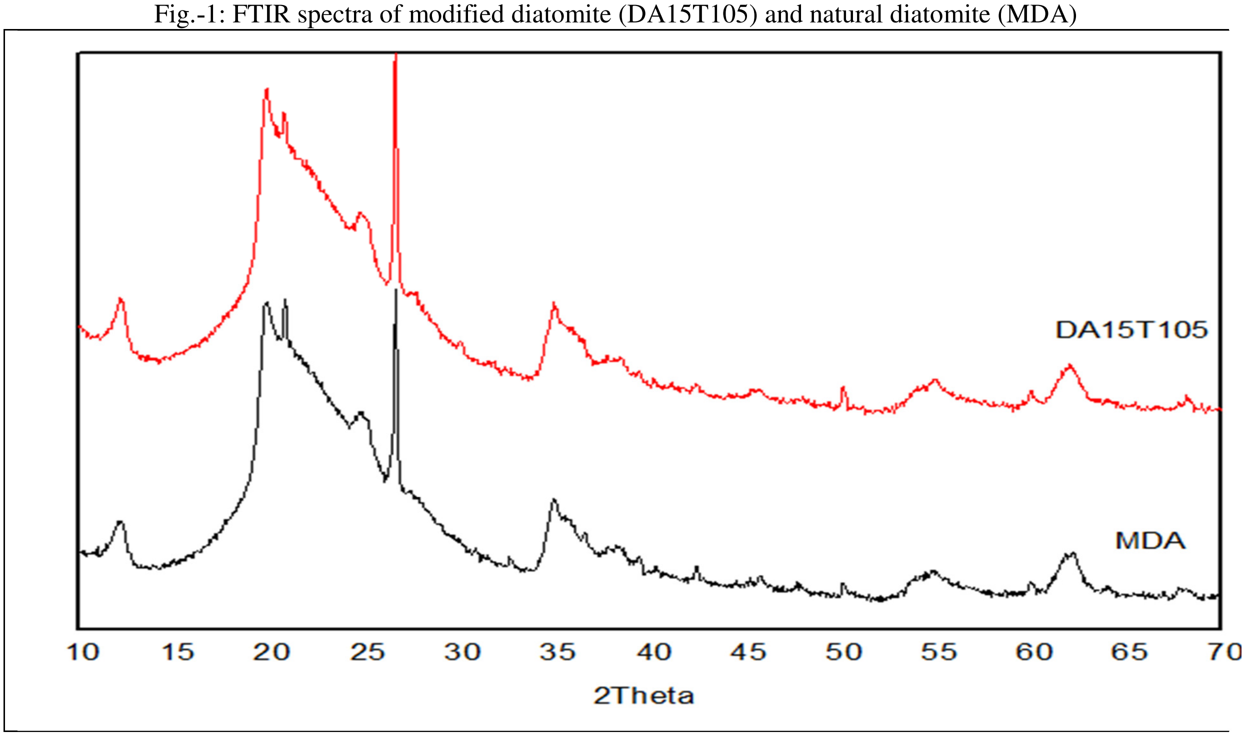
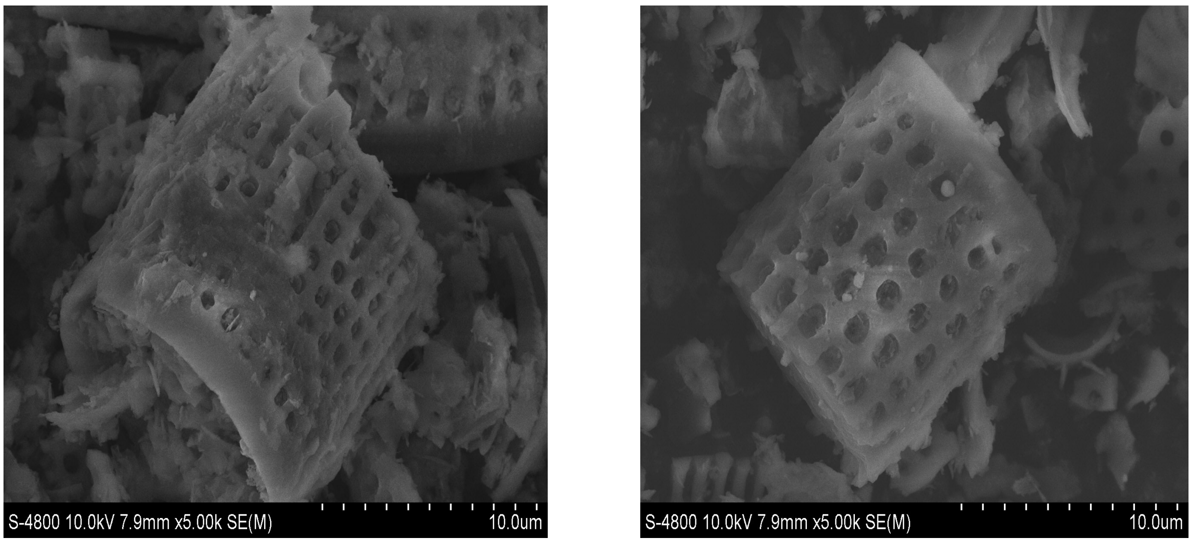


Fig.-2: XRD patterns of modified diatomite (DA) and natural diatomite (MDA)

The removal efficacy was increased from 78 to 95% for natural diatomite and modified diatomite with 60 g/L, respectively and decreased to 86% when the concentration of $BaCl_2$ was increased to 100 g/L. The results showed that the best concentration of the $BaCl_2$ solution for the diatomite chemical modification was 15 g/L. At optimized concentration of the $BaCl_2$ solution for the diatomite chemical modification, the several dried temperatures are conducted. As results, when calcination temperature was increased from 105 to 500 ^oC, the adsorption efficiency was decreased. The maximum adsorption efficiency was at 105 ^oC (Figure-5).



(a) (b)

Fig.-3: SEM images of – (a) diatomite; (b) modified diatomite

Effect of Initial Dye Concentration

The effect of initial concentration on the MB removal was shown in Figure 6. As results, it is remarkable that an increase in the initial concentration (50–200 ppm) of MB led to a decrease in the removal efficiency of diatomite at various contact times. This can be attributed to the mass transfer effects and the driving force of the concentration gradient being directly proportional to the initial concentrations. The plateau values indicated that the adsorption equilibrium was gradually attained. The maximum removal efficiencies were obtained within 2 min for all concentrations. The removal efficiencies were 98, 91 and 76 for concentrations of 50, 100 and 200 ppm, respectively. The removal efficiency dropped to 64% for natural diatomite at concentration of 100 ppm. Particularly, the UV-Vis absorption spectrum of MB at t = 0 min was highest due to no adsorption between diatomite with MB molecules. Otherwise, the lowest absorption spectrum of MB was more than 4 min (Figure-7).

The dependence of MB dye adsorption on diatomite dosage was studied by varying the adsorbent amount from 0.05 to 0.2 g while keeping the volume, 50 mL, of the dye solution constant (100 ppm). The results indicate that the percentage adsorption increases with increasing amount of adsorbent. The increase in the percentage adsorption with increasing amount of the sorbent is due to the greater availability of the adsorption sites at higher concentrations of the adsorbent (Figure-8).

Effect of various textile dyes

A study of adsorption capacity of various textile dyes on the modified diatomite under the best condition in aqueous solution was conducted; the results are shown in Figure-9. As can be seen, different textile dyes showed various removal efficiencies. The results show that methyl blue, methyl red and cationic blue adsorption on diatomite is very fast compared to that of reactive red and reactive yellow.

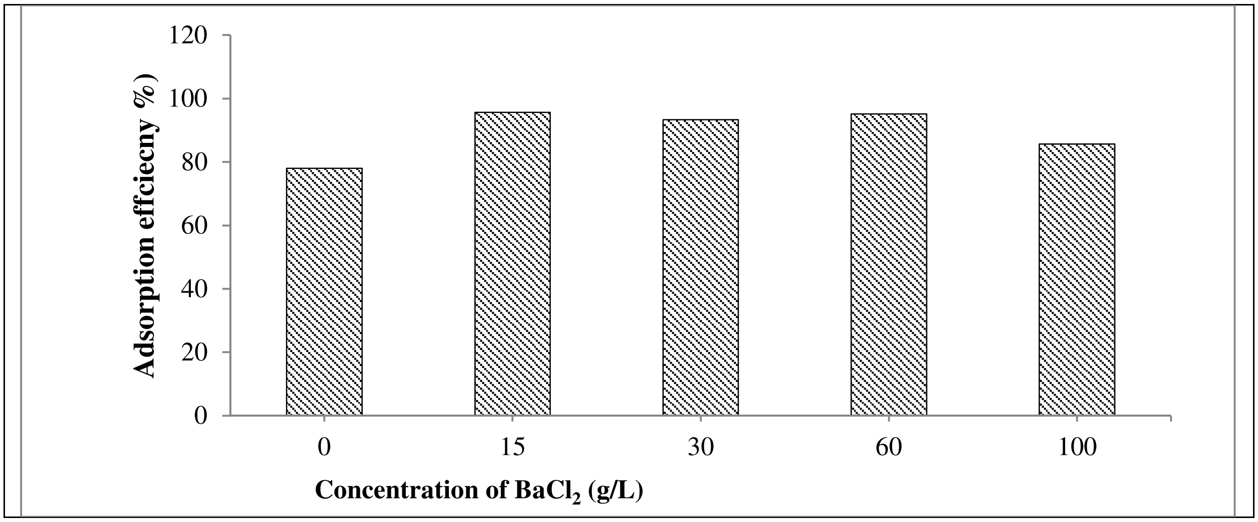


Fig.-4: The influence of the $BaCl_2$ solution concentration on the removal efficiency.

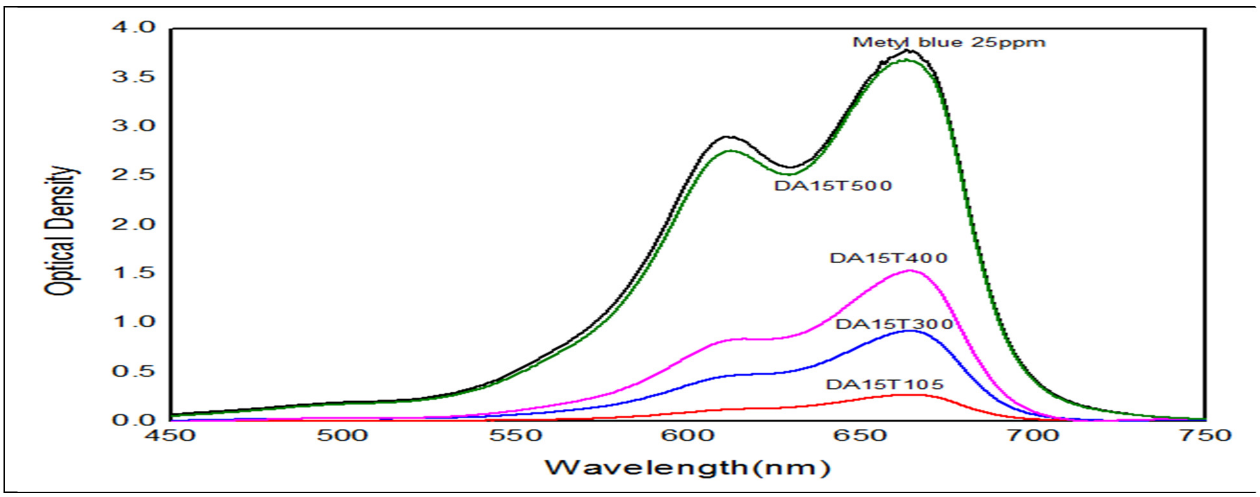


Fig.-5: The change in absorption spectra of MB for adsorption onto diatomite modification with $BaCl_2$ 15g/L dried at the various calcination temperatures.

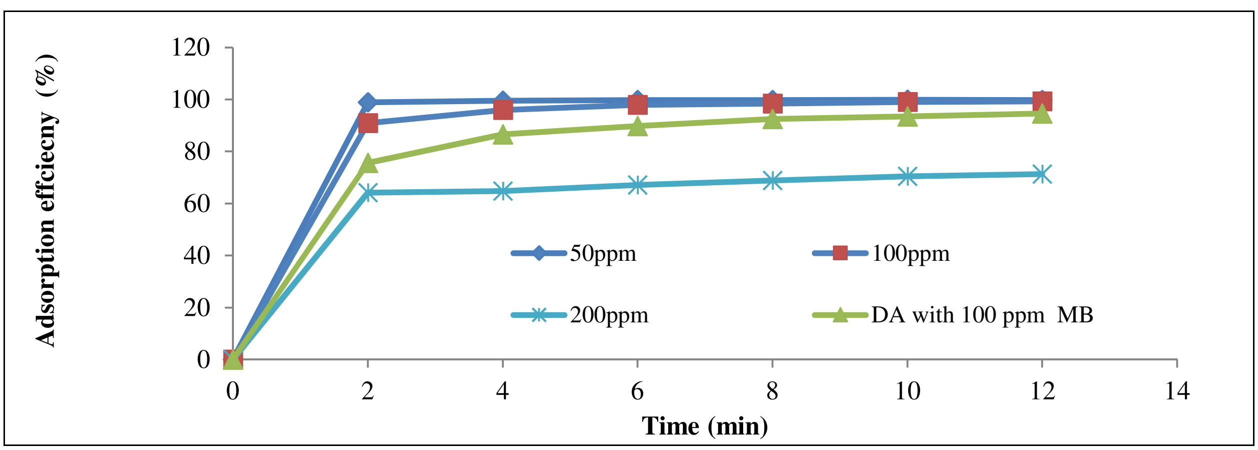


Fig.-6: Effect of initial concentration and contact time on equilibrium adsorption.

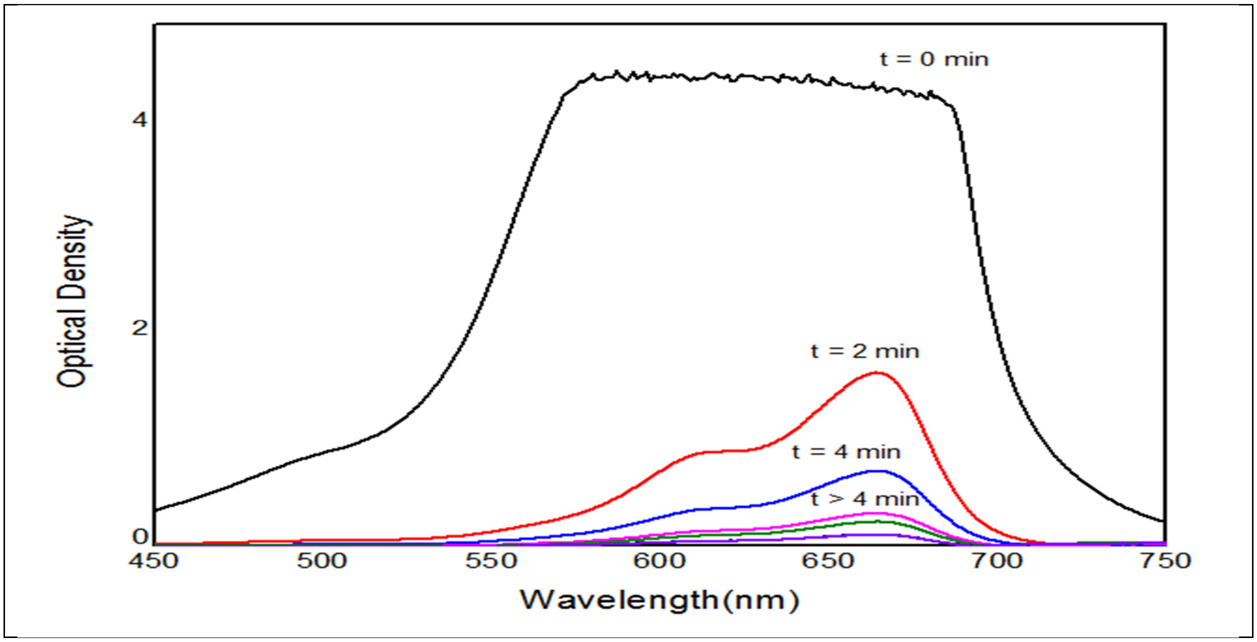


Fig.-7: The change in absorption spectra of MB for concentration of 100 ppm, modification of $BaCl_2$ 15g/L at 105°C.

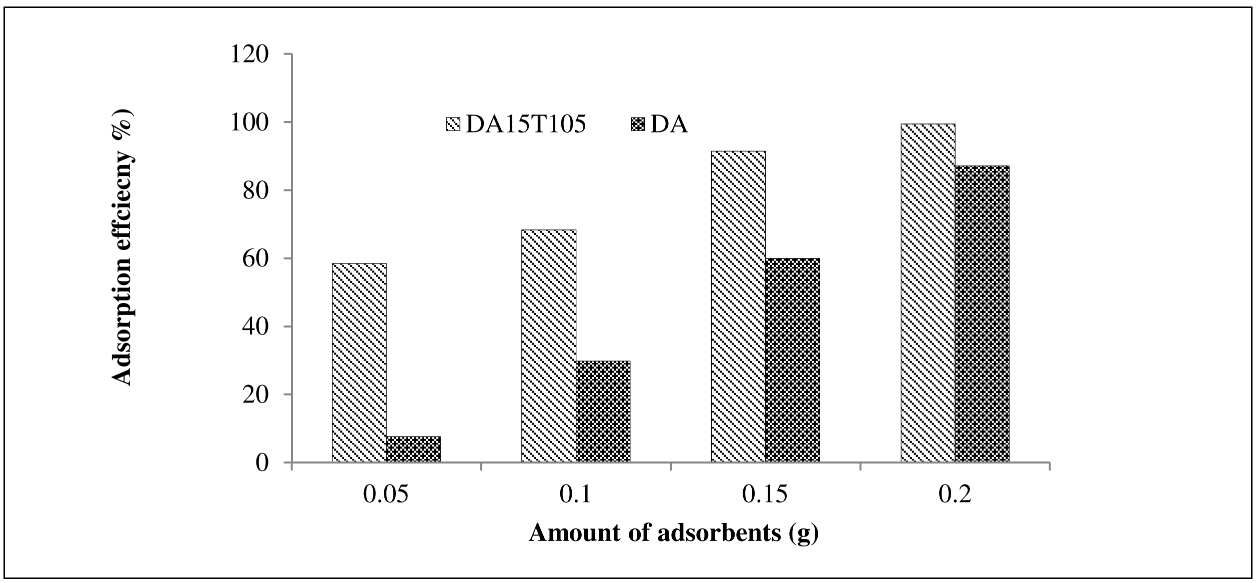


Fig.-8: Adsorption efficiency of MB onto different amount of diatomite (initial concentration of MB: 100 ppm; solution volume: 100 mL).

Removal of Pb^{2+}

Figure-10 showed that the curve of removal efficiency of Pb^{2+} on modified diatomite with various concentration of $BaCl_2$. The efficiency was increased with increasing of the $BaCl_2$ solution concentration. At low concentration, the deposition of $BaSO_4$, which was obtained from the reaction of $BaCl_2$ and H_2SO_4 led to improve pore structure of the diatomite. Additionally, the impurities on the diatomite surface were eliminated by rubbing of $BaSO_4$, and the inner-channels in the diatomite were under-propped by $BaSO_4$, this was favorable for adsorption of Pb^{2+} onto the diatomite. At high concentration, the deposition of

$BaSO_4$ restrained adsorption of Pb^{2+} on the diatomite due to its block; this led to decrease of the diatomite adsorption capacity against Pb^{2+}.

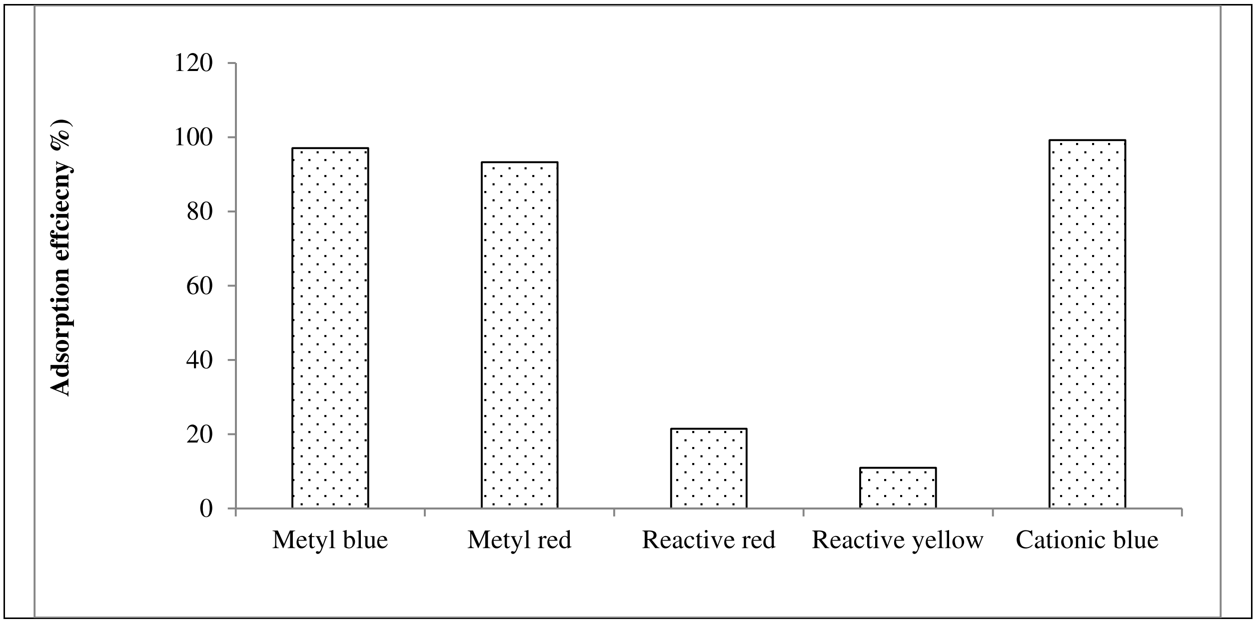


Fig.-9: Effect of pH of dye solution on removal efficiency.

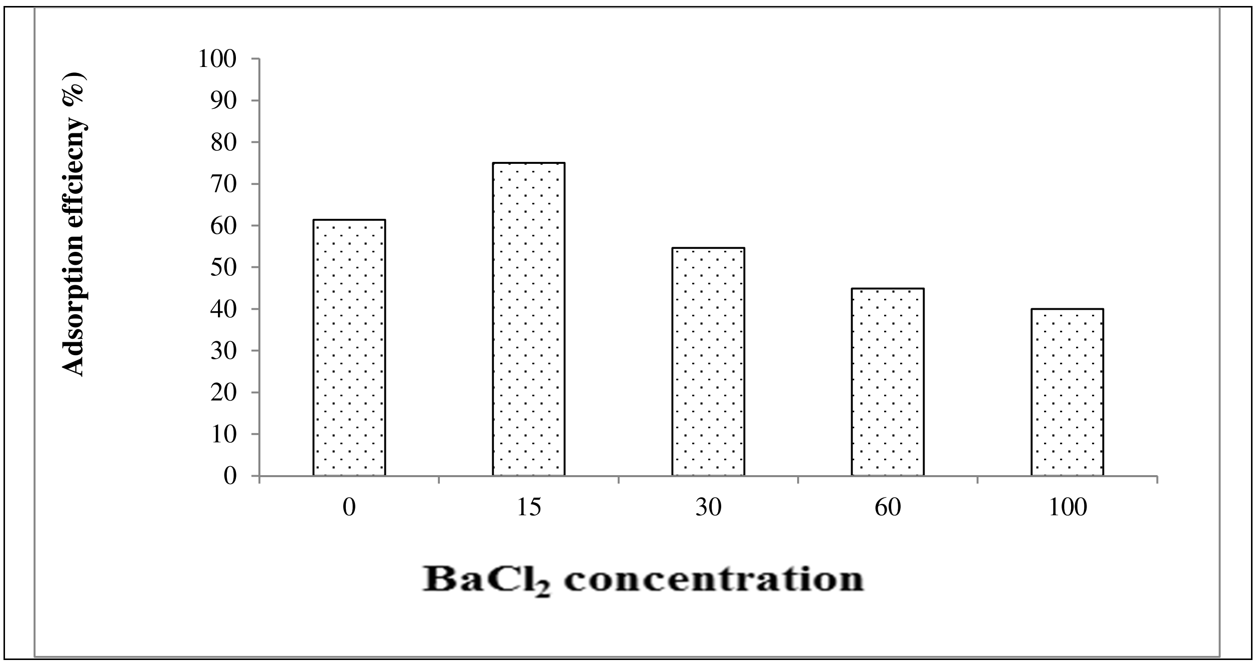


Fig.-10: The effect of $BaCl_2$ concentration on the removal efficiency of Pb^{2+}

CONCLUSION

In this present study, the modification of diatomite by $BaCl_2$ has successfully prepared and characterized. This study shows that diatomite is potential sorbent for removal of textile dyes from water. Diatomite is a locally available, low-cost adsorbent in Viet Nam. Comparing with the natural diatomite, the adsorption

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efficiency for textile dyes on modified diatomite was higher than that of natural diatomite. Additionally, the adsorption efficiency for the lead ions increased from 61% to 75%, indicating that Ba-diatomite was an effective absorbent for removing lead ions from wastewater.

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