THE STUDY ON THE ADSORPTION OF METHYLENE BLUE (MB) ONTO MAGNETICALLY MODIFIED SPENT COFFEE GROUNDS (MSCG)

Đến tòa soạn 16 - 6 - 2015

Bùi Xuân Vững, Ngô Văn Thông
Chemistry Department, Danang Education University

TÓM TẮT

NGHIÊN CỨU HẤP PHỤ THUỐC NHUỘM METHYLEN XANH BẰNG VẬT LIỆU BÃ CÀ PHÊ TỪ TÍNH

Bài báo này trình bày kết quả nghiên cứu về khả năng hấp phụ methylene xanh của bã cà phê có từ tính. Vật liệu hấp phụ này nhận được từ việc cho bã cà phê sau khi chiết bằng nước nóng tiếp xúc với dung dịch nano oxit sắt từ Fe_3O_4. Thành phần vật liệu đã được kiểm tra bằng các phân tích SEM và nhiễu xạ tia X. Các yếu tô ảnh hưởng đến sự hấp phụ của methylene xanh lên vật liệu này như thời gian cân bằng hấp phụ, nhiệt độ, pH và nồng độ ban đầu của methylene blue đã được khảo sát. Các số liệu cân bằng hấp phụ được đánh giá bằng phương trình Langmuir. Kết quả cho thấy ở pH 8 và tại nhiệt độ phòng, thời gian cân bằng hấp phụ khoảng 60 phút và dung lượng cực đại hấp phụ là 30.67 mg.g-1. Vật liệu sau khi hấp phụ được thu hồi dễ dàng từ dung dịch nước bởi một nam châm vĩnh cửu. Các kết quả thu được đã chứng minh cho khả năng sử dụng bã cà phê được từ tính hóa để loại bỏ các thuốc nhuộm trong nước thải.

1. INTRODUCTION

One of the most effective physical processes for the removal of pollutants from wastewater is adsorption [1]. The adsorbent widely used in industrial applications is activated charcoal due to its excellent adsorption capacity. However, this adsorbent has high costs and difficult generation [2]. That is the reason why there have been a lot of efforts, in recent times, to produce low-cost adsorbents replacing activated charcoal.

Spent coffee grounds (SCG) are the main waste discharged with a very large amount from the production of instant coffee by thermal water extraction from roasted coffee bean. The main composition of this waste is polysaccharides such as cellulose and galactomannans that are insoluble solids during the extraction process [3].

SCG can be used as compost and feedstock, yet most of them are burned as a waste, which leads to the production of CO_2, the green house gas [4]. Clearly, it is necessary to find out the way of reusing this waste for more useful purposes. In recent times, spent coffee grounds have been used as an adsorbent for removal of lead [5], chromium [6] and other heavy metal ions [7-9].

Magnetic separation is a promising technique for adsorption of target compounds from difficult-to-handle samples. Magnetic modification of inexpensive adsorbents and carriers can lead to materials suitable for large-scale biotechnology and environmental applications [10]. MSCG were prepared as a possible inexpensive adsorbent and its potential for the adsorption to remove organic dyes from aqueous solutions.

In the current work, we have investigated the adsorption of MB, a common cationic dye, onto MSCG prepared by contacting the material with a ferrofluid containing magnetite nanoparticles.

2. EXPERIMENTAL

2.1. Material and experimental methods

Raw spent coffee grounds obtained from a coffee shop in Danang city. Ferrous chloride ($FeCl_2 \cdot 4H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), Acid perchloric (70 wt.% in water), hydrogen chloride, sodium hydroxide, methyl alcohol and MB were purchased from China. All other chemicals were of analytical grade.

2.2 Preparation of adsorbent

The raw spent coffee grounds were washed with hot water until the washing solution was colorless so that soluble and coloured compounds were completely removed. The solid was then dried at 60 °C for 24 h. Lastly, the resulting spent coffee grounds were ground, sieved to < 0.5 mm and stored at room temperature in the dark until use.

2.3 Preparation of magnetically modified spent coffee grounds

The preparation of aqueous ferrofluid was based on the procedure reported by Berger et al.[11] with some modifications. Magnetite (Fe_3O_4) nanoparticles were first produced by combining 4 mL of 1M $FeCl_3$ solution and 4 mL of 0.5 M $FeCl_2$ and then adding very slowly 150 mL of aqueous 0.1 M ammonia solution whilst stirring. After the addition was complete, stop stirring. The black precipitate were magnetically decanted by a strong magnet and rinsed several times with distilled water to remove water-soluble impurities. Finally, the solid was resuspended in 2M perchloric acid solution. For preparation of the magnetically modified material, 5.00 g of the spent coffee grounds were suspended in 40 mL methanol with 5 mL of the ferrofluid. The suspension was stirred for 1 h at room temperature. Then, the magnetically modified spent coffee grounds were repeatedly washed with methanol and air dried.

2.4 Characterization of prepared MSCG

MSCG samples were sent to Institute of Materials Science belonged to Vietnam Academy of Science and Technology for analysis. The morphological analysis of SCGs samples was performed by a scanning electron microscope (SEM S-4800, Hitachi, Japan). X-ray diffraction

(XRD) analysis was carried out with a Siemens D5000 diffractometer (Siemens, Germany) using Cu Kα radiation at λ = 1.54056 Å. Diffraction patterns were recorded from 20° to 90° 2θ at a scan rate of $1°.min^{-1}$.

2.5 Adsorption Experiments

Adsorption experiments were performed in batch mode. MSCG and the dye solution were initially loaded into glass flasks, which were stirred with agitation rate of 150 rpm at determined temperature for the required time. After that, the adsorbent was separated from the heterogeneous mixture using a permanent magnet and then the solution was analyzed for dye concentration. The concentration of MB was determined spectrophotometrically at 665 nm [14], using UV–VIS LAMBDA spectrometer (USA).

In the current work, the adsorption of MB onto the MSCG as a function of pH, contact time, temperature in equilibrium and initial MB concentration was investigated.

The effect of pH was conducted by mixing 0.1 g of the adsorbent with 30 mL of 50 mg/L MB solution at temperature of 25°C, magnetically stirring the mixture with 150 rpm for 01 h. The pH value, ranging between 4 and 9, was kept constant throughout the adsorption process by micro-additions of HNO_3 (0.01 mol/L) or NaOH (0.01 mol/L).

To determine the effect of the mass of adsorbent, experiments were carried out varying the dosage (0.05–0.5 g of the MSCG/30 mL of 50 $mg.L^{-1}$MB solution) and keeping constant all the other parameters: pH free; 25 °C; 150 rpm; 1 h.

All parameters of experiments to determine the effect of contact time were kept constant: dosage (0.1g of the MSCG/30 mL of 50 $mg.L^{-1}$MB solution); pH free; 25 °C; 150 rpm. After the time interval of 10 minutes, the remaining concentration of MB in the solution was spectrophotometrically determined until the total adsorption time was 90 mimutes. Similarly, the effect of temperature in equilibrium was investigated when temperature was changed in the range from 25 °C to 60 °C.

The effect of initial MB concentration on equilibrium was observed by mixing 0.1 g of the MSCG with 30 mL of dye solutions of different initial MB concentrations (10–60 mg/L).The suspensions were stirred for 01 h at pH free in water bath at 25 °C (agitation rate = 150 rpm). The equilibrium data were analyzed by the Langmuir and the Freundlich models.

3. RESULTS AND DISCUSSION

3.1. Characterization of the MSCG

3.1.1. SEM analysis

Figure 1 shows the SEM images of the SCG (left) and the prepared MSCG (right). As can be seen from these SEM micrographs, the SCG has porous structures and many cavities, which allow adsorbing Fe_3O_4 nano particles in the ferrofluid. A little bit of differences in surface morphology were observed between untreated and magnetically modified SCG supporting the fact that the deposition of Fe_3O_4 nano particles onto the surfaces of the MSCG took place.

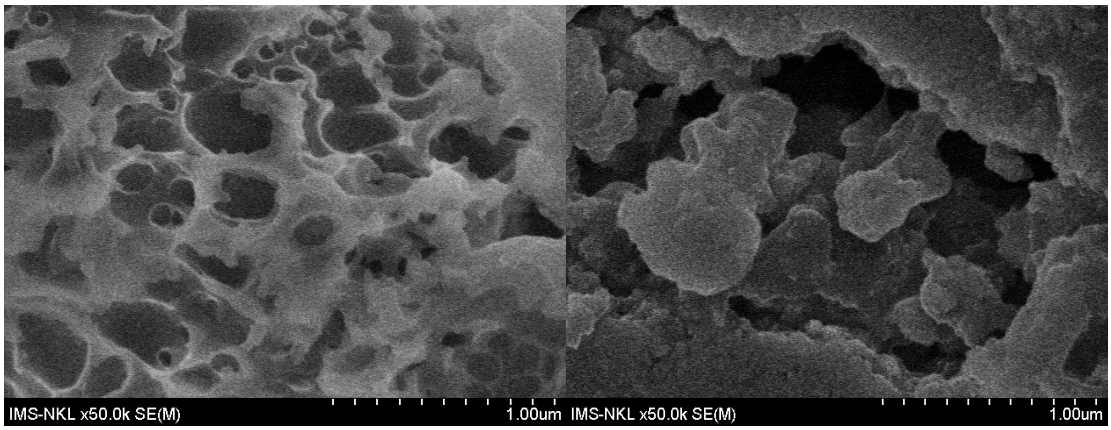

Figure 1: Scanning Electron Micrograph of the SCG (left) and the prepared MSCG (right).

3.1.2. X-ray diffraction analysis

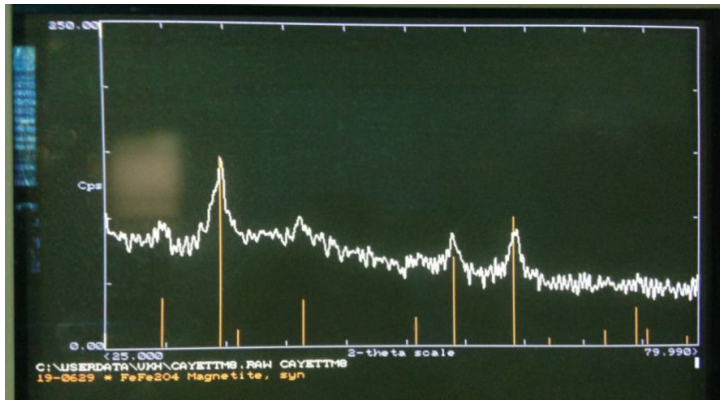

Figure 2: XRD pattern of the MSCG with the characteristic peaks of magnetite

The XRD pattern of the prepared magnetically modified SCG was presented in Figure 2. We can see from this figure the five characteristic peaks at 2θ = 29.9°, 35.6°, 42.8°, 53.2° and 56.9° correspond to the planes (220), (311), (400), (422) and (511) of magnetite (Fe_3O_4). This demonstrates that the magnetic particles are deposited on the surface of the SCG when we made the exposure of the SCG to the water-based ferrofluid leading to the formation of the magnetic adsorbent. The average size of magnetite crystallites was estimated from the strongest diffraction peak (at 2θ = 35.6°) by the Scherrer equation:

$$D = \frac{0.89\lambda}{B.cos\theta}$$

where D is the average crystallite size, λ is the wavelength of Cu Kα radiation = 1,54056Å , β is the full-width at half maximum of the peak and θ is the Bragg diffraction angle. The average size D = 4.15 nm. Figure 3 shows the images of the prepared magnetically modified SCG and the separation of this material from the suspensions by a permanent magnet.

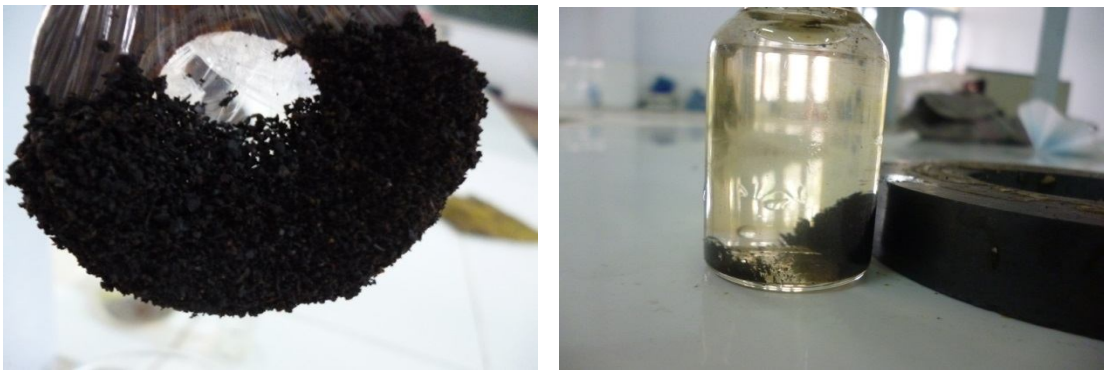

Figure 3: The prepared MSCG (left) and the separation of the MSCG by a permanent magnet (right)

3.2. Adsorption Experiments

3.2.1. Effect of pH

The effect of pH on the adsorption of MB onto the magnetic SCG is presented in Figure 4. In general, the higher dye uptakes were showed in basic pH-region. MB is a potent cationic dye and at basic pH values, the surface of the magnetic adsorbent can be easily charged negatively due to the excess of OH^- groups in the solution. Therefore, the negatively charged adsorbent can be easily charged negatively due to the excess of OH^- groups in the sites of the adsorbent can interact with the positive amino groups of MB, forming a strong bond between adsorbent and dye.

At pH> 8, more than 95% of MB adsorbed onto the adsorbent.

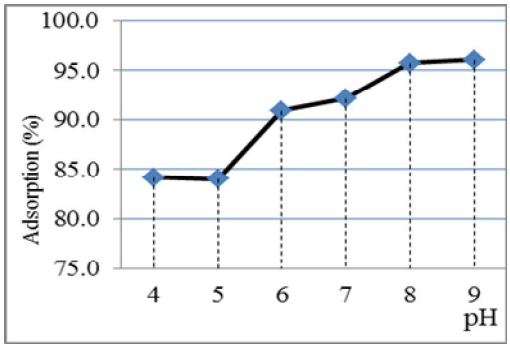

Figure 4: Effect of pH on the adsorption

3.2.2. Effect of contact time

Figure 5 shows the effect of contact time on MB adsorption with the magnetic adsorbent. It can be seen from the figure that the adsorption was rapid at the initial 20 minutes stage of the contact, but it gradually slowed down until the equilibrium at about 60 minutes. The fast adsorption at the initial stage can be explained by the fact that a large number of surface sites were available for adsorption. When time lapsed away, the remaining surface sites were difficult to be occupied because the repulsion between the solute molecules of the solid and bulk phases made it take long time to reach equilibrium [12].

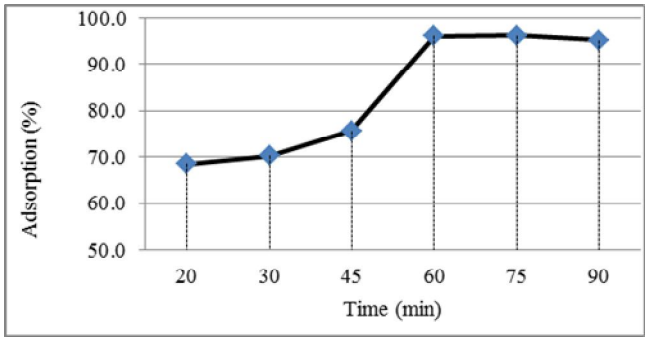

Figure 5: Effect of the contact time

3.2.3. Effect of the dosage of adsorbent

Figure 6 illustrates data from the MB adsorption onto the prepared magnetic material by varying the dosage of adsorbent. It is obvious that increasing the adsorbent's dosage, adsorption efficiency is higher. For the dosage 0.5g/30 mL of 50 ppm MB, the adsorption efficiency is nearly 100%.

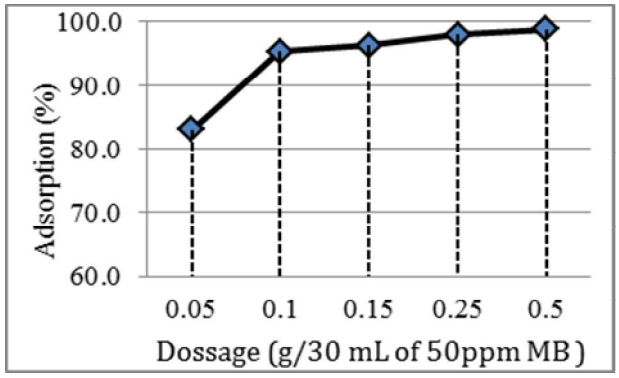

Figure 6: Effect of the dosage

3.2.4. Effect of the initial MB concentration- Isotherms

The equilibrium data were analyzed by the Langmuir and the Freundlich models:

$$q_e = q_{\max} \frac{b.C_e}{1+b.C_e} \quad (2)$$

$$q_e = K_f.C_e^{1/n} \quad (3)$$

Equation (2) and (3) can be rearranged to obtain respectively the linear forms as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}.b} + \frac{C_e}{q_{\max}} \quad (4)$$

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad (5)$$

where C_e and q_e are the equilibrium concentrations in the liquid and solid phases, q_{max} is the maximum adsorption capacity, b is the Langmuir equilibrium constant, and K_f and n are the Freundlich constants.

As can be seen from Figure 7, the Langmuir model provided a more accurate

description of the adsorption process. The maximum adsorption capacity (q_{max}) of MB on the magnetic material estimated from linear Langmuir isotherm equation (4) is 30.7 $mg.g^{-1}$ at pH 7. An examination of the literature reveals that the adsorption capacity of the MSCG for MB is smaller activated charcoal (150 $mg.g^{-1}$) [12] but significantly higher than some low-cost adsorbents such as pine sawdust (16.75 $mg.g^{-1}$), sugar extracted spent rice biomass (8.13 $mg.g^{-1}$), wheat shells (21.50 $mg.g^{-1}$),…[13]. The Freundlich constants drawn from fitting equilibrium isotherm data according to equation (5) are n = 1.42 and K_f = 8.31.

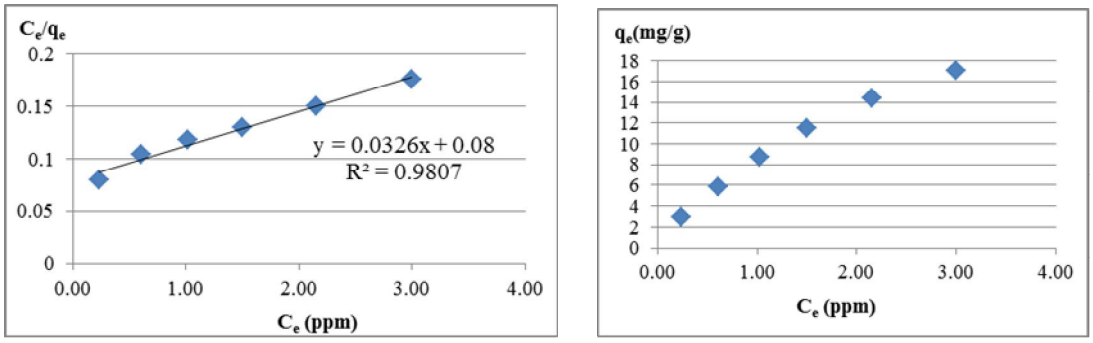

Figure 7: Langmuir adsorption isotherm data (left) and linear Langmuir isotherm form (right)

4. CONCLUSIONS

The results of this study clearly demonstrate that MSCG can be easily prepared by the exposure of SCG, a waste material from the coffee industry, to the water-based ferrofluid, leading to the fact that the magnetic material can be easily separated from the suspensions by a permanent magnetic. The effects such as pH, contact time, dosages of the adsorbent, initial MB concentration on the MB adsorption onto MSCG have been investigated. The estimated maximum adsorption capacity of the MSCG from Langmuir isotherm modes was 30.7 $mg.g^{-1}$ at pH 7, the temperature of 25°C, the contact time of 60 min and the agitated rate of 150 rpm. These results make the MSCG highly suitable as a new low-cost adsorbent for the large-scale removal of pollutants from wastewaters.

REFERENCES

[1] Dabrowski A., (2001). *Adsorption, from theory to practice*. Adv. Colloid Int. Sci., 93, 135–224.

[2] San M.G., Lambert S.D., Graham N.J., (2001). *The regeneration of field-spent granular-activated carbons.* Water Res., 35, 2740–2748.

[3] Jooste T., Garcia-Aparicio M.P., Brienzo M., Van Zyl W.H., Görgens J.F., (2013). *Enzymatic hydrolysis of spent coffee ground.* Appl Biochem Biotechnol, 169(8):2248-62.

[4] Silva M.A., Nebra S.A., Silva M.J.M., Sanchez C.G., (1998). *The use of biomass residues in the Brazilian soluble coffee industry*. Bio-mass Bioenerg, 14:457–467.

[5] Tokimoto T., Kawasaki N., Nakamura T., Akutagawa J., Tanada S., (2005). *Removal of lead ions in drinking water by coffee grounds as vegetable biomass.* J Colloid Interface Sci., 281:56–61.

[6] Fiol N., Escudero C., Villaescusa I., (2008). *Re-use of exhausted ground coffee waste for Cr(VI) sorption.* Sep Sci Technol., 43:582–596.

[7] Djati Utomo H., Hunter K.A., (2006). *Adsorption of heavy metals by exhausted coffee grounds as a potential treatment method for waste waters.* E-J Surf Sci Nanotech, 4:504–506.

[8] Djati Utomo H., Hunter K.A., (2006). *Adsorption of divalent copper, zinc, cadmium and lead ions from aqueous solution by wastetea and coffee adsorbents*. Environ Technol., 27:25–32.

[9]. Yasuda M., Sonda T., Hasegawa N., Kumagawa K., (2003). *Removal of heavy metals with fresh and used coffee grounds*. J Home Econ Jpn, 54:827–832.

[10] Safarik I., Horska K., Svobodova B., Safarikova M., (2012). *Magnetically modified spent coffee grounds for dyes removal*. Eur Food Res Technol., 234:345–350.

[11] Berger P., Adelman N.B., Beckman K.J., Campbell D.J., Ellis A.B., Lisensky G.C., (1999). *Preparation and properties of an aqueous ferrofluid.* J. Chem. Educ., 76, 943–948.

[12] Ahmad, M.A.; Rahman, N.K., (2011). *Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon*. Chem. Eng. J., 170, 154–161.

[13] Mohammed M.A., Shitu A. and Ibrahim A., (2014). *Removal of Methylene Blue Using Low Cost Adsorbent: A Review.* Research Journal of Chemical Sciences, Vol. 4(1), 91-102.

[14] Zuorro A., Battista A.D., Lavecchia R., (2013). *Magnetically Modified Coffee Silverskin for the Removal of Xenobiotics from Wastewater*; Chemical engineering transactions, Vol. 35, 1375-1380.