Research on the manufacturing of Fe_2O_3/TiO_2-based adsorbent granules for application in treating Pb^{2+}-contaminated water

Ngo Minh Tien, Tran Van Chinh*

Institute of Materials, Biology and Environment, Academy of Military Science and Technology, 17 Hoang Sam, Nghia Do, Hanoi, Vietnam.

*Corresponding author: chinhpkkq@gmail.com

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ABSTRACT

In this paper, Fe_2O_3/TiO_2 adsorbent granules were fabricated via a drum-type granulation method with bentonite as a binder. The granulation process included three steps: mixing Fe_2O_3/TiO_2 mixture of powder and fine coal dust into a homogeneous mixture, granulating by spraying water mist, drying the beads, and calcining at 500 °C for 1 h to form pores. The characteristic structures of composite materials after fabrication are evaluated by various methods, such as X-ray diffraction and scanning electron microscopy with energy dispersive X-ray spectroscopy. The performance evaluation of the fabricated adsorbent granulation for removing Pb^{2+} from polluted water was studied using a fixed-bed adsorption column. The factors affecting the adsorption performance, such as height of the adsorption column, flow rate, and inlet Pb^{2+} concentration, were determined. In column mode, the longest exit time was 450 minutes, the saturation time was 723 minutes, and the adsorption efficiency was 78.202% at the initial concentration of 5 mg/l, column height of 16 cm, and flow rate of 5 ml/min. The adsorption data with three well-established fixed-bed adsorption models, namely the Adam-Bohart, Thomas, and Yoon-Nelson models, with a correlation coefficient, $R^2 > 0.95$.

Keywords: Adsorbent granulation; Fe_2O_3/TiO_2 composite; Heavy metals; Pb^{2+}; Column adsorption.

1. INTRODUCTION

Water contaminated with heavy metals is a global problem in terms of environmental pollution and public health. Among them, water contaminated with heavy metals Pb^{2+} in wastewater from factories and domestic water from wells with Pb^{2+} concentrations higher than the safe use regulations must be mentioned. Lead can affect almost every organ and system in the human body. In particular, children aged below 6 years are most sensitive to the effects of lead exposure. Low concentrations of lead in children's blood can cause hearing and learning problems, anemia, behavior anomalies, slowed growth, lower intelligence quotient, and hyperactivity [1-3]. According to the European Community Directive, the World Health Organization, and the National technical regulation QCVN 01-1:2018/BYT have set the maximum acceptable lead limits in tap water as 0.01 mg/liter. Therefore, it is necessary to treat contaminated water containing Pb^{2+} exceeding the allowable level before using or discharging it into the environment. To date, several hundred publications have been reported on the removal of lead ions from an aqueous solution, such as chemical precipitation, adsorption, coagulation, ion exchange, membrane filtration, electrolysis, reverse osmosis, and biology. Among them, adsorption is a widely used technology to remove water sources due to its low cost, good efficiency, and easy operation [3, 4]. Materials capable of absorbing heavy metals such as activated carbon, manganese sand, zeolite, silica gel, alginate, laterite, graphene Oxide, chitosan, organic adsorbents, and biological adsorbents [5]. Fe_2O_3/TiO_2 composite materials have been synthesized and applied by many authors in the adsorption and removal of Pb^{2+}. Studies on Fe_2O_3/TiO_2 materials in the form of fine powder, with a size range of 50 ÷ 400 nm, limit practical application because it often requires secondary treatment, such as high-speed centrifugal filtration, to separate the material from the water environment. The process of converting Fe_2O_3/TiO_2 powder materials into porous particles increases permeability, allowing a large amount of wastewater to pass through easily. Granular materials, with increased porosity, increase adsorption capacity and reduce bulk density, so they will be a more practical filter material to remove heavy metals in polluted water sources [6-8].

In this study, Fe_2O_3/TiO_2-based adsorbent granules were fabricated via the drum granulation method with bentonite as the binder. The adsorbent granules were evaluated for their ability to remove Pb^{2+} from aqueous media using the column adsorption method. Factors affecting the adsorption process, such as initial Pb^{2+} concentration, flow rate, and column height were studied and the optimal parameters were determined. The Thomas, Yoon–Nelson, and Adams–Bohart kinetic models were applied to analyze the experimental data, revealing that the Pb^{2+} adsorption process was more consistent with the Thomas and Yoon–Nelson models.

2. EXPERIMENTS

2.1. Chemicals

The main chemicals used include: Titanium slag - Binh Dinh Minerals Joint Stock Company; H_2SO_4, 98% - Xilong; $Pb(NO_3)_2$ 98% - Xilong; bentonite - India; coal dust 95% - Xilong; distilled water.

2.2. Granulation method

First, the Fe_2O_3/TiO_2 composite material was fabricated according to the published process of the authors [8], specifically as follows: 20 g of titanium slag was mixed with 100 ml of 20% sulfuric acid for 30 min. Thereafter, the solid residue was washed with water several times to remove diluted salts and then dried at 100 ^oC for 6 h. The resulting solid was calcined for 3 h at 600 ^oC. The product was then allowed to cool down to ambient temperature and ground in a steel-made milling cell using 2 ÷ 5 mm diameter zirconia balls at room temperature for 45 min. The Fe_2O_3/TiO_2 composites were vacuum-filtered and dried at 100 ^oC for 6 h to obtain the Fe_2O_3/TiO_2 composites. The Fe_2O_3/TiO_2 composite material, bentonite binder and coal dust in the mass ratio of 1 : 0.08 : 0.08 were put into a disc granulator with an inclined angle of 45^o and a rotation speed of 90 rpm. The mixture was mixed well for 10 minutes, and then water mist was slowly sprayed into the disc to a humidity of about 15%. The granulation process lasted for 45 minutes, the adsorbent beads were taken out and dried at 150 ^oC for 8 hours, and the sieve was used to collect beads with a size of 2 ÷ 5 mm. Then, the adsorbent granulations were calcined at 500 ^oC for 1 hour to form porous capillaries.

2.3. Analysis and evaluation methods

2.3.1. Material characterization method

The phase composition of the materials was determined by X-ray diffraction (XRD) on the X'Pert instrument, using CuKα X-ray source with λ = 1.5406 Å, 45 kV, 40 mA, scanning step 0.1 ^{o}/s. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX, Hitachi S-4800, Tokyo, Japan) was employed to investigate the morphology, particle size, and elemental composition of the Fe_2O_3/TiO_2 composite.

2.3.2. Column adsorption experiment method

The adsorption column is a glass tube with a diameter of 4 cm and a height of 20 cm. The adsorption column is connected to a tank containing Pb^{2+} solution with a flow control valve. Before being packed into the column, the adsorbent beads are soaked in water to remove all air bubbles and particles attached to the material surface. The top and bottom of the adsorbent beads are blocked by a PUF foam layer. Dynamic adsorption is performed by letting Pb^{2+} solution with an initial concentration of C_o run through the column and taking samples after each time point to analyze and evaluate the efficiency.

The column adsorption experiment is carried out at room temperature, the breakthrough time t_b is the time when the output concentration is 10% of the initial concentration $C_t = 0.1C_o$. Similarly, the saturation time ts is determined as the time at which $C_t = 0.9C_o$ [9].

Effect of adsorption column height: The experiment was conducted at the height of the adsorbent bed of 4 cm, 8 cm, 12 cm and 16 cm, corresponding to the adsorbent mass of 45 g, 90 g, 135 g and 180 g, respectively. The initial concentration of Pb^{2+} solution was 10 mg/l, the flow rate was 10 ml/min and pH = 7.

Effect of flow rate: The flow rates were 5 ml/min, 8 ml/min and 10 ml/min, respectively; the height of the adsorption column was 16 cm; the initial concentration of Pb^{2+} solution was 10 mg/l; pH = 7.

Effect of initial concentration of Pb^{2+} solution: The initial concentration of Pb^{2+} solution was 5 mg/l, 10 mg/l and 15 mg/l, respectively, at the flow rate of 5 ml/min; the height of the column was 16 cm; pH = 7.

Column adsorption kinetics study: The Pb^{2+} adsorption kinetics of the fabricated adsorbent beads were evaluated using three models: Thomas, Yoon-Nelson and Adams-Bohart, with linear equations (1), (2) and (3), respectively:

$$\ln\left(\frac{C_o}{C_e}-1\right)=\frac{K_T q_0 M}{Q}-K_T C_o t \tag{1}$$

$$\ln\left(\frac{C_e}{C_o-C_e}\right)=k_{YN}t-\tau k_{YN} \tag{2}$$

$$\ln\left(\frac{C_e}{C_o}\right)=K_{AB}C_o t-\frac{K_{AB}N_o H}{Q} \tag{3}$$

In which: K_T (ml/min.mg), k_{YN} (min^{-1}), K_{AB} (l/mg.min) are the kinetic constants Thomas, Yoon-Nelson and Adams-Bohart respectively; C_o and C_e are the input and output concentrations of the solution (mg/l) respectively; q_o: Adsorption capacity (mg/g); M: Mass of adsorbent (g); Q: Flow rate (ml/min); τ: Time for 50% of the adsorbed substance to escape (min); No: Saturation concentration of the adsorbed substance (mg/l) [9, 10].

3. RESULTS AND DISCUSSION

3.1. Characteristics of adsorbent granules

Figure 1a shows the image of adsorbent particles with sizes from 2 ÷ 5 mm after calcining, these particles have a relatively round and uniform shape. The phase composition of the materials was determined by X-ray diffraction (XRD), figure 1b. It was found that the adsorbent granules had two main phase components, TiO_2 (JCPDS standard card 01-083-2243) and α-Fe_2O_3, hematite (standard card 01-089-8104). The TiO_2 anatase phase appears clearly at $2\theta \approx 25.3°$ and 48.0°, corresponding to the (101) and (200) planes. The α-Fe_2O_3 phase appears at $2\theta \approx 27.4°$, 35.6°, 40.8°, and 54.1°, corresponding to the (012), (110), (113), and (116) planes. The crystallite sizes of TiO_2 and Fe_2O_3 were calculated using the Bragg-Scherrer equation at $2\theta = 25.3°$ and 27.4°, and were found to be 20.3 nm and 23.7 nm, respectively.

Figure 1c shows the surface of the adsorbent, showing the appearance of capillaries and porous channels in the adsorbent. These capillaries and porous channels are formed by the combustion of coal dust, which will be favorable for the removal of pollutants in the water environment. To clarify the composition of elements in the adsorbent particles after calcining, it is shown in figure 1d and table 1. It can be seen that the EDX spectrum shows peaks of the elements O, Ti, Fe, Si, Al and Mn, in which the Ti content is the highest at 38.51%, followed by

Fe at 12.58%, followed by Si, Al, Mn with contents of 4.10%, 2.05% and 2.28% respectively. The presence of Si, Al, and Mn in the EDS spectrum shown in figure 1d is consistent with the elemental composition of the titanium slag used to fabricate the Fe_2O_3/TiO_2 composite.

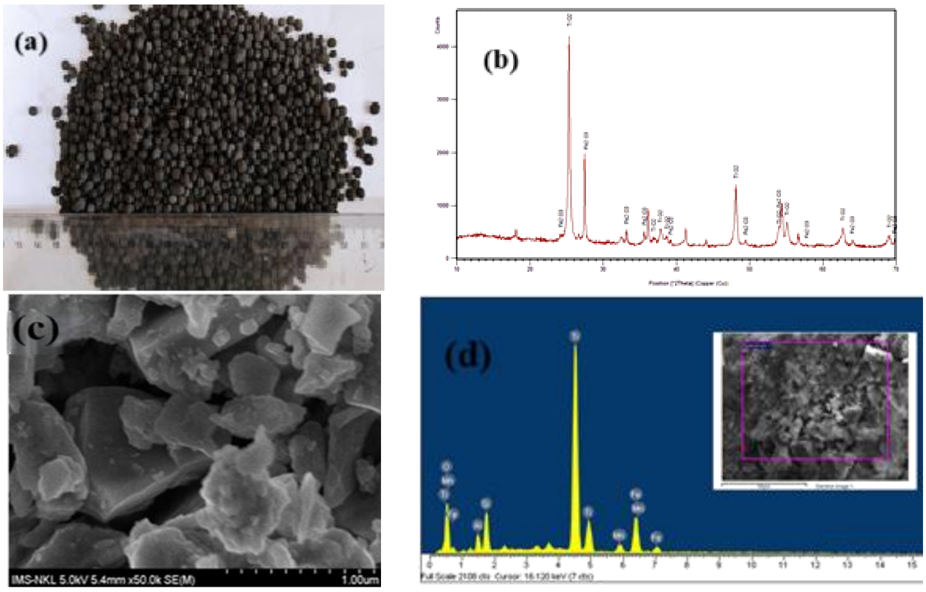

Figure 1. *(a) Adsorbent granules, (b) X-ray diffraction of the adsorbent, (c) SEM image of the adsorbent granules surface, (d) EDX spectrum of adsorbent granules.*

Table 1. *Elemental composition in adsorbent particles.*

Element	% Mass	% Atomic
O K	40.49	66.19
Ti K	38.51	21.03
Fe K	12.58	5.89
Si K	4.10	3.82
Al K	2.05	1.99
Mn K	2.28	1.09
Tổng	100	100

3.2. Factors affecting the column adsorption process

The effect of column height on Pb^{2+} adsorption capacity is illustrated by the escape curve shown in figure 2a. At column height H = 4 cm, the escape time and saturation time for Pb^{2+} are 30 min and 150 min. When the adsorption column height is increased to 8 cm, 12 cm and 16 cm, the escape time, saturation time and total time all increase. This shows that the height of the adsorption column greatly affects the adsorption efficiency of heavy metal ions in dynamic mode, due to increasing the surface area and the number of available adsorption sites on the material, the efficiency increases as the column height increases, from 44,457% to 63,766% for Pb^{2+}.

Effect of flow rate: The leaching curve of Pb^{2+} with different flow rates is shown in figure 2b. The adsorption efficiency reached the highest value when the inlet flow rate was the lowest and gradually decreased as the flow rate increased. When the flow rate was 5 ml/min, the adsorption efficiency was 74.853% with a saturation time of 577 min. Thus, the smaller the inlet flow rate, the higher the adsorption efficiency, which is because the longer the contact between the liquid and solid phases, the more the amount of adsorbed substance diffuses from the liquid phase into the solid. On the contrary, when the flow rate is high, it leads to a shorter contact time, which limits the diffusion of metal ions into the adsorbent.

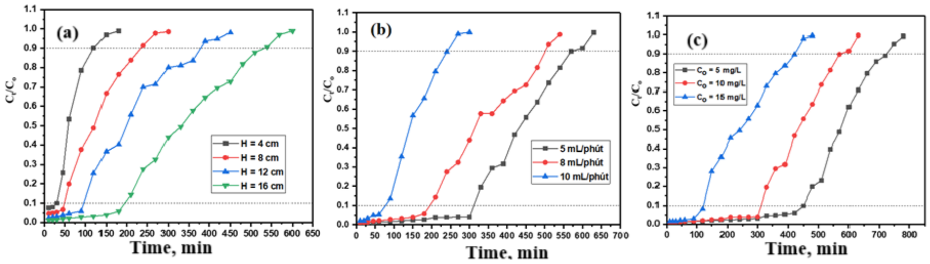

Figure 2. *Escape curves of* Pb^{2+} *adsorption for different (a) column height, (b) flow rate and (c) initial concentration.*

Effect of initial Pb^{2+} *solution concentration:* The escape curve of Pb^{2+} adsorption process at different initial concentrations is shown in figure 2c, it is seen that when increasing the inlet concentration under the same conditions (column height, flow rate), the escape curve tends to be shorter. At low metal ion concentrations, the diffusion coefficient and adsorption of metal ions on the material surface are slower, the amount of metal ions adsorbed on the material is lower, on the contrary, when the metal ion concentration is high, more metal ions are adsorbed due to the faster movement of metal ions to the material surface, leading to a shorter column working time. The optimal Pb^{2+} adsorption capacity at the longest release time was 450 min, the saturation time was 723 min and the adsorption efficiency was 78.202% at the initial concentration of 5 mg/l. This result is equivalent to some published studies, such as the adsorption efficiency of Steel slag 85.6%; Fly ash-containing geopolymer monoliths 68%; Sago waste activated carbon 67%; Coffee residue activated with zinc chloride đạt 75%; Fly ash 90%; Chemically modified moso bamboo 85%; Sawdust 70.9% [3].

From the above research results on factors affecting the adsorption process of and Pb^{2+}, it can be seen that the optimal conditions for the adsorption process of and Pb^{2+} are H = 16 cm, Q = 5 ml/min and Co = 5 mg/l.

3.3. Column adsorption kinetics model

From the experimental data, the kinetic models Thomas, Yoon-Nelson and Adam-Bohart were performed to evaluate the adsorption process of Pb^{2+} when changing the column height, flow rate and initial solution concentration. The results are shown in figures 3 to 5, respectively. The kinetic parameters were calculated, the results shown in table 2 show that the Thomas and Yoon-Nelson models both have quite large R^2 values (> 0.95). Meanwhile, the R^2 value according to the Bohart-Adam model is lower than that of the Thomas and Yoon-Nelson models under constant experimental conditions.

Thus, the Thomas and Yoon-Nelson models can be applied to explain the Pb^{2+} removal process in column systems. The Thomas model ignores the mass transfer resistance on the boundary membrane between the particles and the liquid membrane. Therefore, this model assumes that the surface reaction between the ions and the unadsorbed centers determines the adsorption rate. According to the Yoon-Nelson model, it is assumed that the adsorption rate of the substances is proportional to the adsorption and desorption rates.

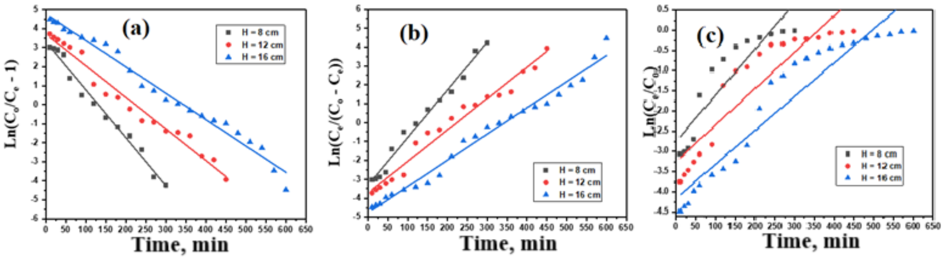

Figure 3. *Linear (a) Thomas, (b) Yoon-Nelson (b) and (c) Bohart-Adam kinetic equations for* Pb^{2+} *at different adsorption column heights.*

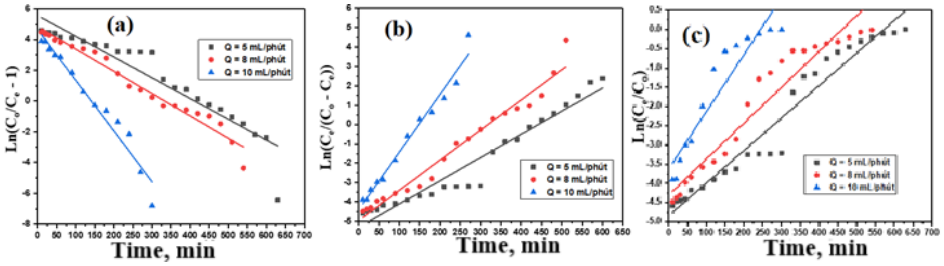

Figure 4. *Linear (a) Thomas, (b) Yoon-Nelson (b) and (c) Bohart-Adam kinetic equations for* Pb^{2+} *at different flow rates.*

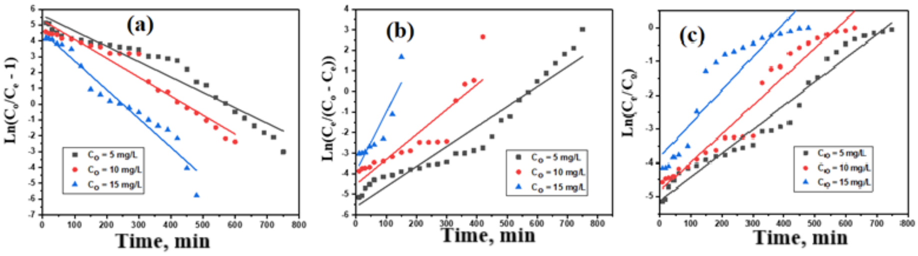

Figure 5. *Linear (a) Thomas, (b) Yoon-Nelson (b) and (c) Bohart-Adam kinetic equations for* Pb^{2+} *at different initial concentrations.*

Table 2*. Parameters in the kinetic equations of* Pb^{2+} *adsorption on adsorbent particles.*

Biến số			**Thomas**			**Yoon-Nelson**			**Bohart-Adam**		
H, cm	**Q, ml/phút**	**C$_o$, mg/l**	**K$_T$, ml/phút.mg**	**q$_o$, mg/g**	**R^2**	**K$_{YN}$, phút^{-1}**	**τ, phút**	**R^2**	**K$_{AB}$, l/mg.phút**	**N$_o$, mg/l**	**R^2**
8	8	10	0.00252	116.656	0.9828	0.0252	131.28	0.9828	0.00114	2406.58	0.8094
12	8	10	0.00166	132.594	0.9718	0.0166	223.75	0.9718	0.00090	2403.78	0.8257
16	8	10	0.00139	152.368	0.9809	0.0139	342.83	0.9809	0.00084	2471.55	0.9068
16	10	10	0.00329	78.4450	0.9558	0.0329	141.20	0.9740	0.00148	1529.39	0.8816
16	5	10	0.00135	114.438	0.8839	0.0135	411.98	0.9438	0.00085	1779.45	0.9497
16	5	5	0.00190	81.8450	0.9223	0.0097	577.13	0.9222	0.00142	1130.19	0.9643
16	5	15	0.00120	105.236	0.9499	0.0182	249.79	0.7651	0.00066	1814.44	0.8459

4. CONCLUSIONS

This study successfully granulated Fe_2O_3/TiO_2 composite materials on a disk-shaped device, using bentonite and coal dust as binders to create porosity for the particles. The adsorbent particles had a size of 2 ÷ 5 mm and were calcined at 500 ºC for 1 hour to create hollow capillaries observed through SEM images. The adsorption capacity of Pb^{2+} of the particles depends on the initial concentration, column height and flow rate. In column mode, the longest exit time was 450 minutes, the saturation time was 723 minutes and the adsorption efficiency was 78.202% at the initial concentration of 5 mg/l, column height of 16 cm and flow rate of 5 ml/min. The Thomas, Yoon-Nelson and AdamBohart kinetic models were used to evaluate the experimental data, showing that the adsorption process of Pb^{2+} was more consistent with the Thomas and Yoon-Nelson models. The fabricated adsorbent beads have the potential for practical application in the treatment of water sources polluted by heavy metals.

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TÓM TẮT

Nghiên cứu chế tạo hạt hấp phụ trên cơ sở Fe_2O_3/TiO_2 ứng dụng trong xử lý nước nhiễm Pb^{2+}

Trong bài báo này, các hạt hấp phụ Fe_2O_3/TiO_2 được chế tạo thông qua phương pháp tạo hạt dạng trống với bentonit làm chất kết dính. Quá trình tạo hạt bao gồm ba bước: trộn hỗn hợp bột Fe_2O_3/TiO_2 và bụi than mịn thành hỗn hợp đồng nhất; tạo hạt bằng cách phun sương nước; sấy khô hạt và nung ở 500 °C trong 1 giờ để tạo các lỗ xốp. Cấu trúc đặc trưng của vật liệu composit sau khi chế tạo được đánh giá bằng nhiều phương pháp khác nhau như nhiễu xạ tia X và kính hiển vi điện tử quét với phổ tia X phân tán năng lượng. Đánh giá hiệu suất các hạt hấp phụ chế tạo để loại bỏ Pb^{2+} khỏi môi trường nước ô nhiễm đã được nghiên cứu bằng cách sử dụng cột hấp phụ cố định. Các yếu tố ảnh hưởng đến hiệu suất hấp phụ như: chiều cao cột hấp phụ, lưu lượng và nồng độ Pb^{2+} đầu vào đã được xác định. Ở chế độ cột, thời gian thoát ra dài nhất là 450 phút, thời gian bão hòa là 723 phút và hiệu suất hấp phụ là 78,202% ở nồng độ ban đầu là 5 mg/l, chiều cao cột là 16 cm và tốc độ dòng chảy là 5 ml/phút. Dữ liệu hấp phụ với ba mô hình hấp phụ cố định đã được thiết lập tốt, cụ thể là các mô hình Adam-Bohart, Thomas và Yoon-Nelson, với hệ số tương quan, $R^2 > 0,95$.

Từ khóa: Hạt hấp phụ; Composit Fe_2O_3/TiO_2; Kim loại nặng; Pb^{2+}; Hấp phụ cột.