REMOVAL LEAD FROM WASTE WATER IN BATTERY RECYCLE VILLAGE OF VIET NAM BY LOW COST ADSORBENT CREATED FROM TREATED FY ASH AND POLYURETHANE FOAM

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Abstract: *The objective of this research is to create a low cost material with high heavy metal removal capacity. Our study focuses on preparing a composit which can remove lead from wastewater of battery recycle villages of Vietnam, based on treated fly ash (TFA) and polyurethane (PU) foam. Fly ash after treating by thermal and NaOH has the surface area of 250.12 m2/g which leads to its high adsorption capacity, monolayer adsorption capactity* Q^0 *= 3gPb/g. The preparation of PU foam and treated fly ash (TFA) process was conducted by mixing TFA and PU foam then treated withthermal. The TFA supported PU can increase the absorption capacty of PU. The PU/TFA composit was performed its removal of 87% lead in wastewater of batery recycle village. In this research, we successfully created a low cost adsorbent that can be used in recycle villages in Vietnam where heavy metal contaminated wastewater has not been treated properly.*

Keywords: Battery recycle village, low cost adsorbent, material removal, polyurethane foam, treated fly ash.

1. INTRODUCTION

Heavy metal contamination in wastewater has become widespread and hard to be solved due to the poor management and treatment of waste water in metal recycle villages in Viet Nam. In Dong Mai village, Van Lam, Hung Yen, there are 269 of 570 households doing metal recyle from disposed batteries. Untreated water is released directly to water bodies that affects to environment and peoples health. There were 283 adults and 335 children in village were being poisoned by lead in blood (NASP). Up to now, the common methods for heavy metals removal are advanced like cation exchange, ion exchange, membrane filtration, and carbon adsorption. However, these methods have not been widely applied at large scale because the requirements of high cost and high skill in operatation and mantainance. Ion-exchange is an efficient method, with moderate electivity since it can not only remove the heavy metal ions but also exchange Ca2+, Mg2+ ions (Li, Su et al. 2007).

Intensive wide spread contamination of the surface water related to adverse industrial operations has been of great concern and call for the development of better adsorbents. The modern approach towards metal removal mainly concenns to use low cost materials. The synthesis of fly ash, generated during the combustion of coal for energy production consists of fine, spherical, either solid or hollow, and mostly glassy can create a prosperous absorbant. The main compositions of fly ash are silica, alumina, iron oxide and un-burned carbon which favour the heavy metal adsorption (Visa, Bogatu et al. 2010). The fly ash modification process is easy, low cost and sustainable, using alkali solutions of average concentration.

Reyad Shawabkeh et al. 2004 shown that zeolite sythesised from fly ash successfully removes lead and cadmium from waste water with the adsorption capacity of 70.58 mg lead/g-zeolite and 95.6 mg cadmium/g-zeolite). Fly ash

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modified by the hydrothermal treatment method can increase from 2 to 25 times the adsorption capacity (AC) comparing to its original capacity (Nascimento, Soares et al. 2009). In recent years, scientists have tried to develop cation oxides on treated fly ash based ceramic to improve antibacterial capability of the material.

Polyurethane (PU) foam have been used as adsorbents for wastewater and treated wastewater because they are cheap and can be used without prior treatment. Polyurehthane (PU foam) is composed of Polyether polyol, Isophoronediisocyanate, Dibutyltindilaurate and sodium bicacbonate. It is normaly used in industry as a foam underlay or on top as a coating. In medical, its purpose is tubing, hospital bedding, surgical drapes, wound dressings and a variety of injection-molded devices. Recently, scientists have discovered a number of applications of PU foam in environmental treatment.

Hydroxyapatite/polyurehthane (HAp/PU) composite foamwith two different HAp contents of 20 and 50 weight % (wt.%) can effetively remove Pb2+ ions from aqueous solutions (Jang, Min et al. 2008). PU foam can possess a high surface area because of their open porous structures and thus can be used as matrices to immobilize various adsorbents (Harikrishnan, Singh et al. 2010). Wei Li el al prepared composite adsorbents by supporting activated carbon on PU foam (Li and Liu 2012). Different adsorbent materials were supported on polyurethane foam to investigate nitrogen and toluene adsorption (Pinto 2004).

In our knowledge, PU foam and treated fly ash have been known as a low cost adsorbents for metal removal but there has not been any absorbent combined of these two materials in wastewater treatment. In this research, we created a new low cost adsorbent by integration of the PU foam and treated fly and investigated its potential of Pb removal from wastewater in battery recycle village.

2. MATERIALS AND METHODS

2.1. Zeolite preparation

Fly ash samples were collected from Pha Lai thermal power plan located the Northern part of Viet Nam. These samples passed the 1 mm mesh were collected before modification. The remaining ash was grinded and stored in closed and dark container at room temperature.

Zeolite synthesis was conducted by mixing fly ash with sodium hydroxide, ratio 1:2 in weight. Then this composite was put in the reaction vessels and transferred to the oven and kept in 4 hours at 600 ^oC. After that, the product was cooled down at room temperature before mixing with water in ratio of 1:5 in weight. Then the slurry was stired in 9 hours before crystallizing in 3 hours at temperature of 100^oC. After the activation period, the product was washed several times by distilled water until pH reached 6.5, dried at 105 ^oC, then stored in a closed container for analysis.

2.2. Cation exchange capacity

Four (4) grams of sample was mixed with 33 mL of 1.0 N sodium acetate solution in triplicate. Then the samples were washed three times with 33 mL isopropyl alcohol, three times with 33 mL of ammonium acetate. These sollution was collected and analyzed by the Thermo Element Atomic Absorption Apectrophotometer (AAS).

2.3. Adsorption experiment

Adsorption isotherms

An amount of 0.1 g treated fly ash were added to 100 mL lead solutions with different initial concentrations. Solutions were placed in a shaker at room temperature for a fixed period of time to allow complete equilibration. Similar procedure was performed on blank samples by the addition of zeolite into deionized water for the purpose of comparison. The pH was buffered at a value of 5.5 for all solutions. The equilibrated solutions were analyzed by the Thermo Elemental atomic absorption spectrophotometer.

Langmuir isotherm

The Langmuir equation is written as

$$\frac{Ce}{qe} = \frac{1}{Q^o\, b} + \left(\frac{1}{Q^o}\right) C_e \qquad (1)$$

Where q_e is the amount of soluted adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/Lmg/L), Q^0 is monolayer adsorption capactity (mg/g) and b is the constant related to free energy adsorption. It is the reciprocal of the concentration at which half of the saturation of the adsorbent is obtained.

Freundlich isotherm

The Frenundlich isotherm was written as

Log q_e = log K_F + $\frac{1}{n}$ log C_e (2)

Where q_e is the amount of solute adsorded per unit weight of adsorbent (mg/g). C_e is the equlibrium concentration of solute in bulk solution (mg/L), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g), $\frac{1}{n}$ is the constant indicative of the intensity of the adsorption.

2.4. PU foam/treated fly ash composite

The required amount of treated fly ash was added to the mold, and a strong stirring with water was applied during 15 ± 2 s. The percentage of synthesis fly ash in foam/treated fly ash composite in weight is 5%. After stirring, the slugde including TFA and water was mixed with PU foam in 30 mminutes then left unsturbed for 1 hour for foam forming. The foarm was then put in to oven for 30 minutes at 90^0C to 300^0C.

2.5. Material characteration

The characteristics of synthesis fly ash and PU foam/treated fly ash composite were determined by Brunauer–Emmett–Teller (BET) method to determine surface area, total pore volume and pore size distribution. The samples were determined from N2 adsorption–desorption isotherms obtained at 77.350 K using an automatic adsorption. The surface morphology and channel structure of the carbon foam materials were observed by a scanning electron microscope (SEM).

2.6. Sampling and filltration experiment

Four (4) waste water samples were collected from sewers of 4 households doing battery recycle. Lead concentration of these samples were analyzed by AAS method. The average lead concentration of above sample was used to conduct filltration experiment.

In the filltration experiment, PUfoam/ TFAcomposite layers (5 cm thickness and 60mm in diameter) was installed in a tube for lead contaminated water filltration. The Fig.1 shows the design of the experiment. The contaminated water was filtered through PUfoam/TFAcomposite. Lead concentration of filtered water was analized by by AAS.

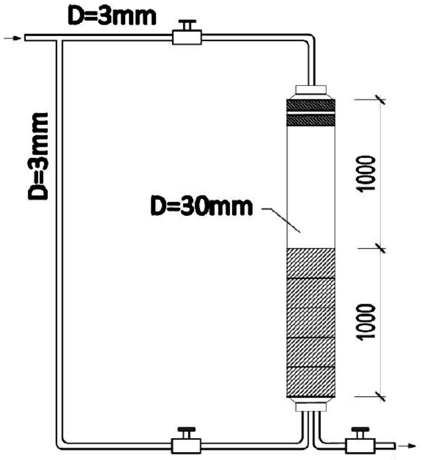

Fig.1. Diagram of filltration experiment

3. RESULTS AND DISCUSSION

3.1. Characterization of treated fly ash

The composition of fly ash from Pha Lai has been determined as: SiO2: 58.05 wt.%; Al2O3: 24.21 wt.%; Na2O: 0.05 wt.%; K2O: 0.3 9wt.%; Fe2O3: 6.07 wt.%; SO3: 0.09 wt.%; other: 0.7 wt.%. It can be categorized as Class F fly ash in terms of ASTM C618-99 specification.

SEM image showed that, in Fig 2, original fly ash consites of uniform spherical particles. The Fig 3 illustrates that, all the surface of fly ash was destroyed by sodium hydroxide to form crystals. Crack was also generated in the matrix of glass which maybe responsible for an increase in adsorbent pore volume. The treated fly ash has smaller particle size compared to fly ash sample. This decrease is possibly attributed to the crush and transformation of crystal. Additionally, it could be explained due to an increase increase of spheroidal nature of the magnetic particles formed from the transformation of some hematite phases into magnetite. According to Bhatia *et al*. 1989, fly ash was mixed with NaOH reacted flowing reaction:

$$NaOH + ash \rightarrow Na_{\alpha}(AlO_2)_c.NaOH.H_2O \rightarrow Na_j(AlO_2)_j(SiO_2).H_2O \quad (3)$$

The unbalance between the aluminium atoms and the four oxygen atoms in the silica and the forming crystal structure of product caused adsorption. Cation-exchange capacity (CEC) plays an important indicator for lead removal effectively of the products. In this research, the CEC value of TFA was 40.4 cmol$_c$ kg^{-1} which is significantly high comparing to activated carbon ranged from 30-40 cmol$_c$ kg^{-1}.

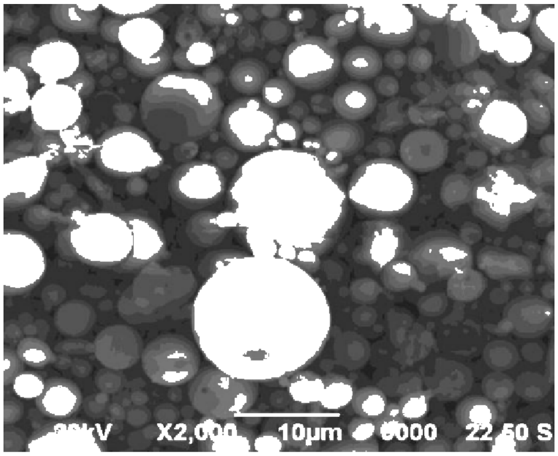

Fig2. Original fly ash in Pha Lai thermal porwer plant, Viet Nam

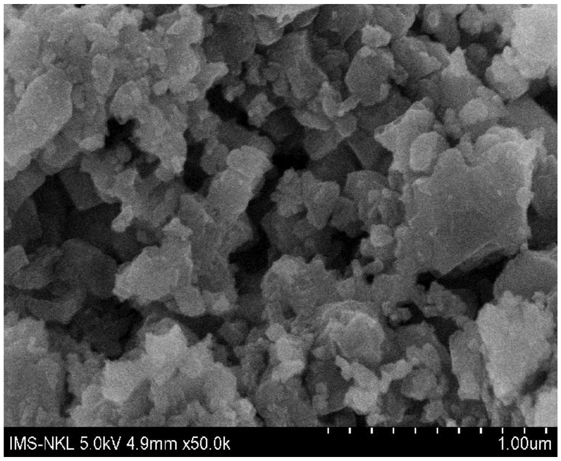

Fig 3. Treated fly ash by NaOH

The BET surface area of TFA was 250.1232 m2 g−1 which is similar as the BET surface area of the zeolite synthesized from fly ash of Qiu et al, 2009(Qiu and Zheng 2009). The Type IV adsorption isotherm of TFA implies the mesoporous structure of materials (Occur on porous adsorbents with pores in the range of 1.5 – 100nm. At higher pressures, the slope shows increased uptake of adsorbate as pores become filled, inflecxion point typically occurs near completion of the first monolayer.

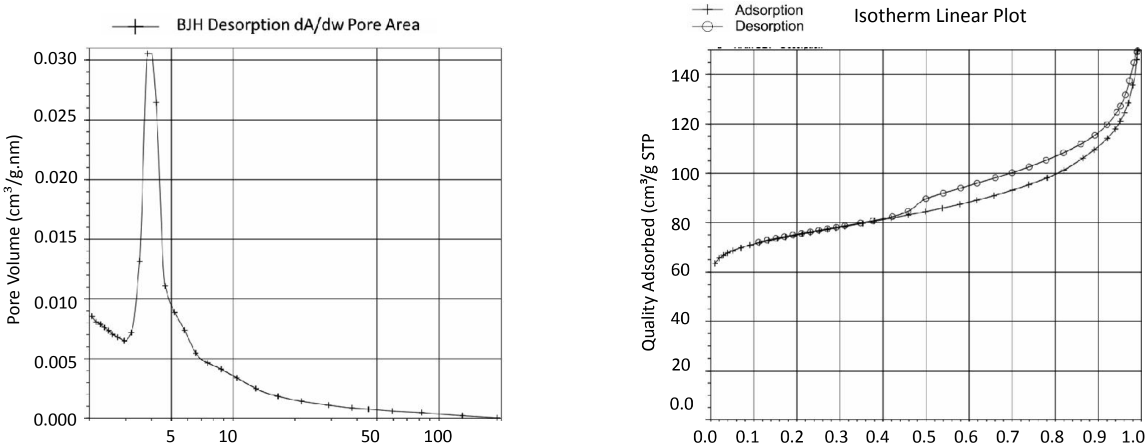

Fig 4. Nitrogen adsorption–desorption isotherm of TFA

The pore size distribution confirms that the pore size of TFA ranged from in 17˚A (1 ˚A= 0.1 nm) to 300A˚. However, it should be noted that the pore sizes are of the secondary pores between the cancrinite crystals rather than the pores in the cancrinite framework. The mesoporous pore structure may be favourable for the ion exchange process as it provides easy accesses for sorbate cations to approach the inner micropores in the cancrinite framework since most heavy metal cations are below 5A°. The Correlation Coefficient Langmuir Surface Area was 0.999789.

3.2. Equilibrium isotherms of TFA

The ion exchange isotherm can be mathematically described by the Langmuir adsorption isotherm, the equation is written as in equation (1).

This study found that, the amount of lead adsorbed on to treated fly ash (qe) inceased with the lead concentration in solution (Ce). It indicated that the higher concentration of the cations enabled the ion exchange process at the less active exchangeable sites on treated fly ash. The adsorption experiment of TFA is fit with the parameters of Langmuir equation ($R^2 = 0.998$) and Q^o = 3gPb/g. As shown in Fig 5b, the Frenundlich isotherm parameters obtained by experiment has n = -0.4 and K_F = 10^2.47. In comparison, the dataset fit langmuir model ($R^2 = 0.998$) more than the Frenundlich model ($R^2 = 0.796$).

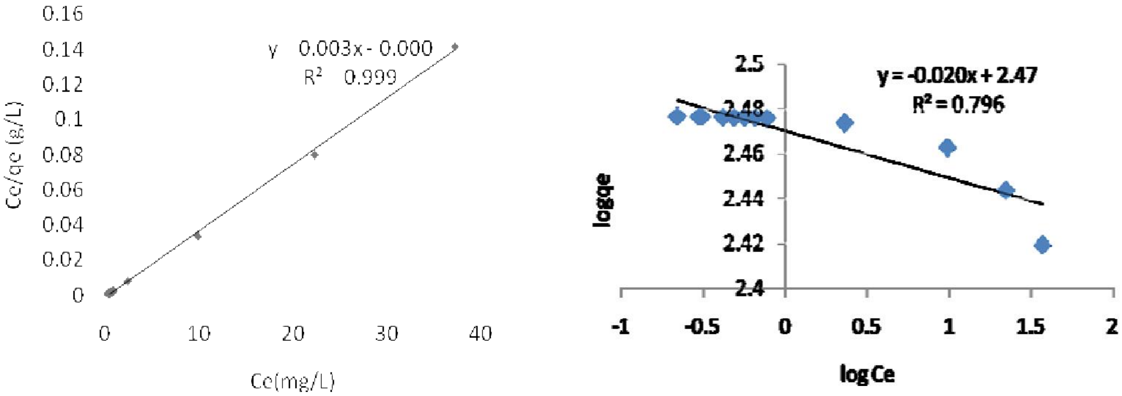

Fig 5. a) Langmuir liner adsorption isotherms *b) Frenundlich adsorption isotherms*

3.3. Chacteration of PU foam/TFA composite and Pb2 + adsorption ability

The sample contaminated Pb2+ with the initial concentration is 0.77mg/L was collected from wastewater system of Dong Mai village, one of the big lead recycle area in Viet Nam. This sample was leached through PU/TFA composite. The lead concentration after treating by PU/TFA composite is 0.1 mg/L with is lower than the allow of water quality release according to the Viet Nam National Standard. The reasion for Pb2+ capacity of this material is because following characterations of PU foam/TFA composite:

First, according to the treated PU/TFA composite experiment by thermal, the weight of the composite stated to loss when the temperature at 100°C. The weight of PU/TFA was almost constant from 100 to 200°C. The reason of the weight loss is at higher 100°C, water and other vapour adsorbed was removed. There is highly decrease in weight of the composite at temperature 200°C to 300°C. This may be caused by the decomposition of PU to diisocyanate, isocyanine and polyol, then to lamide, ethylene and CO2 (Robaina, Soriano et al. 2009).

Second, The Fig 6 shown the interaction between PU and TFA. The composite foam in this study possessed well-developed open cell network with a non-uniform distribution of AC. It is believed that the open cell structures of the composite can allow better lead access to the TFA supported on PU foam. The image illustrated that adsorption ability PU/TFA composite treated by thermal developed cell structure is better than the untreated composite.

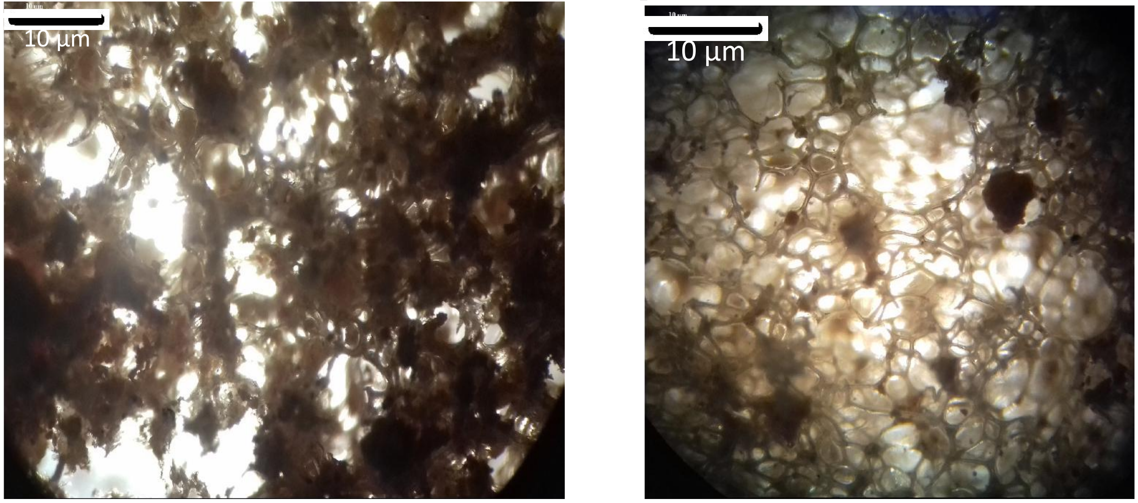

Fig 6. a) Images of the PU/TFA composite before thermal treatment (scale X4,000 10µm)

b) Images of the PU/TFA composite after thermal treatment (scale X4,000 10µm)

Third, the Fig 7 shows the BET result of PU/TFA composite. The sharply increased N2 adsorption capacity when $P/P_0 > 0.3$ and the presence of a hysteresis loop are characterized of a mesoporous structure. For PU/AC composite, the N2 adsorption capacity was much lower, and both slope and size of the hysteresis loop increased compared with those of TFA indicate the increaseing of macroporous structure.

The BET surface area of PU/TFA composite is 70.23 m^2/g much lower than the BET surface area of TFA. The reason of this is because the percent of TFA in the composit is 5% and the surface area of PU foam is lower than those of TFA. The higher percentage of TFA in the composite would have higher surface area. Moreover, the lead adsorption of PU/TFA as mentioned above not only because of high surface area but also because of cation exchange with TFA. So the opened cell structure with macroporous size would allow better accessibility of pollutants to the TFA adsorbent. Further more, PU/TFA composite is easy to shape and is suitable for operator in large scall with less by-product.

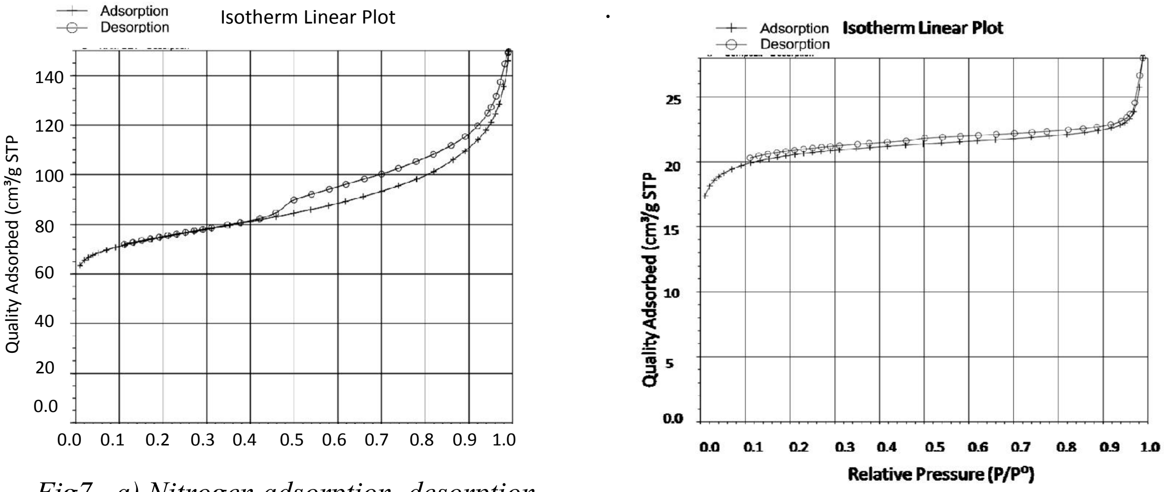

Fig7. a) Nitrogen adsorption–desorption

b) Nitrogen adsorption–desorption isotherm

isotherm of PU/TFA composite

of TFA

The result of equilibrium isotherms of PU/TFA shows that, the adsorption experiment of TFA is fit with the parameters of Langmuir equation ($R^2 = 0.992$) and Qo = 30mgPb/g. The langmuir equation is y = 0.0065x-0.0036.

4. CONCLUSIONS

In conclusion, this study successfully created the residual product from recycling fly ash with high surface area (250.1232 m2 g−1) and high monolayer adsorption capacity Q_o = 3gPb/g. The PU/TFA composit treated by thermal develop cell structure well and increased surface area for adsorption. This new material can remove 87% lead contaminated wastewater from battery recycle village. Moreover, this composite is a highly potental material in water and wastewater treatment due to low cost, light material and easily shaping.

5. ACKNOWLEDGEMENT

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Tóm tắt:

XỬ LÝ NƯỚC BỊ Ô NHIỄM CHÌ TẠI LÀNG TÁI CHẾ CHÌ Ở VIỆT NAM BẰNG VẬT LIỆU COMPOSIT CHI PHÍ THẤP TỪ TRO BAY BIẾN TÍNH VÀ POLYURETHANE FOAM

Trong nghiên cứu này chúng tôi tập trung chế tạo vật liệu chi phí thấp có khả năng xử lý ô nhiễm kim loại trong môi trường nước. Đây là loại vật liệu composit được hình thành từ tro bay biến tính ở Phả Lại và chất PU foam tạo xốp trong công nghiệp. Kết quả nghiên cứu cho thấy, tro bay biến tính sau khi được hoạt hóa bằng NaOH có diện tích bề mặt lớn là 250.12 m2/g và đương lượng hấp phụ lớp đơn phân tử lớn nhất là Q^0 *= 3gPb/g và chỉ số CEC trao đổi cao là 40.4* $cmol_c\ kg^{-1}$ *Vật liệu composit từ PU foam và tro bay biến tính (chiếm 5% khối lượng vật liệu) được tạo thành có diện tích bề mặt hấp phụ là 37,2* m^2/g *có khả năng hấpphụ 87% chì trong nước với nồng độ chì ban đầu là 0,77mg/L nước đầu vào lấy tại vùng nước mặt làng nghề tái chế chì Đông Mai, Hưng Yên. Ngoài khả năng xử lí chì tốt, loại vật liệu này rất dễ tạo khuôn, thích hợp cho việc lắp ráp vào các thiết bị xử lý có hình dạng khác nhau trong quá trình ứng dụng.*

Từ khóa: Làng tái chế chì, vật liệu hấp phụ chi phí thấp, xử lý kim loại nặng, polyurethane foam, tro bay biến tính

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