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Adsorption of Cr(VI) by material synthesized from red mud and rice husk ash

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Abstract:

In this work, the efficiency of a material prepared from red mud and rice husk ash (ZRM), in Cr(VI) absorption, without the use of acid to neutralize raw red mud (RM), was examined. The physico-chemical characteristics of the obtained material were determined by several methods, including BET nitrogen adsorption, XRD, SEM, and TEM. ZRM was employed in the adsorption of Cr(VI) in solution at 25°C with a Cr(VI) concentration of 20 ppm. The results showed that the nano particles of material were formed within the size range of 30-50 nm, and that the specific surface area of the material was 70.76 m^2/g. The conditions of the adsorption process (i.e., the initial pH of the solution, the stirring rate, and the material content) were seen to significantly affect the efficiency of Cr(VI) adsorption at the material's surface. The optimum conditions for Cr(VI) adsorption via ZRM were determined as pH=2, a stirring rate of 300 rpm, and a material content of 10 g/l. With these conditions, the maximum adsorption capacity for Cr(VI) in a solution of ZRM was found to be 23.32 mg/g.

Keywords: **Cr(VI) adsorption, material, red mud, rice husk ash.**

Classification number: **2.2**

Introduction

Nowadays, a multitude of hazardous waste is being produced as a result of rapid industrial development, with some environmental effects being particularly serious - including those involving water resources. Toxic organic compounds such as metallic ions of Cu, Zn, Pb, Ni, are some of the waste products released from petroleum oil processing, and the leather, electronics, electroplating, textile and dyeing industries. These waste compounds have been directly related to serious genetic changes, and to cancer, as well as to environmental degradation, even in small quantities. Cr(VI) can be considered one of the most hazardous of these substances. It is commonly found in waste water from a variety of industries, such as tanning, electroplating, textile dyeing, etc. Cr(VI), even in low concentrations in waste water, can cause damage to the kidneys, lungs, liver, as well as stomach [1, 2]. As a result of research, various techniques have been applied to remove Cr(VI) from waste water, including membrane filtration, ion exchange, electrolysis, adsorption, and biological techniques [3-5]. Among these, adsorption is the most attractive because of its economic efficiency [6, 7]. Discovering an appropriate adsorbent material, with high adsorption capacity and low cost, is the purpose of many current researches.

RM is one type of industrial waste which can be reused to produce low-cost adsorbent material. RM is known in the aluminium industry as a toxic waste resulting from the Bayer's process for the manufacturing of alumina from bauxite ore, following bauxite leaching by an alkali. The main components of RM are Fe_2O_3, Al_2O_3, SiO_2, CaO, and Na_2O. In Vietnam, according to the government's projection up to 2025, 15 million tons of alumina will be produced and more than 20 million tons of RM will be wasted yearly. More than 200 million tons of RM will be wasted over 10 years, therefore, this amount rising to more than 1.15 billion tons

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over 50 years [8]. There has been much research focused on recycling and increasing the value of RM. Recently, some studies have shown that it can be used as an adsorbent to remove pollutants such as arsenic [9], mercury [10], dyeing [11], as well chromium [12] from waste water. However, this involves a large amount of acid being used to neutralize the RM.

Rice husk ash (RHA) is mainly composed of SiO_2 (at about 95%), and other trace elements such as potassium, calcium, magnesium, iron, copper, manganese, and zinc. An attempt was made to investigate the synthesis of a material, with a partial zeolite structure, from RHA and RM, and with a high pH, so that the alkalinity did not require to be neutralized or acidified, thus reducing the cost of this process. The special feature of this study is that it examines synthesis of the adsorbent without processing residual alkali - an approach not previously published.

In this study, a new kind of adsorbent material was synthesized from RM and RHA, and the effect of various factors on the adsorption process of Cr(VI) investigated. The advantage of this process is not only using an agriculatural by-product, but also reusing the remaining caustic soda in RM without neutralizing it with acid.

Methods and materials

The main chemicals used in the synthesis process and the testing of the adsorption properties of the material on Cr(VI) were oxalic acid (99%, Merck), $K_2Cr_2O_7$ (99.9%, Merck), and diphenylcarbazite as an indicator.

RM was obtained from Tan Rai factory, Lam Dong province, Vietnam with the composition as follows [13]: 64.2% Fe_2O_3, 12.6% Al_2O_3, 4.5% Na_2O, 3.7% SiO_2, 4.13% CaO, 9.3% P_2O_5, 0.235% TiO_2.

RHA was collected from Sa Dec industrial park in Dong Thap province, Vietnam. After undergoing the calcination process for 2 hrs at 700°C, the composition of the RHA was as follows [13]: 95.2% SiO_2, 0.375% P_2O_5, 1.02% K_2O, 0.584% CaO.

The physico-chemical properties of the synthesized material were characterized using a variety of methods. An X-ray diffractometer (XRD, Bruker D8 Advance, Germany) with CuK_α radiation (λ=0.15406) was used to determine the structure and crystallite phase. The morphology of the material was investigated through use of a Scan Electronic Microscope SEM (FESEM, S4800-Hitachi, Japan) and a Transmission Electronic Microscope (TEM, JEM 1400, JEOL, Japan). The specific surface area of the synthesized powder was tested by BET (NOVA 3200e, Quantachrome Instruments, USA).

The absorbent material (ZRM) was synthesized from RM and RHA using the process as described in [13] with the ratio of SiO_2/Al_2O_3 at 1.8. The remaining caustic in the RM did not require neutralizing by acid, which is an advantage of this process. ZRM was applied to test its adsorption activity on Cr(VI). In this process, a 250 ml solution of Cr(VI) was poured into a beaker in which 10 grs of ZRM had been placed. The affecting factors were then investigated, including the pH of the initial Cr(VI) solution (2-7), the initial concentration of the Cr(VI) solutions (10-40 mg/l), and stirring rates (200-400 rpm). All experiments were conducted at room temperature (25°C). The resulting mixtures were centrifuged to separate solids from liquids, diluted with the ratio of 1:5 times, and then analyzed via UV-Vis equipment (Shimadzu, Japan) with diphenylcarbazite as an indicator at a wavelength of λ=540 nm.

For analysis of the Cr(VI) concentration in the sample according to adsorption time, the calibration curve with the dependence of Cr(VI) concentration (C = 0; 0.5; 1.0; 2.0; 3.0; and 4.0 mg/l) on absorbance (Abs) was constructed as follows:

$$C_i = 0.579*(Abs) \quad (1)$$

The adsorption yield was calculated by the equation (2):

$$H = (C_o - C_e)*100/C_o \quad (2)$$

where C_o and C_e correspond to the initial and equilibrium concentrations of Cr(VI) (mg/l).

Equilibrium Cr(VI) concentration (C_e) was determined at the point at which Cr(VI) adsorption was saturated [Cr(VI) concentration did not change over time].

Results and discussion

Physico-chemical characteristics of catalysts

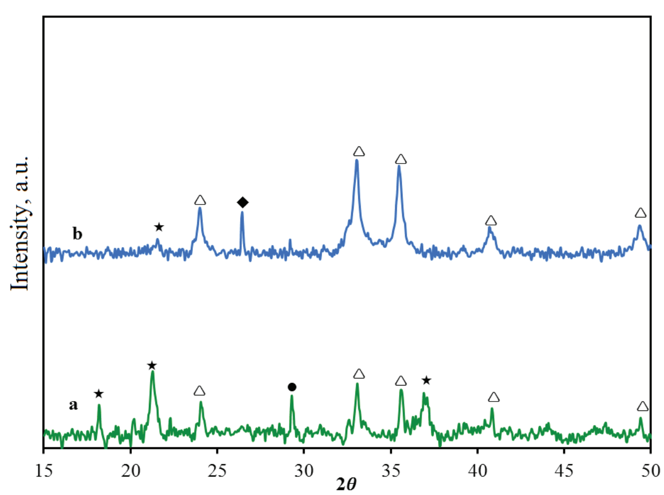
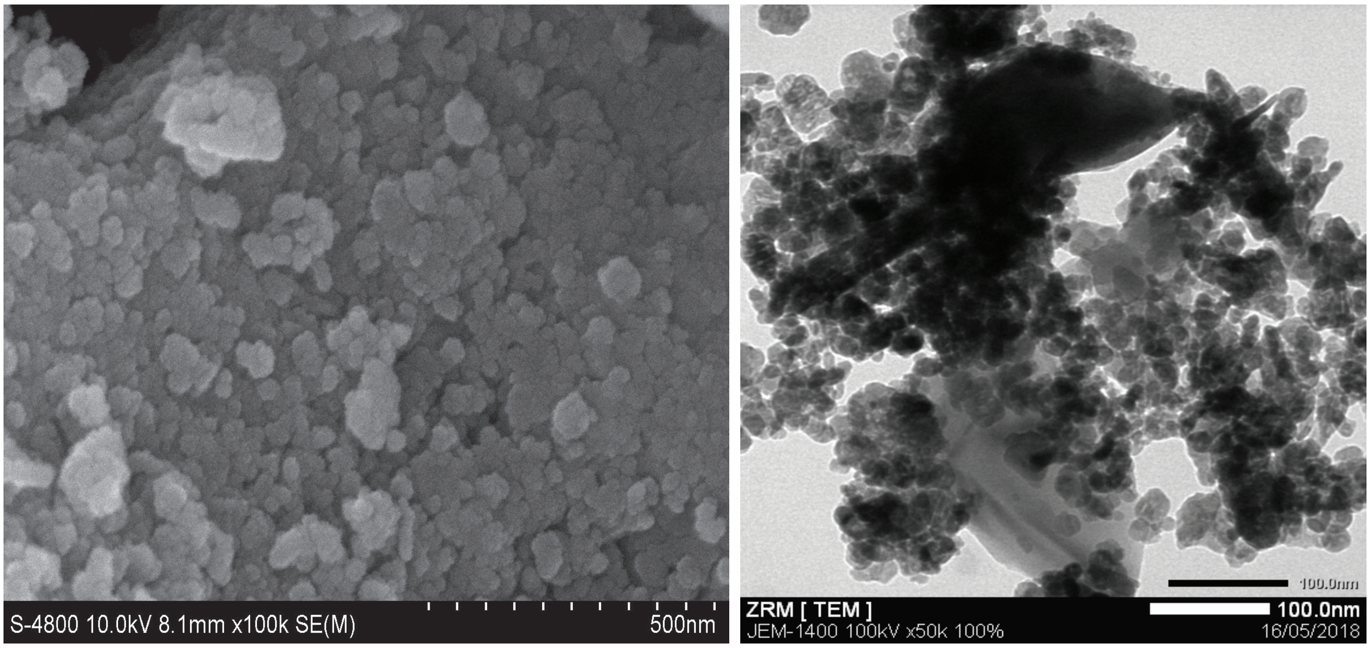


Fig. 1. XRD patterns of raw RM (a) and ZRM (b).



(A) (B)

Fig. 2. SEM (A) and TEM (B) images of ZRM.

The XRD patterns in Fig. 1 show that RM is mainly composed of hematite (2θ = 24, 33, 35.5, 41, and 49.4°) and gibbsite (2θ = 18, 21.2, and 37°), besides the peak of calcite (2θ=29°) [14]. The patterns for ZRM show that the peaks of gibbsite and calcite have disappeared, with the peaks for hematite in the same position but higher and sharper compared to that of raw RM.

The results of the specific surface areas obtained by BET analysis for RM, RHA, and ZRM were: 23.59, 28.35, and 70.76 m^2/g, respectively. According to these results, the specific surface area of ZRM is triple that of raw RM. This finding could be explained by the small amount of zeolite in phase A, formed during the synthesis process, as shown in the XRD patterns (2θ=27°), and the organic compounds on the surface of raw RM being destroyed during the calcination process. The material synthesized by ZRM has an average pore diameter of 18Å and a pore volume of 0.051 cm^3/g.

The SEM image in Fig. 2 shows that particle size on the surface of ZRM is rather uniform, in the range of 30-50 nm. Furthermore, it can be seen that ZRM has high porosity and low aggregation at its surface. The TEM results for ZRM as shown in Fig. 2 show some pores on the surface were covered by other compounds found in RM, such as Fe_2O_3, with the result that the spcific surface area for ZRM is not so high.

Adsorption of Cr(VI) by ZRM

Comparison of Cr(VI) adsorption between raw RM and ZRM:

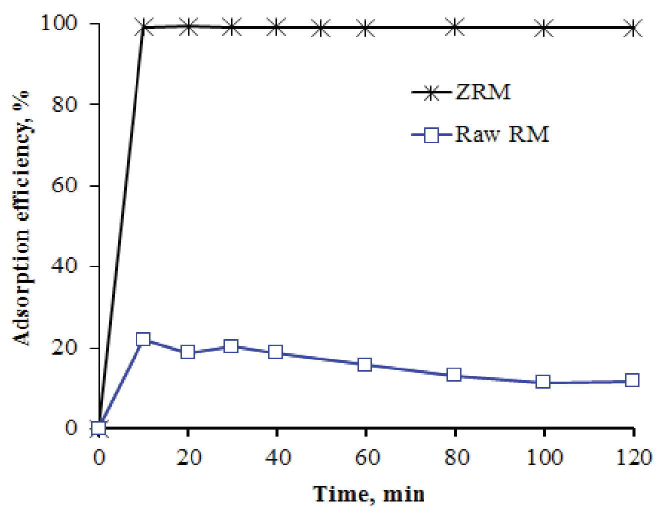


Fig. 3. Cr(VI) adsorption by raw RM and ZRM.

The adsorption capacity of raw RM and ZRM for Cr(VI) was studied at stirring velocity conditions of 300 rpm, at a temperature of 25°C, and at pH=2 (which was adjusted by use of oxalic acid); the initial concentration of Cr(VI) was 20 ppm, where the mass ratio of adsorbency was 10 g/l. The results are shown in Fig. 3. It can be seen that ZRM's capacity for absorption of Cr(VI) is much higher than that of raw RM; just 10 minutes into the adsorption process, the adsorption yield of ZRM reached 100%. This meant the absorbance (Abs) of the solution is approximately zero, while it is about 12% with raw RM.

Effect of the conditions on efficiency of ZRM's absorption of Cr(VI):

The capacity of ZRM for absorbing Cr(VI) was studied with various values of stirring capacity - from 200 rpm to 400 rpm, at pH=2, and with all other conditions remaining the same as the previous experiment. The results are shown in Fig. 4. When the stirring velocity was 200 rpm, the adsorption capacity was low, at around 40% after 30-40 min; at 300 rpm and higher, however, the adsorption yield reached 100% after 15 min with no further change.

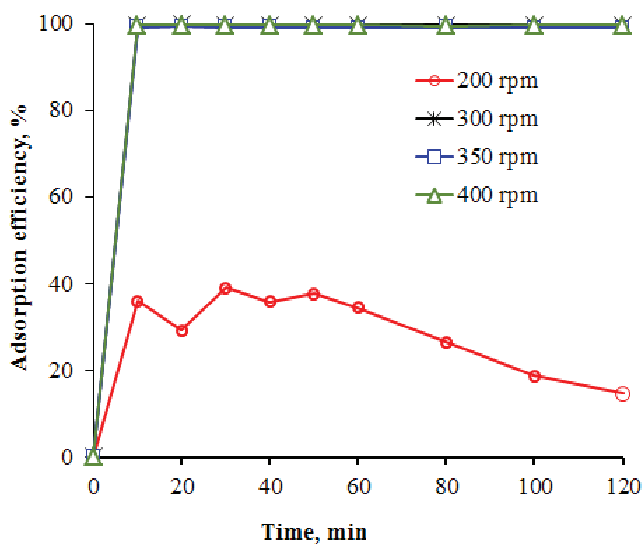


Fig. 4. Effect of stirring rate on ZRM's efficiency in absorbing Cr(VI).

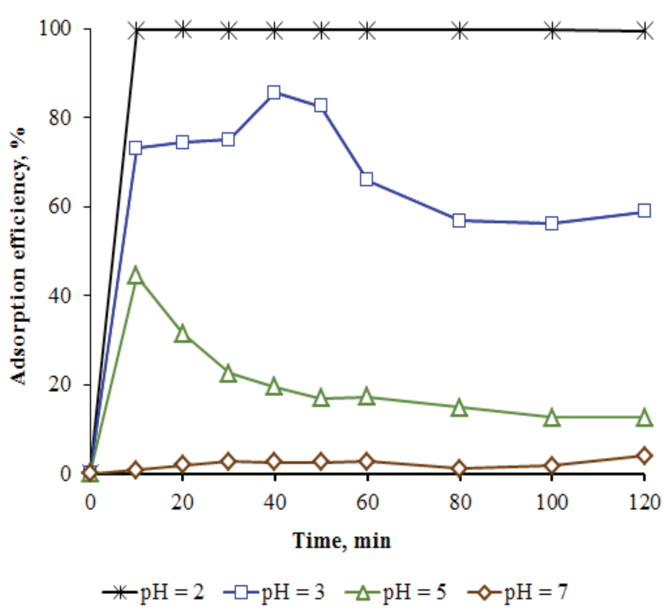


Fig. 5. Effect of pH on ZRM's efficiency in absorbing Cr(VI).

pH is one of the factors strongly affecting the adsorption of heavy metal ions. The effect of pH, adjusted by oxalic acid, on ZRM's adsorption of Cr(VI), is shown in Fig. 5, at a stirring velocity of 300 rpm and all other conditions remaining the same as in the previous experiments. The results show that when the pH is increased from 2 to 7, the adsorption capacity of ZRM is decreased. The highest adsorption yield was determined as being at pH=2, and this value is 99.73% after 10 min. This can be explained by the material surface being assembled H^+ and subsequently Cr(VI) being more easily adsorbed by the process of ion exchange. The reducing of absorption capacity when the pH is increased, might be because of the process of hydrolysis, which prevents the dispersion step in the adsorption process [15].

To determine the effect of the content of ZRM in the solution, the adsorption process was carried out with the same conditions as the previous experiments, where this varied from 5 to 15 g/l. Fig. 6 shows that when the ZRM concentration is increased, the adsorption yield also increases. However, if the ZRM concentration reaches 20 g/l, then the adsorption yield is decreased. This might be explained by the fact that at concentrations greater than 15 g/l, aggregation of the material will occur, leading to a reduction of the adsorption surface. With a ZRM concentration of 10 g/l, the maximum Cr(VI) adsorption is 23.32 mg/g which is higher than that of RM modified cetyltrimethylammonium bromide (22.20 mg/g), as reported in the work of Li, et al. [15].

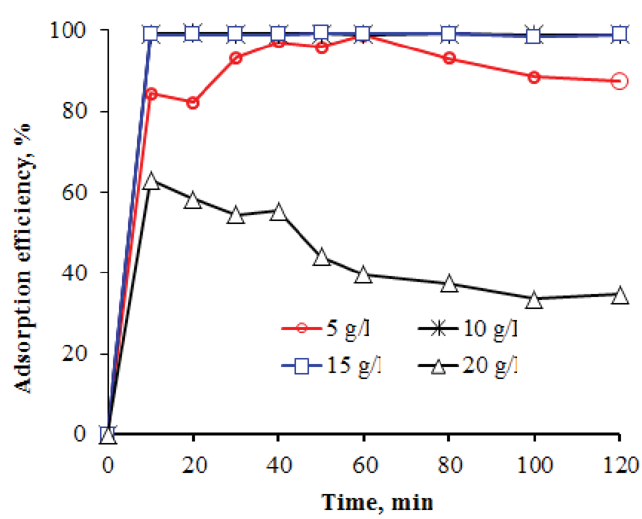


Fig. 6. Effect of ZRM concentration in the solution, on adsorption of Cr(VI).

Conclusions

The material ZRM for adsorption of Cr(VI) in solution, synthesized from RM and RHA without the use of acid to neutralize it, has a surface area of 70.76 m^2/g and a particle size of 30-50 nm. The optimum conditions for Cr(VI) adsorption by ZRM at 25^oC were determined as pH=2, a stirring rate of 300 rpm, and material content of 10 g/l. With these conditions, based on the equilibrium adsorption result, the maximum adsorption capacity for Cr(VI) in a solution of ZRM is 23.32 mg/g - three times higher than that of raw RM. This study has suggested a way of synthesizing cheap material from two waste resources, RM and RHA, for Cr(VI) adsorption in solution, and with high efficiency.

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The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

[1] Muhammad Mahmood-ul-Hassan, Vishandas Suthor, Ejaz Rafique, and Muhammad Yasin (2015), "Removal of Cd, Cr, and Pb from aqueous solution by unmodified and modified agricultural wastes", *Environmental Monitoring and Assessment*, **187**, p.19.

[2] Waseem Daoud, Taghi Ebadi, and Ahmad Fahimifar (2015), "Optimization of hexavalent chromium removal from aqueous solution using acid-modified granular activated carbon as adsorbent through response surface methodology", *Korean Journal of Chemical Engineering*, **32**, pp.1119-1128.

[3] Mojdeh Owlad, Mohamed Kheireddine Aroua, Wan Ashri Wan Daud, and Saeid Baroutian (2009), "Removal of hexavalent chromium-contaminated water and wastewater: a review", *Water, Air, and Soil Pollution*, **200**, pp.59-77.

[4] Saroj K. Sharma, Branislav Petrusevski, and Gary Amy (2008), "Chromium removal from water: a review", *Journal of Water Supply: Research and Technology-AQUA*, **57**, pp.541-553.

[5] M. Arthy and M.P. Saravanakumar (2013), "Isotherm modeling, kinetic study and optimization of batch parameters for effective removal of acid blue 45 using tannery waste", *Journal of Molecular Liquids,* **187**, pp.189-200.

[6] M. Ahmaruzzaman (2011), "Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals", *Advances in Colloid and Interface Science*, **166**, pp.36-59.

[7] Lin Tang, Gui-De Yang, Guang-Ming Zeng, Ye Cai, Si-Si Li, Yao-Yu Zhou, et al. (2014), "Synergistic effect of iron doped ordered mesoporous carbon on adsorption-coupled reduction of hexavalent chromium and the relative mechanism study", *Chemical Engineering Journal,* **239**, pp.114-122.

[8] Tran Manh Hung (2012), *Research the physico-chemical properties of RM and its application in the environment*, masters, University of Natural Sciences.

[9] Hülya Genç-Fuhrman, Henrik Bregnhøj, and David McConchie (2005), "Arsenate removal from water using sand-RM columns", *Water Research,* **39**, pp.2944-2954.

[10] David A Rubinos and María Teresa Barral (2015), "Use of RM (bauxite residue) for the retention of aqueous inorganic mercury (II)", *Environmental Science and Pollution Research*, **22**, pp.17550-17568.

[11] C. Namasivayam and D.J.S.E. Arasi (1997), "Removal of congo red from wastewater by adsorption onto waste RM", *Chemosphere*, **34**, pp.401-417.

[12] You-Wei Cui, Jie Li, Zhao-Fu Du, and Yong-Zhen Peng (2016), "Cr(VI) adsorption on RM modified by lanthanum: performance, kinetics and mechanisms", *PLOS ONE,* **11**, p.e0161780.

[13] Dinh Thi Ngoc Quyen, Luu Cam Loc, Huynh Ky Phuong Ha, Dang Thi Hang Nga, Nguyen Tri, and Nguyen Thi Thuy Van (2017), "Synthesis of adsorbent with zeolite structure from RM and RHA and its properties", *The 3rd Int. Conf. on Chem. Eng. Food BioTech.*, Ho Chi Minh city, Vietnam.

[14] Harjeet Nath and Abanti Sahoo (2014), "A study on the characterization of RM", *International Journal on Applied Bioengineering*, **8(1)**, pp.1-4.

[15] Deliang Li, Ying Ding, Lingling Li, Zhixian Chang, Zhengyong Rao, and Ling Lu (2015), "Removal of hexavalent chromium by using RM activated with cetyltrimethylammonium bromide", *Environmental Technology*, **36**, pp.1084-1090.