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Evaluating the Removal of Hexavalent Chromium (Cr -VI) in Wastewater by Low-Cost Adsorbent Modified from Waste Fly Ash

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The Cr (VI) is a toxic element to human and other organisms. In this paper, the adsorption of Cr (VI) to fly ash zeolite (FAZ) was investigated in batch modes. The effect of pH (2 – 9), initial Cr (VI) concentration (0.2 – 1.4 mg/L), adsorbent amount (0.01 – 3.00 g), and contact time (0 – 5 h) was investigated. These experiments were carried out in an Erlenmeyer flask containing 50 mL solution of Cr (VI) at room temperature. The Langmuir and Freundlich models were applied for determining the adsorption characteristic and isotherms. The FAZ was tested for removing Cr (VI) containing in actual metal plating industry effluent. The result showed that in the investigated values of pH the adsorption ability decreased when pH increased. The adsorbent dose of FAZ provided the best capacity at 0.05g FAZ in 50 mL solution; the suitable adsorption time was observed at 3 h duration; the 0.8 mg/L of Cr (VI) concentration was appropriated in this study. The Langmuir model was matched to the experimental records (R^2 = 0.9922) which demonstrated that the Cr (VI) adsorption on FAZ belonged to monolayer type. In order reach the standard regulation at the column B, QCVN 40:2011/BTNMT for effluent industrial wastewater (Cr (VI) concentration is under 0.1 mg/L), it took 6 h duration for the adsorption to drop the initial Cr (VI) concentration of 0.803 mg/L to 0.091 mg/L. It can be suggested that FAZ is a good material for treating of Cr (VI) in aqueous solution and industrial wastewater.

1. Introduction

People have been facing the dark side of industrialization all around the world which is environmental pollution. The main concerns about surface and ground water resources are the contamination of organic matters, nutrients, microorganisms and heavy metal (Malise et al., 2020). The representative members of heavy metals include cadmium, arsenic, chromium, copper, lead, and mercury (Ru et al., 2021). Heavy metals are contained with high concentration in the effluent of many industries such as metal processing, landfill leachate, mining, pulp and paper; and pesticides (Guo et al., 2020). It has been well-known that heavy metal ions can destroy the enzyme system in living organs, thus cause many diseases related to nervous, digestive, respiratory, reproductive, and circulatory systems (Abbas et al., 2016). Chromium is reported to be the seventh most abundant elements on earth. It can enter the plants cells by penetrating through the ion channels on the membrane, accumulate in the food chain and become poisons to animal and human. It has been recorded that Cr can destroy many organs such as kidney, lung, brain and immune system. Therefore, the study of heavy metals, especially Cr removal in water by appropriate agents is very essential for the suitable development of the world. The environmental engineers have been developing new material that can achieve high treatment efficiency with low cost (Duan et al., 2020). Among them, the application of adsorption from waste is considered an expected trend as it could achieve both economic and environmental benefits at once (Kang et al., 2020)
The electric generation from coal is main energy sector in the world. It was reported that about 750,000 t of ash are generated annually worldwide in which the coal fly ash proportion is estimated as 40 % (Xing et al., 2019). People have been tried to reuse the waste coal fly ash in several fields such as construction materials (Muthusamy et al., 2020); catalytic synthesis (Sikarwar et al., 2018) ,and adsorbents (Kobayashi et al., 2020). A large amount of this waste has been dumped and this process could cause pollution for the soil, the ground

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water, and the air and then further made negative effect to the human health or other organisms (Asl et al., 2019). The advantages of developing FA-based adsorbent are including: low cost; recycle waste fly ash; environmental protection; and high efficiency (Pham and Le, 2021). It is necessary to find a suitable approach to convert this coal fly ash to useful product and apply in the environmental remediation. This study aims to investigate the hexavalent chromium removal by using zeolite modified from waste fly ash of power plant.

2. Materials and methods

2.1 Chemical reagents and materials

The chemicals including NaOH, HCl, and $K_2Cr_2O_7$ were in analytical level (Merck, Germany). Distilled water that used for diluting and dissolving reagents during experiment was prepared by Aquatron water still equipment (Stuart, England). The waste fly ash was taken from Duyen hai thermal power plant, pretreatment and further alkali modification to be FAZ. Before doing the experiment, characteristic of FAZ sample was determined by BET machine (SURFER, Thermo Fisher Scientific Co., US). As a result, this FAZ had surface space of 66.4 m^2/g, the pore volume was 15.3 cm^3/g.
The specific Cr (VI) concentration was synthesized by dissolving $K_2C_{r2}O_7$ reagent in distilled water with desired weight. The actual electroplating industry wastewater was collected from Mocal Company in Protrade Industrial Park in An Tay, Ben Cat Town, Binh Duong Province, Vietnam. In the treatment system of the factory, wastewater was separated into different lines according to its characteristic. In the line which contained chromic acid, the treatment went through steps of: pre-treatment, oxidation-reaction; and then adsorption by activated carbon to achieve the required standard before discharging. In this study, the the Cr (VI) removal test was carried out using wastewater collected from the treatment systems of the factory before the adsorption step. A volume of 50 mL wastewater containing Cr (VI) (C = 0.803 mg/L) was used for the FAZ adsorption test.

2.2 Experimental procedure

Batch experiments of Cr (VI) removal by FAZ were performed an Erlenmeyer containing 50 mL of Cr (VI) solutions with designed concentrations. Tested solution was shaken at 120 rpm in ambient condition. The effects of initial pH (2– 9), contact time (0 – 5 h), adsorbent dose (0.01 – 0.30 g), and Cr (VI) concentration (0.2 – 1.4 mg/L) were investigated. The NaOH 0.1 M or HCl 0.1 M solutions was used for pH adjustment. In order to determine the potential of adsorbent in Cr (VI), the adsorption capacity (Eq(1)) and removal rate (Eq(2)) are shown as bellow:

$$q_e = \frac{(C_0 - C_e) * V}{M} \tag{1}$$

$$R = \frac{(C_0 - C_e)}{C_0} * 100\% \tag{2}$$

where: C_o is the original concentration of adsorbate (mg/L); C_e and q_e are the concentration of adsorbate (mg/L) and the adsorption ability (mg/g) at the balance stage; V is the experimental volume (L); M is the adsorbent weight (g).

2.3 Analysis

During the experimental batches, liquid samples from the reactor were withdrawn from the reactor after a designed time. After that, samples were filtered by 0.45 µm pore filter paper, the obtained filtrate was used to analyze the Cr (VI) concentration. The quantitative of chromium in liquid samples was processed by following the instruction in TCVN 6658:2000. By following the instruction, chromium (VI) calibration curve was established; before analyzing, the samples those contained Cr (VI) were reacted with 1,5-diphenylcarbazide reagent to turn up a specific color and then further measured by spectrophotometer at 540 nm wavelength by UV – VIS (TCVN, 6658:2000).

2.4 Adsorption isotherm models

Langmuir model was widely applied to define the monolayer adsorption. The Freundlich model has been used to describe both monolayer and multilayer processes. In Langmuir model, it is assumed that: the adsorption happens on the surface of the material; the adsorption is homogeneous at all points at the surface; there is no reaction between adsorbent and the target adsorbate (Ru et al., 2021). The Langmuir model (Eq(3)) and Freundlich model (Eq(4)) are indicated below:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

$$\ln(q_e) = \ln(K_F) + \left[\frac{1}{n}\right] \ln C_e \quad (4)$$

Where: C_e, concentration of pollutant at the equilibrium stage (mg/l); q_e, adsorption ability at the balance stage (mg/L); q_m and b, K_F the adsorption constants (L/mg); n, the adsorbent intensity.

3. Results and discussion

3.1 Effect of pH on Cr (VI) adsorption

Figure 1 illustrates the effect of pH on Cr (VI) removal of the FAZ. The result indicated that the removal adsorption capacity decreased when pH was increased. The adsorption capacity gradually dropped from 0.79 to 0.46 mg/g together with the change of pH from 2 to 9. In the previous study, Mor et al. (2007) demonstrated that the removal of Cr (VI) ions from aqueous solution by activated charcoal was strongly affected by pH, the removal efficiency decreased from 99 % at pH 2 to 60 % at pH 10. The same trend of Cr (VI) removal in different pH value was also elucidated by other authors (Jang et al., 2020). This phenomenon can be explained that in the solution happens the chemical equilibrium: $2CrO_4^- + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$. In the acidic condition the $Cr_2O_7^{2-}$ is the dominant and CrO_4^- is dominant alkaline condition. The present of $Cr_2O_7^{2-}$ and H^+ ions can provide the favor environment for the adsorption process (Asl et al., 2013). When pH increases, the present of OH^- in the solution could complete with CrO_4^{2-} in attaching to the surface of adsorbent resulting in the reduction of adsorption capacity (Mor et al., 2007).

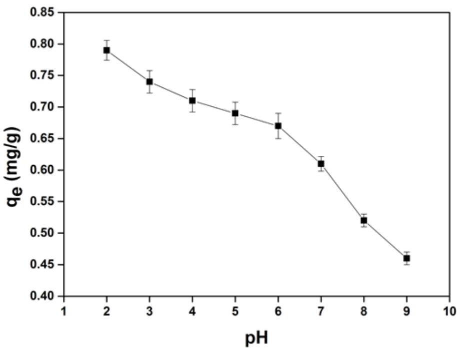

Figure 1: The effect of pH on Cr (VI) removal of FAZ adsorbent

3.2 Effect of FAZ dosage and contact time on Cr (VI) adsorption

The effect of FAZ dosage on removal efficiency and adsorption capacity is shown in Figure 2a. The results demonstrated that when the FAZ dosage increased from 0.01 to 0.30 g, the removal rate was improved but the adsorption capacity was reduced. Remarkably, the highest adsorption capacity was achieved at the dosage of 0.01 g however the removal efficiency at this dosage was only 50.8 %. At the adsorbent dosage of 0.05 g the removal efficiency reached 94.6 % and it was not increased significantly when the adsorption dosage increased in later level up to 0.30 g. This dose was chosen for the other experiments in this study. Figure 2b describes the removal rate during operational time. It is noticeable that the removal rate sharply increased in the first two hours of the operational time and to reach 91.2 % at the contact time of 3 h and the adsorption ability at this point was as 0.74 mg/g. The removal efficiency was eligible improve in later phase at contact time of 4 h (94.2 %) and 5 h (94.6 %). This could be explained by the fact that the active positions were stepwise saturated, so the chromium ions had no ability to compete with the functional groups in the material. Previous studies have described that an initial Cr (VI) concentration of 10 mg/L in the dose of adsorbent 0.5 g/100 mL solution could reach the equilibrium after 120 min (Mor et al., 2007). Dakiky et al. (2002) also found out that the necessary contact time for achieving equilibrium condition of Cr (VI) is 2 h (Dakiky et al., 2002). It can be assumed that the treatment of Cr (VI) by fly ash based adsorbent could obtain the equilibrium condition after 3 h contact time.

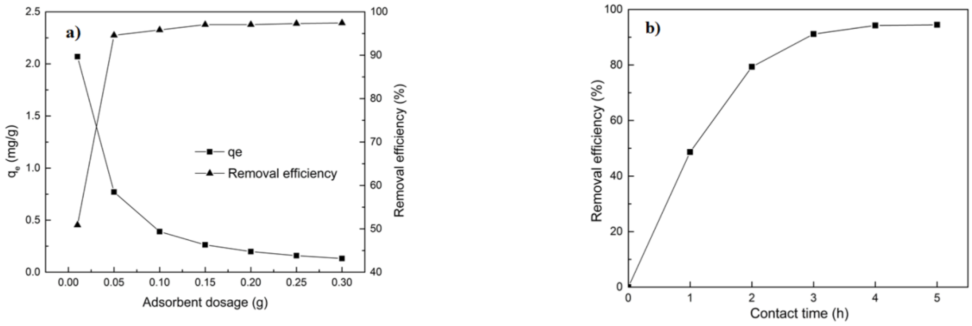

Figure 2: The effect adsorbent dosage (a) and contact time (b) on Cr (VI) adsorption

3.3 Effect of adsorbate concentration on adsorption capacity

The experiment was carried out in various concentrations in the range of 0.2 to 1.4 mg/L, the amount of adsorbent was fixed at 0.05 g of FAZ in 50 mL solution for each batch test; pH value was adjusted at 3. The result indicated that the adsorption ability of Cr (VI) by FAZ was enhanced with the enlargement of initial concentration from 0.2 to 0.8 mg/L corresponding to improved adsorption ability from 0.18 to 0.62 mg/g. When the chromium (VI) concentration was changed from 0.8 to 1; 1.2; and 1.4 mg/l, the adsorption capacity was insignificantly improved (Figure 3). In the earlier study, Khan et al investigated the removal of chromium (VI) by using rice husk carbon adsorbent and revealed that the removal rate of Cr (VI) decreased from 62.7 to 43.2 % when the concentration of Cr (VI) risen from 60 to 120 mg/L (Khan et al., 2016). It was elucidated that when the amount of adsorbent was constant, the higher adsorbate concentration the less active sites and capillaries of adsorbent were available. In other words, the adsorbent became saturated resulting the decrease of adsorption capacity in the later phase of the experiment (Mor et al., 2007).

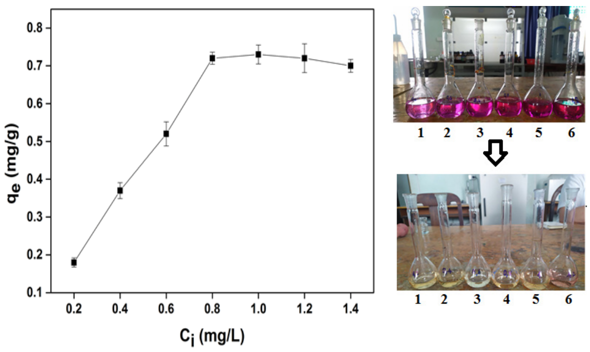

Figure 3: The effect initial Cr (VI) concentration on adsorption capacity

3.4 Adsorption isotherms

After conducting experiments, the adsorption kinetics of FAZ was determined. Based on the Langmuir model, the good linear relationship between C_e/q_e on the Ce was obtained which indicated at high the correlation coefficient (R^2 = 0.9922) (Figure 4a). The maximum adsorption level was calculated as q_m = 0.797 mg/g. From the observed data, the adsorption trend (R_L) that equals to 1/(1+ bC_0) was calculated, R_L value of 0.806. Previous researches introduced the status of isotherm in the value range of R_L as following: $R_L > 1$: unfavorable; $R_L = 1$: linear; $0 < R_L < 1$: favorable; and $R_L = 0$: irreversible (Ma et al., 2019). For that reason, the value of R_L in this study is in the expected range. Therefore, it can be assumed that the adsorption route was fixed with Langmuir isotherm and it can be considered that the adsorption of Cr (VI) on FAZ is monolayer type. Figure 4b shows the relationship between $\ln q_e$ and $\ln C_e$ by applying Freundlich model. The obtained straight line showed R^2 as 0.6084. It meant that Freundlich model is not appropriate for the observed data from this experiment and this model is not suitable to describe the adsorption process of Cr (VI) on FAZ in this study. The better match of the Langmuir equation than that Freundlich model in study of removing Cr (VI) in the solution by different adsorbents was also found out in the former researches (Mor et al., 2007).

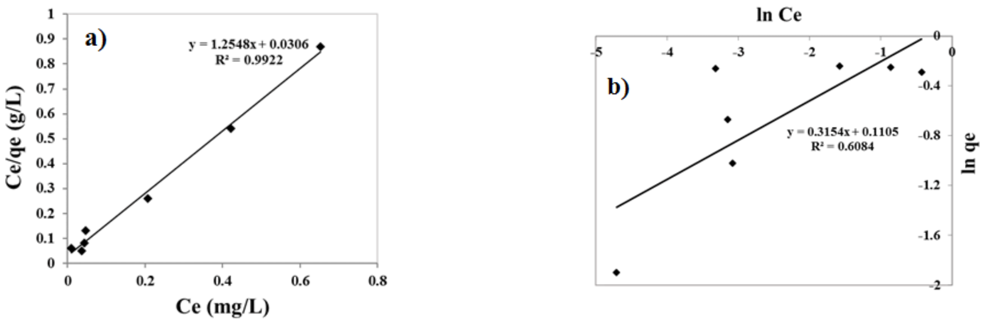

Figure 4: The isotherm schemes of Cr (VI) adsorption by FAZ: a) Langmuir model; b) Freundlich model

3.5 The Cr (VI) removal in actual metal plating industry wastewater

The change of chromium concentration in the solution during the experimental period is illustrated in the Figure 5. It is clear to observe that the adsorption capacity was gradually increased from 0 to 5 h with the increase of removal efficiency from 48.00 % to 87.96 % and it reached 88.63 % after 6 h operation corresponding to the Cr (VI) concentration as 0.091 mg/L. This effluent value of Cr (VI) could satisfy the required standard regulated at the column B, QCVN 40: 2011/BTNMT for effluent industrial wastewater (QCVN, 2011). It was demonstrated that the actual metal plating industry wastewater which contained competitive ions from many other metals could affect the adsorption of chromium to the adsorbent (Wen et al., 2011). From the experimental result, it can be demonstrated that the FAZ could provide a feasible approach in the treatment of Cr (VI) in the electroplating industry wastewater.

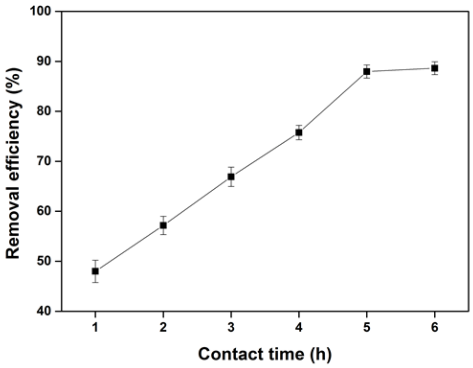

Figure 5: The removal Cr (VI) in metal plating industry wastewater by FAZ

4. Conclusions

This study found out that the FAZ is effective to remove Cr (VI) containing in synthesis and actual electroplating industry wastewater. The results suggests that he suitable operational conditions of the tests as at acidic condition, pH = 2. At the adsorption dosage of 0.05 g, FAZ could perform well for the treatment of 50 mL Cr (VI) (C = 0.8 mg/L) at contact time of 3 h. The study of adsorption isotherms revealed the best suitable of the Langmuir model in this case study with the correlation coefficient of 0.9922. The adsorbent also demonstrated the high potential of treatment Cr (VI) electroplating industry wastewater. The FAZ adsorbent could remove Cr (VI) from 0.803 g/L to 0.091 mg/L after 6 h to achieve the requirement of Cr (VI) level containing in industry effluent (under 0.1 mg/L) indicated in QCVN 40:2011/BTNMT. In order to have fully understanding in this process, it is necessary to conduct further experiment to investigate the effect of other operational factors such as temperature. The adsorption of concomitant heavy metals in actual wastewater is essential to investigate.

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