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Immobilization of Coal Fly Ash in Alginate Beads for Adsorption of Fe (III) Ions

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ABSTRACT. Various industrial, agricultural, household, mining, smelting, and chemical industrial activities can generate waste containing heavy metals such as Fe(III). Fly ash has the potential as an effective adsorbent to capture heavy metals in wastewater. This study aims to immobilize coal fly ash in alginate beads for the adsorption of Fe(III) ions from synthetic waste solution. To test the adsorption capability of fly ash-alginate beads was performed by varying the contact time (1-24 hours), the mass of fly ash-alginate beads (5, 15, 35, 45, and 55 g), and the initial concentration of Fe (III) ions at 6, 8, and 10 ppm. The determination of the concentration after adsorption was done using a UV-Vis spectrophotometer. The results showed that fly ash-alginate beads were able to remove Fe(III) ions up to 68.60% at a bead mass of 55 g, ion concentration of 10 ppm, and the equilibrium contact time was reached after 5 hours. The analysis results indicated that the adsorption mechanism followed the Freundlich isotherm model due to the heterogeneous surface exhibited.

1. INTRODUCTION

Water is Earth's most abundant natural resource, but only a small fraction (about 1.0%) is fresh and accessible to humans. Freshwater quality is declining worldwide due to pollution from organic and inorganic contaminants. While having positive impacts, population growth, modernization, industrial development, and economic progress also bring negative consequences, such as water pollution. This is a serious concern as it can harm living organisms and the environment [1].

Wastewater from various sources, such as industry, agriculture, households, mining, smelting, chemical manufacturing, and battery production, can release heavy metals into surface water and soil. Some industries, such as steel tempering, coal coking, and mining, often release significant amounts of iron, nickel, copper, and zinc into the environment. Iron is present in the aquatic environment in the form of salt compounds Fe(II) and Fe(III) bound to organic or inorganic substances. While iron is an essential metal required by living organisms in certain quantities, too much iron can be toxic. High concentrations of iron can have negative effects on human health, including poisoning, digestive disorders, joint inflammation, congenital disabilities, gum bleeding, increased cancer risk, kidney damage, constipation, diabetes, diarrhoea, dizziness, fatigue, hepatitis, high blood pressure, insomnia, premature ageing, and even sudden death [2].

Fly ash is a fine-grained waste product from coal-fired power plants, with a global production of around 600 million tons per year. The composition of fly ash varies depending on the type of coal used and the combustion temperature. Alumina (Al_2O_3), hematite (α-Fe_2O_3), silica (Si), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), and titanium oxide (TiO_2) are the major components in fly ash [3]. Over the past two decades, research has shown that fly ash can be used effectively to remove heavy metals from wastewater at a low cost, both for cleaning gases and water [4].

Extensive research has been undertaken on removing heavy metals, in this case iron, using fly ash. One such investigation explored Fe adsorption using 150-180 mesh fly ash powder activated by concentrated H_2SO_4, yielding a 94% Fe adsorption efficiency [5]. Although the results were encouraging, they were ineffective in the following phases due to the difficulty separating fly ash from wastewater. Researchers typically use fly ash in the form of a suspension. However, using fly ash in this suspended form encounters challenges in separating and

retrieving or recycling the adsorbent, which is time-consuming and costly. In this research, this issue is resolved by immobilizing fly ash particles using alginate, a support material. Alginate will keep the fly ash particles in place, making them easier to remove from the wastewater after they have captured the heavy metals.

Alginate is a cheap, natural, and biodegradable polymer that is good at forming complexes with many different heavy metals. Furthermore, sodium alginate is a highly suitable material as a carrier matrix because it is a natural polymer, biodegradable, biocompatible, non-toxic, and highly hydrophilic, making it well-suited for absorbing water-soluble toxic substances [6].

In our previous research, we successfully made fly ash-alginate beads and tested their ability to remove Rhodamine-B dye from water. The results indicated a reduction in the concentration of Rhodamine-B by 31.15% from the initial solution concentration after a 300-minute adsorption process using 35 g of beads. Furthermore, based on BET characterization, the fly ash-alginate beads are classified as mesoporous materials with a pore diameter of 10 nm, a total pore volume of 5.332×10^{-3} cc/g, and a specific surface area of 2.133 m^2/g [7].

In this study, we are focusing on the application of fly ash-alginate beads for the removal of Fe(III) ions from wastewater, as well as observing the mechanism of Fe(III) ion removal using well-known adsorption isotherm models such as Langmuir and Freundlich. Furthermore, metal ion concentration was measured in this investigation using a UV-Vis spectrophotometer. Although an atomic absorption spectrophotometer (AAS) is used to assess heavy metal concentrations according to the Indonesian National Standard (SNI), its availability is still restricted. A UV-Vis spectrophotometer is another approach that may be employed. Due to the employment of a ligand as a complexing agent for Fe(III) ions, measuring the concentration of Fe(III) ions using a UV-Vis spectrophotometer is considerably easier, simpler, and has acceptable accuracy [8].

2. MATERIALS AND METHODS

2.1. Materials and Tools

The materials used in this research are waste synthesis made from anhydrous FeCl$_3$, fly ash derived from coal combustion in a boiler, distilled water (aquadest), sodium alginate obtained from Himedia, CaCl$_2$.2H$_2$O, KSCN 2M complexing agent, and 4M HNO$_3$. The primary tools used to create the fly ash-alginate beads include an oven, a 100-mesh sieve, a magnetic stirrer, a 5 mL syringe, and a Shimadzu UVmini-1240 spectrophotometer.

2.2. Immobilization of Fly Ash Forming Fly Ash-Alginate Beads

The immobilization process of fly ash in calcium alginate to be used as an adsorbent is divided into two stages. In the initial stage, 1% w/v sodium alginate is dissolved in 100 mL of distilled water and stirred until homogeneous. Then, 0.5g of dried fly ash, which has been sieved through a 100-mesh sieve, is added to the sodium alginate solution and stirred for 30 minutes until the fly ash powder is evenly suspended in the solution, as indicated by the absence of fly ash agglomeration in the solution. The second stage involves extruding the mixture of fly ash and alginate using a 5 mL syringe to form slowly dripping spherical droplets into a 100 mL solution of 0.1 M CaCl$_2$ hardening solution that is stirred at a constant speed. They are immersed in the CaCl2 solution to harden the alginate beads for 24 hours. Afterwards, the beads are filtered, washed three times with distilled water, and stored by soaking them in distilled water at room temperature for later use as an adsorption test for Fe(III) ions. The beads of fly ash-alginate produced using this method are presented in Figure 1.b.
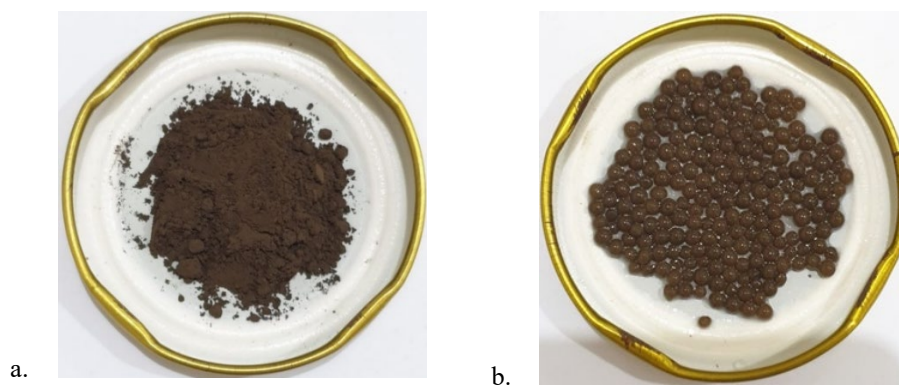
Figure 1. (a) Fly Ash after being dried and sieved to 100 mesh, (B) Fly Ash-Alginate Beads

Based on random measurements of the diameter of fly ash-alginate beads, particle sizes were found to be relatively uniform, approximately +/- 3 mm (Figure 2).
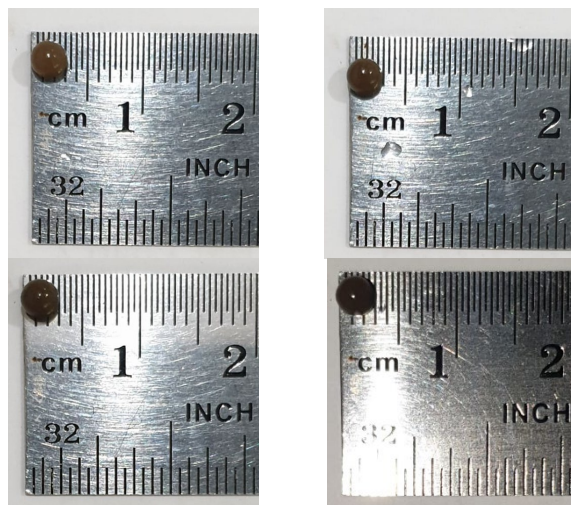
Figure 2. Random Measurement of Fly Ash-Alginate Beads Diameter

2.3. Ion Fe(III) Adsorption

A 100 ppm Fe(III) stock solution for synthetic wastewater is prepared by dissolving 0.01 g of anhydrous $FeCl_3$ in 100 mL of distilled water. The adsorbate concentrations needed for standard curve determination and adsorption process experiments are 0.5, 2, 4, 6, 8, and 10 ppm. These concentrations are achieved by sequentially diluting the stock solution to the appropriate volumes.

The adsorption experiment of Fe(III) ions was carried out in a batch system without stirred using a 250 mL beaker, with a 100 mL test solution containing varying concentrations (6, 8, and 10 ppm) and the mass of the fly ash-alginate beads (5, 15, 35, 45, and 55 g). At the end of the predetermined time intervals, the concentration of Fe(III) ions in the test solution was measured using a spectrophotometer at a specific wavelength. The adsorption process was conducted by observing the influence of contact time (1-24 hours), the mass of beads added to the adsorbate (5-55 g), and the initial metal concentration (6-10 ppm) on the removal of Fe (II) ions, which was calculated using an equation:

$$\%R = \left(1 - \frac{c_t}{c_o}\right) \times 100 \tag{1}$$

Given that %R is the percentage removal of Fe(III), Co is the initial concentration of Fe(III) in the solution, and C_t is the concentration of Fe(III) in the solution at a given time t.

3. RESULTS AND DISCUSSION

This study presents a spectrophotometric method to measure Fe(III) concentration in a test solution, optimizes the adsorption process using fly ash coal immobilized on an alginate matrix hardened with $CaCl_2$ solution, and investigates the mechanism of Fe (III) ion removal.

3.1. Standard curve

To measure the concentration of Fe(III) ions in a test solution using a UV-Vis spectrophotometer, a complexing agent is needed to form an orange-coloured $Fe(SCN)_3$ compound. Potassium thiocyanate (KSCN) is one example of a complexing agent that can be used. The higher the concentration of Fe (III) ions in the solution, the darker the orange colour will be. Nitric acid is added to create an acidic environment, allowing KSCN to react with $FeCl_3$ following the reaction mechanism as follows [9]:

$$FeCl_{3(aq)} + 3\ HNO_{3(aq)} \rightarrow Fe(NO_3)_{3(aq)} + 3\ HCl_{(aq)} \tag{2}$$

$$Fe(NO_3)_{3(aq)} + 3\ KSCN_{(aq)} \rightarrow Fe(SCN)_{3(aq)} + 3\ KNO_{(aq)} \tag{3}$$

The determination of the concentration of the test solution begins with the preparation of a calibration curve. This curve is used as a standard to calculate the concentration of Fe(III) ions in the test solution. The wavelength used for the calibration curve was 490 nm, which resulted in the highest absorbance measurement using a 100 ppm standard solution. The absorbance measurement results for various Fe(III) ion concentrations in the test solution are shown in Figure 3. The linearization plot of the x-axis (absorbance) and y-axis (Fe(III) ion concentration in ppm) data resulted in a linear equation

$$y = 210,7792\,x - 0,9280 \tag{4}$$

The strong linear correlation between absorbance and concentration, as evidenced by the determination coefficient (R^2) of 0.9520 in Equation 4, demonstrates that the equation can accurately represent the data shown in the linear plot in Figure 3.
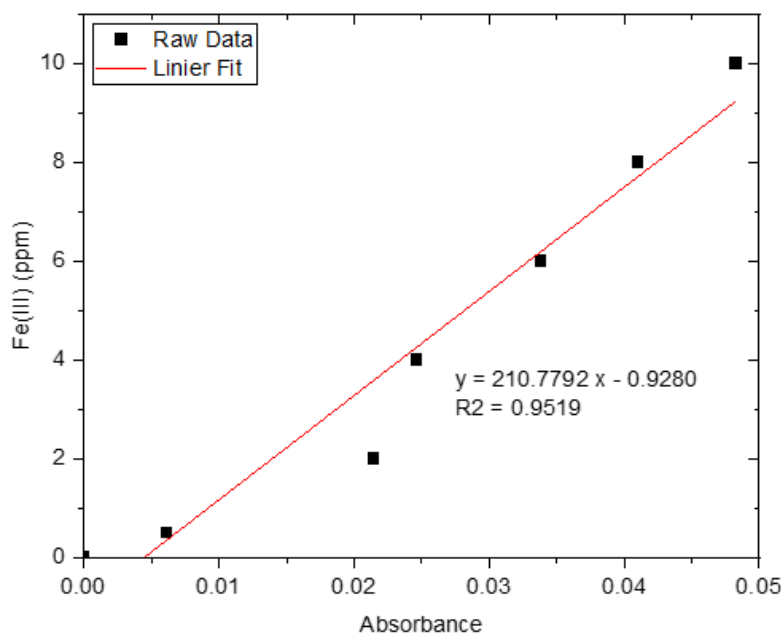

Figure 3. Fe(III) Ion Curve Standard

3.2. Effect of Adsorbent Mass

Increasing the mass of the adsorbent generally leads to a higher percentage of pollutant removal. This is because more adsorption sites are available, as evidenced by the results of the study shown in Figure 4. The immobilization method used in this research prevents the formation of agglomeration when more fly ash is added to the sample, due to the small particle size. This is confirmed by the fact that the percentage of Fe(III) ion removal does not decrease as the mass of fly ash-alginate beads increases. The lowest percentage of Fe(III) ion removal (59.33%) was obtained with a mass of 15 g of fly ash-alginate beads and an initial concentration of 10 ppm after 5 hours. The highest percentage of removal (68.60%) was obtained with a mass of 55 g of fly ash-alginate beads and the same period.
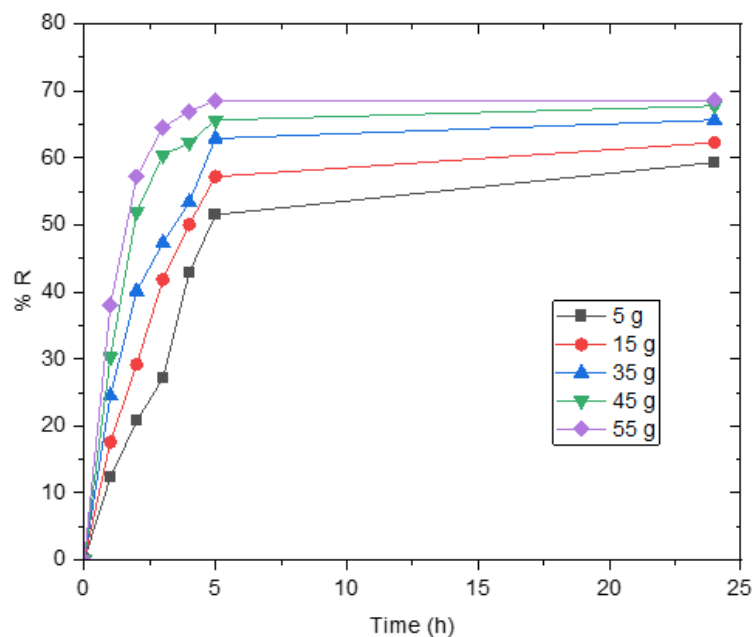
Gambar 4. Effect of the Mass of Fly Ash-Alginate Beads on the Percentage Removal of Fe (III) Ions.

3.3. Effect of Adsorbate Concentration

The effectiveness of the adsorption process can be observed through the initial concentration of metal ions that are removed. An increase in the initial concentration of metal ions, in this case Fe(III) ions, leads to an increase in the percentage removal of Fe(III) ions in the solution due to the greater driving force for mass transfer at higher concentrations. As shown in Figure 5, using the same mass of beads, which is 55 g, the percentage removal of Fe(III) ions also increases with increasing initial concentration of the adsorbate. This is due to the possibility of interaction between the surface of the adsorbent and the Fe(III) ions. The percentage removal of Fe(III) ions with initial concentrations of 10 ppm, 8 ppm, and 6 ppm after 5 hours, respectively, are 68.68 %, 61.54%, and 48.02%.
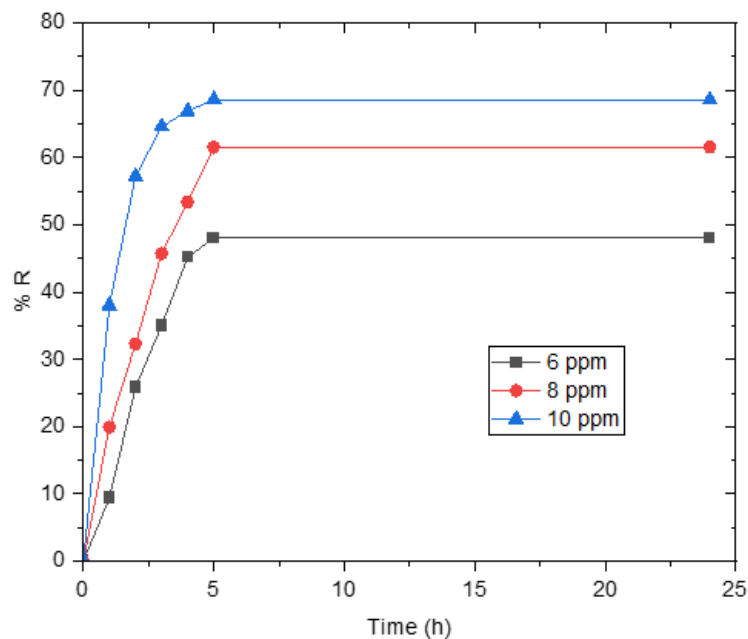
Figure 5. Effect of Fe(III) Ion Concentration on the Percentage Removal of Fe(III) Ions

3.4. Effect of Contact Time

Contact time is crucial in determining the binding and complete usage of the adsorbent in solution during the extraction of heavy metal ions. This is especially crucial for real-world applications because, as contact duration grows, the proportion of metal ion elimination rises and finally achieves equilibrium at a prime moment before becoming constant (Figures 4 and 5). In this study, the saturation limit of Fe(III) ion adsorption on fly ash-alginate beads is shown by the rise in adsorption that persists up to a contact time of five hours and achieves equilibrium at a contact time of twenty-four hours. In this work, the saturation limit was shown by the rise in Fe(III) ion adsorption on fly ash-alginate beads up to a contact period of five hours, which achieved equilibrium after twelve hours.

3.5. Adsorption Mechanism

The Langmuir Isotherm (5) and Freundlich Isotherm (6) equations can be used to explain the mechanism of adsorption of Fe(III) ions on fly ash-alginate beads using linear regression. The heterogeneous, multilayer adsorption process on the surface with varying adsorption energies is described by the Freundlich equation. When there is homogeneous adsorption, every adsorbate molecule has the same adsorption activation energy upon adhering to the surface, referred to as the Langmuir model. When a monolayer of adsorbate layer sticks to a homogeneous surface without any interaction between adsorbed molecules, this method assumes that the adsorbent is in a saturated state [10][11].

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L}\frac{1}{C_e} + \frac{1}{q_{max}} \tag{5}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

The Freundlich isotherm equation shows that a plot of ln q_e (equilibrium adsorption capacity, mg/g) versus ln Ce (equilibrium adsorbate concentration, ppm) from Equation (5) yields a straight line with an intercept at K_F and a slope of 1/n. The Freundlich adsorption coefficient (K_F, mg/g) can indicate the affinity between the adsorbate and adsorbent. The value of n (heterogeneity factor) is related to the energy heterogeneity on the adsorbent surface and determines whether the curve is linear or not. A plot of $1/q_e$ versus $1/C_e$ from the Langmuir isotherm equation also yields a straight line with $1/K_L$ qmax and 1/qmax as the slope and intercept, respectively. K_L is the adsorption energy coefficient (L/mg) and q_{max} is the maximum adsorption capacity (mg/g) [12]. The results of the Langmuir and Freundlich isotherm adsorption analyses for five different masses of fly ash-alginate beads are presented in Figures 6.a and 6.b, and Table 1.

(a)	(b)
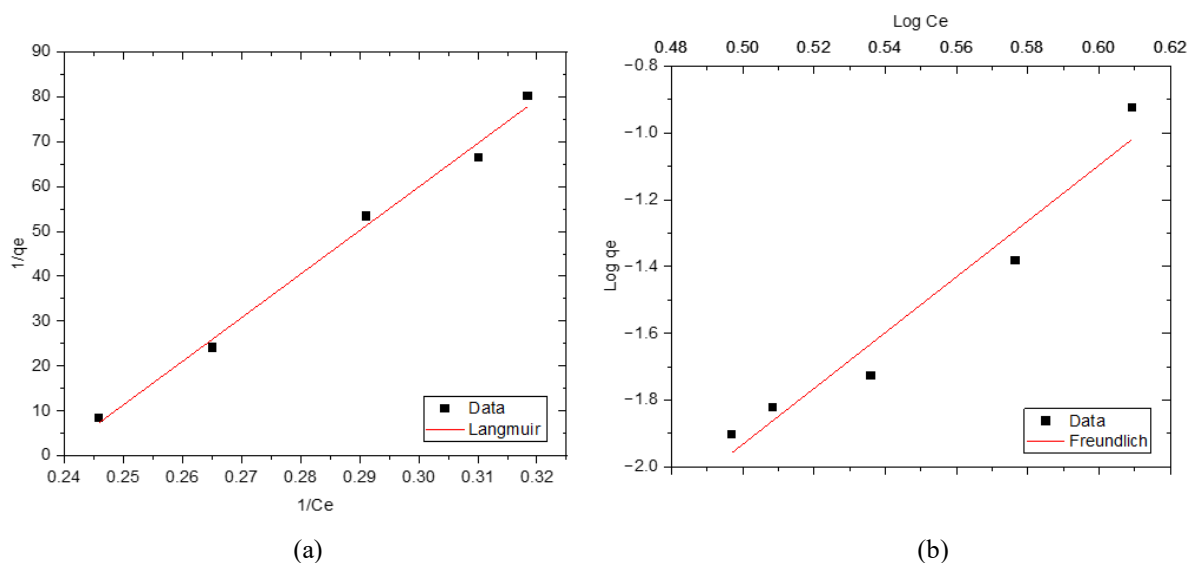
Figure 6. (a) Linier Plot of Adsorbtion Langmuir Isotherm Model, (b) Linier Plot of Adsorbton Freundlich Isotherm Model

Table 1. Parameters of the Freundlich Equation and Langmuir isotherm

Isotherm	Parameter	Value	Isotherm	Parameter	Value
Langmuir	q_m (mg/g)	-0.0043	Freundlich	K_F (L/g)	7.7893E-07
	K_L	-0.2383		N	0.1197
	R^2	0.9927		R^2	0.9535

The linearization plots in Figures 6.a and 6.b show that the Langmuir equation provides a very good mathematical approximation for describing the equilibrium adsorption of Fe(III) ions onto Fly ash-alginate beads, where the Langmuir plot is in good agreement with the experimental data with $R^2 = 0.9927$, which suggests a monolayer adsorption model. However, based on the parameter values, it can be concluded that the Freundlich equation is more suitable for describing the adsorption mechanism, where the linearization plot for all contact times provides positive values for K_F and $1/n$. Conversely, for the Langmuir equation, the linearization results provide negative values for K_L and qm, as listed in Table 1. Therefore, the adsorption of Fe(III) ions onto Fly ash-alginate beads is more likely to occur on a heterogeneous surface.

4. CONCLUSION

Immobilization of fly ash in an alginate matrix is capable of removing Fe(III) ions from test solutions and can be easily separated after the adsorption process is complete. The highest Fe(III) removal was obtained at 68.60% using a mass of 55 g fly ash-alginate beads in 100 mL test solution with a concentration of 10 ppm, and the lowest at 48.02% using 15 g beads in 100 mL test solution with a concentration of 6 ppm. The adsorption mechanism was tested using equilibrium data with the Langmuir and Freundlich isotherm equations. Adsorption of Fe(III) ions using fly ash-alginate beads follows the Freundlich isotherm model.

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