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Advancing Environmental Protection: Monolithic Bentonite and Zeolite-Clay Adsorbents for Fe^{2+} Ion Removal

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Abstract. Clay minerals possess substantial potential for developing innovative functional materials, particularly in the context of environmental protection. This study focuses on the adsorbent zeolite-clay and bentonite-clay, shaped into honeycomb monoliths to efficiently remove Fe^{2+} ions from water. The process involved physically activating powdered zeolite-clay and bentonite-clay through calcination at 600°C. The activated materials were then mixed with distilled water and molded into monolithic shapes through extrusion with stainless steel molds, resulting in cylindrical structures measuring 1.8 cm in diameter and 2 cm in height, featuring 40 perforations. Mechanical characterization aimed to evaluate structural strength and assess pressure drop during operation, revealing superior mechanical strength in bentonite-clay compared to zeolite-clay. The monolithic form exhibited lower pressure drop during operation compared to pellet adsorbents. In terms of adsorption performance, a batch reactor assessed efficiency, isotherm, and kinetics with 2 and 4 ppm Fe2+ ion solutions over a 240-minute period. The zeolite-clay monolith demonstrated the highest capacity, achieving a removal efficiency of up to 65%. Maximal adsorption capacities for bentonite-clay and zeolite-clay were 0.209 and 0.289 mg/g, respectively, with corresponding Langmuir adsorption equilibrium constants (KL) of 0.187 and 0.181 L/g by the Langmuir isotherm model. Kinetic analysis favored the pseudo-first-order non-linear model, indicating rates for zeolite-clay and bentonite-clay adsorbents at 2 and 4 ppm Fe^{2+} ion concentrations of 0.0043, 0.0030, 0.0039, and 0.0038 min^{-1}. This study signifies a significant advancement in solid adsorbents, optimizing the adsorption process for broader applications.

Introduction

The depletion of global water resources results from ecological damage caused by the release of harmful substances into natural surroundings, leading to significant water scarcity for essential applications [1]. Wastewater treatment offers a partial solution to the pressing global water crisis. A prevalent issue in water purification is the elevated levels of ionized iron found in groundwater worldwide, attributed to human activities like quarrying and natural geochemical cycles [2-3]. The rise in iron and other heavy metals in water ecosystems poses risks, as these elements are readily absorbed by living organisms, leading to bio-magnification and health problems. Excessive iron in the bloodstream can result in various medical issues, including mitochondrial dysfunction and tissue damage [4-5]. Despite its essential role in human health, elevated iron levels in groundwater can cause problems such as water discoloration, unpleasant taste, and textile and pipe darkening [7]. To address health concerns, the World Health Organization (WHO) has set a strict permissible limit for iron in drinking water at 0.3 mg/L [8].

Current investigations indicate a range of methods, including chemistry, biology, and physiological processes are employed for eliminating metallic substances from water as well as wastewater. Amongst such things, adsorption is a widely passed strategy for eliminating a multitude of contaminants, such as textile hues and heavy metals [9]. Adsorption emerges as an exceedingly appealing approach owing to its notable efficacy and inherent simplicity. The utilization of this method is prevalent in the treatment of deleterious heavy metals owing to its efficacy and straightforward approach [10]. Clays are being evaluated as prospective and cost-effective alternatives due to their availability, high specific surface area, ion exchange capability, swelling capacity, and cation exchange capacity [11-12]. Clay is a natural, non-toxic, abundant, durable, and high-surface area material extensively used in the adsorption process. Over the years, clay has been employed in various applications, including pottery and the production of construction materials such as bricks and tiles [13-14].

Bentonite clay, widely utilized across various industries, has applications in adsorbent production, cat litter, foundry work, and as a component in drilling and tunneling fluids, aiding lubrication, cooling, and cuttings removal while preventing blowouts [15]. Predominantly composed of montmorillonite, with two tetrahedral silica plates (Si^{4+}) and an octahedral alumina plate (Al^{3+}), bentonite clay's negatively charged surface allows it to expand upon contact with water. Heat treatment can modify its properties, reducing water-induced expansion and enhancing stability for dynamic system applications. Valuable for heavy metal and organic compound removal, bentonite clays possess a hydrophilic nature, high chemical stability, and cation exchange capacity [17].

In contrast, zeolites are inorganic crystalline minerals with structured pores smaller than two nm. Evolving types of zeolites include template-driven high-silica zeolites, natural zeolites, template-free low-silica zeolites, aluminum phosphate zeolites, and heteroatomic zeolites. Used in various sectors such as oil refining, fine chemicals, adsorption, and water treatment, manufactured zeolites are preferred due to large reserves, affordability, and essential constituents [18-20].

Honeycomb monoliths offer advantages, including reduced pressure drops, improved mass efficacy, and compelling physical and thermodynamic properties [21]. Two approaches are available for introducing active materials into the gas flow within these adsorbents: using multiple channels as a framework for an adsorbent film or directly molding monoliths with parallel channels, similar to carbon monoliths [22-24]. Previous research has demonstrated that naturally occurring clays can be easily shaped into honeycomb monoliths, utilized for various ecological purposes, including VOC adsorption, methylene blue removal from water, and biofuel combustion [25]. Clay monolithic adsorbents have been customized for the targeted removal of iron, mercury, and lead contaminants in water [26-29]. The structured pores of natural clays exhibit excellent handling features when exposed to water, enhancing the removal of contaminants during adsorption processes [30].

In the present study, monolith adsorbents were fabricated using zeolite and bentonite materials to investigate their efficacy in adsorbing Fe (II). These monoliths were meticulously prepared by adopting a stable structure through the use of a stainless-steel molder, involving a series of processes encompassing mixing, molding, thermal consolidation, and subsequent drying. Mechanical attributes, such as pressure drop and mechanical strength, were also rigorously examined, as they hold a critical role in the adjustment of operational parameters. The study encompassed an evaluation of the monoliths' performance, involving the assessment of their adsorption efficiency, isotherm behavior, and kinetic characteristics. Furthermore, the potential for future application of earth's resources such as clay, bentonite, and zeolite as customized adsorbents in a monoliths way, as explored in the current research, encompasses the potential to significantly contribute to the elimination and eradication of pollutants from water and wastewater systems.

Experimental

Monolith preparation. The primary materials for crafting monolith adsorbents consisted of clay, zeolite and bentonite. The Bentonite utilized in the current research was purchased through Java Indah Ltd., located in West Java, Indonesia. Similarly, the zeolite and clay samples were obtained from Sigli, a region within the Pidie District of Aceh Province, Indonesia. To properly to prepare the materials, a thorough washing process was conducted on both the clay and zeolite samples. Initially, the samples were washed with distilled water for a duration of 5 minutes. Subsequently, numerous decanting cycles were performed to effectively remove any impurities present in the samples. Then, that resulting slurry was then exposed to a two-day period of air-drying in order to eliminate the remaining water on the surface. The dry clay and zeolite were finally crushed in a ball mill. To ensure homogeneity, clay, zeolite, and bentonite were powdered and sieved through a 100-mesh sieve. Each zeolite and bentonite was then combined with clay in a 2:1 ratio to achieve consistency, with a sufficient amount of water added to form an ideal paste appropriate for molding. The molded monoliths were allowed to air-dry for two days and were later subjected to calcination at 600°C for a duration of 3 hours and stored in vacuum jar.

Characterization of monolith. The study primarily focused on characterizing the adsorbent's mechanical properties, particularly compressive strength and pressure drop. The analyses were essential for understanding how changes in pressure affect the adsorbent structure. Compressive strength was analyzed using a hydraulic universal testing machine (WAW-E-Series). In practical applications for measuring pressure drop within a column, monolithic adsorbents are arranged in series within an adsorption column and packaged for distribution, necessitating a robust structure. Pressure drop analysis involved various adsorbent forms, such as pellets and monoliths. It was conducted using an adsorption column equipped with water pressure sensors at the inlet and outlet, programmed with an Arduino Uno microcontroller to measure pressure differences.

Adsorption process. To prepare the Fe^{2+} metal solution, the iron standard solution ($Fe(NO_3)_2$) (Merck) 1000 ppm was diluted to concentrations of 2 and 4 ppm. In the adsorption process, each zeolite and bentonite monolith were immersed in 250 mL of Fe^{2+} solutions with concentrations of 2 and 4 ppm in separate batch reactors (250 mL Erlenmeyer flasks). The experiment was performed under ambient conditions, specifically at room temperature, with a mixing rate of 110 rotations per minute (rpm) for an entire period of 240 minutes. Following this, 10 mL of the filtrate was extracted, and its absorbance was measured using Atomic Absorption Spectroscopy (AAS) (Shimadzu AA-6300). The present study assessed the effectiveness of the adsorption process through investigation of multiple variables, including adsorption efficiency, isotherm models (namely Langmuir and Freundlich), and kinetics equations (either pseudo-first order or pseudo-second order).

Result and Discussion

Monoliths Characteristics. Compressive strength assessments were conducted to ascertain the load-bearing capacity of zeolite and bentonite adsorbents. The findings obtained through these tests are displayed in Table 1, which includes data on the applied force or load (F, measured in Newtons), the compressive surface area (A, in square millimeters), and the resulting compressive strength (Fc, expressed in Megapascals, MPa) of the monolith adsorbent.

Table 1. Results for compressive strength of monolith adsorbent

Sample	F (N)	A (mm^2)	Fc (MPa)
Zeolite	608	241.78	2.51
Bentonite	2711	166.18	16.31

Analysis of Table 1 reveals that bentonite exhibits the highest compressive strength among the materials tested, owing to its denser pore structure in comparison to the other materials. The compressive strengths of zeolite and bentonite monolith adsorbents were 2.51 MPa and 16.31 MPa, correspondingly. Aside from the chemical bonding factor inside the monolith matrix, increasing porosity might result in a reduction in compressive resistance [31]. It can be inferred that the concentration of zeolite powder has a significant impact on the material's load-bearing capacity [32]. Notably, the compressive strength of the zeolite adsorbent decreases, primarily due to its higher porosity compared to the bentonite monolith.

Pressure drops. Pressure drop is the pressure loss as the fluid passes through the bed. In an adsorption system, pressure drop plays a significant role in purifying a material. A system with too low a pressure drop will have ruined circulation in a bed. Meanwhile, a high-pressure drop of adsorbent will cause more consumption of power to be fed in a packed column [33]. To make sure the adsorbent has the specific pressure drop, calculations in various types of adsorbents at various heights have been done. The results of the pressure drop measurement can be seen in Figure 1.

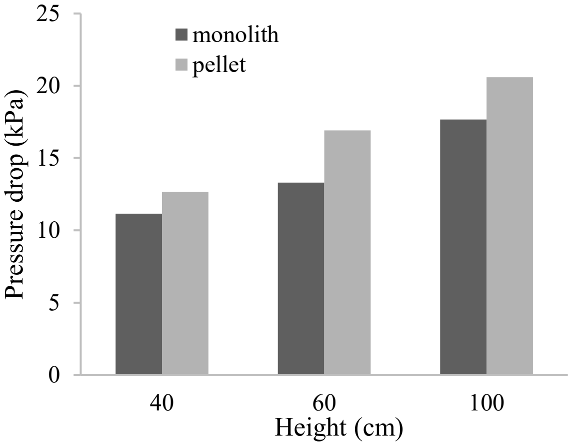

Fig. 1. Pressure drops in the fixed bed adsorber for various types of clay-based adsorbents

The monolith showed a lower pressure drop than the pellet at the three fixed bed heights. At the height of 40 cm, the monolith and pellet pressure drop differ slightly. At the height of 60 cm and 100 cm, the pressure drop of the monolith is also lower than the pellet. Because of Ergun's Equation about pressure drop in a packed bed, solid adsorbents with smaller diameters tend to have a high-pressure drop. Monolith pressure drop performance in a packed bed has a lower pressure drop because of its unique structure. It has a high porosity value because of the presence of channels or cavities [34].

Adsorption Capacity. In this study, the efficiency of zeolite and bentonite monoliths in adsorbing Fe^{2+} metal ions were assessed at various contact times, including 0, 40, 80, 120, 160, 200, and 240 minutes, as depicted in Figure 2a and 2b.

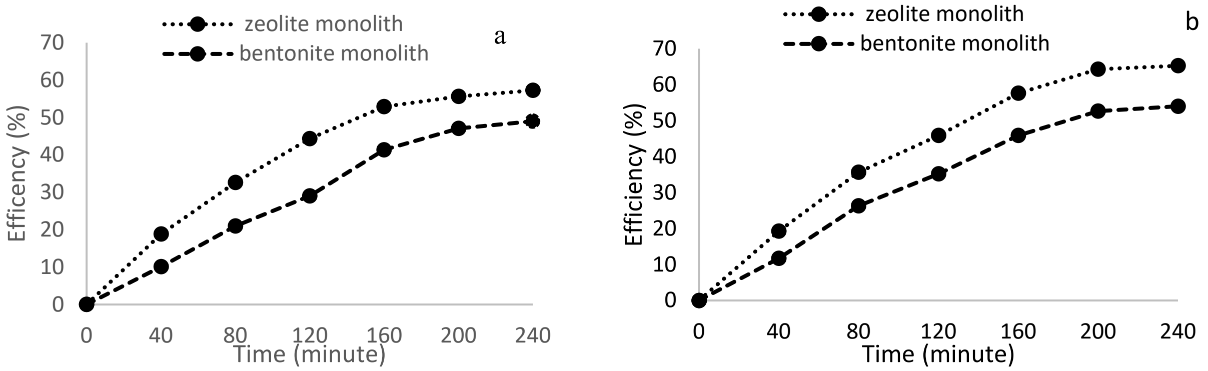

Fig 2. A correlation exists among process period and effectiveness at varied initial concentrations (a) 2 ppm and (b) 4 ppm

These figures portray the relationship among the efficiency and period process. Particularly, there was a substantial elevation in the adsorption efficacy observed during the 240-minute duration, indicating that prolonged contact periods promote enhanced interactions between the Fe^{2+} metallic ions and the adhesion domains of the adsorbent. The maximum efficiency for Fe^{2+} adsorption was observed to be 65.25% when utilizing zeolite monoliths with a 4 ppm Fe^{2+} solution. Conversely, bentonite monoliths exhibited a maximum Fe^{2+} removal efficiency of 54% at a 4 ppm Fe^{2+} concentration. Notably, the two figures demonstrate that the equilibrium stages are reached at 240 minutes, as seen by the stagnation of efficiencies at 200 and 240 minutes. Currently, the adsorption capacity has exhibited stability, providing an indication that the active sites on the adsorbents have reached a state of near-full closure, thus finishing the interactions between the adsorbate and adsorbent. Particularly, the utilization of zeolite monoliths for Fe^{2+} ion adsorption outperformed bentonite due to higher adsorption kinetics due to zeolite's higher cation-exchange potential in compared with bentonite [35].

Isotherm of Adsorption. The adsorption isotherm shows the results of stationary adsorption studies in an instance for a particular period until a state of equilibrium has been reached and defines the adsorbent's maximum performance and adsorbate solution's interaction [36]. Data from batch experiments on equilibrium adsorption were examined through a non-linear approach for identifying the best isotherm model among Langmuir and Freundlich. To determine and optimise the isotherm parameters in non-linear equations, the solver plugin function in Microsoft® Excel was employed. The model with the least SSE (Sum of Square Error) result was identified as the best isotherm model. SSE is recognized as the value of the least objective function for obtaining the optimal isotherm parameters and minimizing the gap between theoretical and experimental data [37].
The formula for equation 1 is the mathematical representation of the Langmuir model [38]:

$$q_e = \frac{KL.Ce}{1+aL.C_e} \tag{1}$$

In this context, qe represents the adsorption capacity of mercury (Hg) in milligrams per gram (mg/g), Ce denotes the equilibrium concentration of Hg in milligrams per liter (mg/L), KL (L/mg) and aL (L/g) are the Langmuir coefficients.
The equation for the Freundlich model can be written as follows [38]:

$$q_e = K_f.{C_e}^{1/n} \tag{2}$$

Within this investigation, the parameters under consideration are defined as follows: qe, denoting the capacity for mercury (Hg) adsorption, expressed in milligrams per gram (mg/g); Ce, representing the equilibrium concentration of Hg in milligrams per liter (mg/L); Kf, indicative of the predicted capacity in the Freundlich Model, measured in (mg/); and n, signifying the intensity of the reaction. Table 2 encapsulates a succinct summary of the optimization procedures derived from the isotherm analysis. The assessment, rooted in the Sum of Squares of Errors (SSE) values, points towards the Langmuir isotherm model exhibiting a commendable fit to the adsorption study. Specifically, the constants KL and aL, pertinent to both zeolite-clay and bentonite-clay adsorbents, are quantified as 0.187 L/g, 0.181 L/g, 0.895 L/mg, and 0.639 L/mg, respectively. In accordance with the Langmuir isotherm, the adsorption process transpires on the adsorbent surface, and the active sites within the outermost layer are characterized as both homogeneous and finite. This mechanism involves the formation of a singular layer (monolayer) on the adsorbent surface, consisting of homogeneous and energetically equivalent active sites. These sites possess a consistent binding energy, ensuring that the adsorbent selectively binds to only one Fe^{2+} metal ion per active site, with no interactions among adjacent Fe^{2+} ions [39].

Table 2. A concise overview of thermodynamic equilibrium and isotherm data.

Adsorbent	Langmuir Isotherm				Freundlich Isotherm		
	K_L (L/g)	a_L (L/mg)	Q_o (K_L/a_L)	SSE	K_f (mg/g)	N	SSE
Zeolite-clay	0.187	0.895	0.209	3.08×10^{-4}	0.064	1.46	4.42×10^{-3}
Bentonite-clay	0.181	0.639	0.284	4.32×10^{-4}	0.074	1.37	5.98×10^{-3}

Kinetics Study. Adsorption kinetics plays a crucial role in elucidating the rate at which iron ions are absorbed, directly associated with the residence time of these ions on the adsorbent's surface. To ascertain the kinetic rate and mechanism governing the adsorption of Fe^{2+} ions onto the adsorbent, two widely employed models, namely the Pseudo First Order rate equation and the Pseudo Second Order equation, are employed [40]. A comparative analysis between these two models is conducted to determine which one better aligns with the experimental data through regression analysis. This comparison involves both linear methods that evaluate the compatibility of equations with experimental observations and non-linear methods that rely on data optimization processes and numerical techniques aimed at minimizing error values [41]. The results of the data processing pertaining to adsorption kinetics are presented in Table 3.

Tabel 3 The adsorption kinetic tabulation data

C_o	Monolith	Parameter	Pseudo first order		Pseudo second order	
			Linear	*non-linear*	*linear*	*non-linear*
2 ppm	Zeolite	qe_{exp}	0.0556	0.0556	0.0556	0.0556
		qe_{cal}	0.0753	0.102	0.408	0.164
		k	0.0012	0.0043	0.0016	0.017
		SSE	-	5.2×10^{-4}	-	5.27×10^{-4}
		R^2	0.861	0.9886	0.2279	0.9882
	Bentonite	qe_{exp}	0.0736	0.0736	0.0736	0.0736
		qe_{cal}	0.102	0.149	0.386	0.262
		k	0.0137	0.0030	0.0027	0.00654
		SSE	-	3.87×10^{-5}	-	4.097×10^{-5}
		R^2	0.9029	0.996	0.6097	0.9957
4 ppm	Zeolite	qe_{exp}	0.192	0.192	0.192	0.192
		qe_{cal}	0.233	0.325	1.072	0.5443
		k	0.0111	0.0039	0.0009	0.004375
		SSE	-	2.30×10^{-4}	-	1.23×10^{-4}
		R^2	0.944	0.9978	0.3431	0.9977
	Bentonite	qe_{exp}	0.234	0.234	0.234	0.234
		qe_{cal}	0.2952	0.396235	0.9146	0.66862528
		k	0.0121	0.0038	0.00167	0.003487
		SSE	-	1.42×10^{-4}	-	1.646×10^{-4}
		R^2	0.943	0.9986	0.7257	0.9983

To determine the most suitable adsorption kinetics model, a comparison of the regression coefficient (R^2) between linear and non-linear models is essential [42]. Examining Table 2, it is evident that at solution concentrations of 2 mg/L and 4 mg/L, the non-linear method yields higher R^2 values (R^2>0.97) compared to the relatively lower R^2 values obtained through the linear method. For solutions with concentrations of 2 mg/L and 4 mg/L, the adsorption kinetics of zeolite and bentonite monoliths align with the pseudo-first order model, as indicated by the smallest Sum of Squared Errors (SSE). This is further substantiated by the proximity of the theoretical adsorption capacity values (qe, calc) obtained from the pseudo-first-order kinetic model to the experimental adsorption capacity values (qe, exp). The pseudo-first-order kinetic model implies that the rate of ion absorption is directly proportional to the availability of active and free ion bonds on the surface of the adsorbent [43]. In accordance with the model, iron ion molecules are assumed to bind to a single active site on the adsorbent's surface, characterizing the adsorption as physical in nature. The pseudo-first-order kinetics is particularly suited for adsorption processes in low-concentration solutions, which aligns with the relatively low concentration of the solutions used in this study, specifically 2 and 4 mg/L [44].

For a solution concentration of 2 mg/L, the pseudo-first-order adsorption rate constant (k1) was determined to be 0.0043 min^{-1} for the zeolite adsorbent and 0.00299 min^{-1} for the bentonite monolith. At a solution concentration of 4 mg/L, the values for k_1 were 0.00389 min^{-1} for zeolite and 0.003852 min^{-1} for bentonite. This trend is in accordance with the theory that posits an inverse relationship between the adsorption rate constant and the initial concentration of the solution. As the concentration of the solution increases, the adsorption rate constant tends to decrease, as it requires more time for the process or reaction to attain equilibrium[45].

Summary

To sum up, this study has successfully developed a unique and compact adsorbent, referred to as monolith, utilizing clay-zeolite and bentonite for the purpose of removing iron from aqueous solutions. Notably, in terms of mechanical properties, bentonite exhibited higher compressive strength, reaching a maximum of 16.3 MPa, in comparison to zeolite. The assessment of pressure drop underscored the monolith's advantage, as it displayed a lower pressure drop compared to pellet-type adsorbents. The efficiency of adsorption highlighted zeolite's exceptional performance in removing Fe^{2+}, pointing at Langmuir equation model in whole adsorption process also achieving an impressive removal efficiency of 65.25%, attributed to zeolite's inherent Fe^{2+} binding capabilities. Furthermore, the kinetics study indicated the most suitable order, with the pseudo-first-order model demonstrating the highest R^2 value and the lowest SSE value, with a kinetic rate of 0.000299 min^{-1}. Based on the outcomes of the study, it becomes evident that zeolite monoliths display a notable capacity for adsorbing Fe^{2+} from water sources. The experimental findings highlight the efficiency and effectiveness of zeolite-based monoliths in the removal of Fe^{2+} ions from aqueous solutions. This characteristic underscores the potential of zeolite monoliths as a promising and reliable adsorption material for addressing water contamination issues, particularly in scenarios where the presence of Fe^{2+} poses environmental and health concerns. The development and application of such innovative adsorbents contribute to sustainable solutions for ensuring water quality and safeguarding both the environment and human health.

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