



Original Article

Kinetic Study of Mg(II) Adsorption on Activated Coal Bottom Ash

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Abstract— The research of adsorption of Mg(II) ions on coal bottom ash as adsorbent has been carried out. The research was conducted by activating the coal bottom ash using concentrated HCl. Characterization of activated coal bottom ash was done by using Fourier Transform Infra-Red (FTIR) spectroscopy and X-Ray Diffraction (XRD) analysis. Parameters of metal adsorption examined in this study include the effect of pH, mass of adsorbent, and interaction time. The concentration of each metal ion remaining in the solution after adsorption and desorption was determined using atomic absorption spectrophotometer. The result showed that activated coal bottom ash has been carried out. The optimum conditions for Mg(II) adsorption using 0.3 g coal bottom ash are at pH 5 with 60 minute contact. The Adsorption kinetics follow Ho model pseudo-second order with the rate constant 0.6182 and 0.998 correlation coefficient. These results highlight the potential of activated coal bottom ash as a low-cost, effective adsorbent for water treatment applications.

Keywords—Adsorption; Coal bottom ash, Kinetics, Mg(II) metal ions.

1. INTRODUCTION

The presence of heavy metals in water bodies has raised serious environmental concerns due to their toxicity and persistence in nature. Magnesium, although essential in trace amounts, it can become problematic at elevated concentrations, especially in industrial effluents originating from activities such as mining, metal processing, and chemical manufacturing. Excessive magnesium levels may harm aquatic ecosystems and potentially affect human health by causing adverse physiological effects [1].

Among the various techniques available for treating metal-contaminated water, adsorption is widely recognized for its simplicity, efficiency, and cost-effectiveness. In recent years, attention has shifted toward the use of industrial by-products as alternative adsorbent materials, aligning with the principles of waste valorization and environmental sustainability. Coal bottom ash, a solid residue from coal combustion in power generation, is one such material with promising adsorptive properties due to its mineral content and porous nature [2]. Despite its potential, untreated bottom ash may exhibit limited adsorption capabilities owing to its relatively low surface area and the presence of unwanted compounds. To overcome these limitations,

activation processes physical or chemical are employed to improve the surface characteristics and adsorption performance of the material. Activated bottom ash has demonstrated enhanced affinity toward various metal ions in solution. This research focuses on the kinetics adsorption of an adsorbent material using activated coal bottom ash, which is applied for the adsorption of Mg(II) metal ions, followed by a study of the chemical adsorption kinetics.

2. EXPERIMENTAL SECTION

2.1. Materials

Coal bottom ash of Pacitan plant; Dithizone (Merck); Ethanol 99% (Merck); Concentrated HCl 37% (Merck); Toluena (Aldrich); Magnesium (II) Sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) (Merck); Cadmium(II) Sulphate, aquadest and aquabidest.

2.2. Instrumentation

Atomic Absorption Spectrophotometers (SSA) Analytik Jena contrAA 300, Shimadzu Infrared Spectrometer FTIR 8201 model, X-ray Diffractometer

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Rigaku miniflex 600, Pyrex quality laboratory glassware (beaker, funnel, measuring, watch glass), Buchner filter, magnetic stirrer, reflux set, 250 mesh sieve, filter paper whatman 42, analytical balance (Metler AE 200), pH meter (TOA Electronics Model HM-5B).

2.3. Activation of Coal Bottom Ash

Coal bottom ash was first ground and sieved to obtain particles of 250 mesh size. Activation was performed by refluxing 20 grams of the sieved ash in 120 mL of diluted hydrochloric acid (1:1 ratio) for a duration of 4 hours. The mixture was then filtered, and the solid residue was thoroughly washed with distilled water until the filtrate reached a neutral pH. The resulting material was subsequently dried in an oven at 160 °C for 6 hours. The activated product was characterized using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy [3].

2.4. Effect of pH Solution

A volume of 30 mL of 50 ppm Mg(II) solution was contacted with 0.1 g of activated coal bottom ash. The pH of the solution was adjusted within a range of 3 to 7. The adsorption process was conducted over a period of 60 minutes. After adsorption, the mixture was filtered, and the concentration of magnesium ions remaining in the filtrate was determined using atomic absorption spectrophotometry (AAS).

2.5. Effect of Adsorbent Mass Variation

A 30 mL solution containing 50 ppm of Mg(II) ions was treated with different dosages of activated coal bottom ash—specifically, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 grams—under the solution's optimum pH conditions. The adsorption process was carried out over a duration of 60 minutes. Following the adsorption, the solid adsorbents were removed by filtration, and the residual concentration of Mg(II) in the filtrate was determined using atomic absorption spectrophotometry (AAS).

2.6. Effect of Adsorption Time Variation

A 30 mL solution of 50 ppm Mg(II) was added to 0.2 g of activated coal bottom ash at the optimal pH level. The adsorption process was performed with varying contact times of 5, 15, 30, 45, 60, and 90 minutes. After the process, the adsorbent was filtered, and the concentration of magnesium in the filtrate was measured using atomic absorption spectrophotometry.

3. RESULT AND DISCUSSION

3.1. Activation of Coal Bottom Ash

The primary characterization before and after activation using an infrared spectrophotometer is intended to identify the functional groups present in the adsorbent. The infrared spectra, both before and after activation, are shown in **Figure 1**.

The spectra in **Figure 1** show a broad absorption at 3425 cm⁻¹, which indicates the presence of OH group vibrations in Si-OH and water molecules in coal bottom

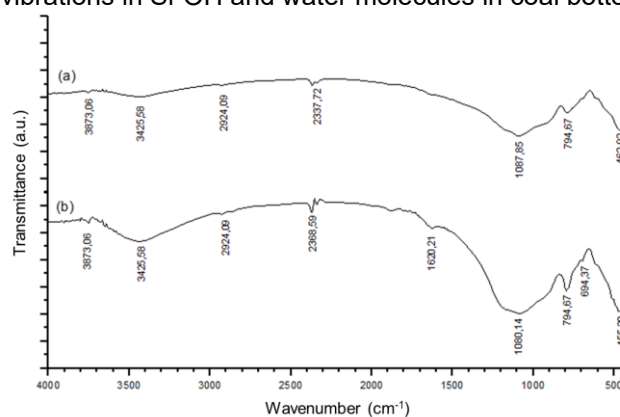


Figure 1. Infrared spectra of (a) coal bottom ash before activation and (b) coal bottom ash after activation

ash. This absorption is intensified by the bending vibration of O-H at 1620 cm⁻¹. A peak at 1087 cm⁻¹ corresponds to the stretching vibration of Si-O in the Si-O-Si and Si-O-Al groups in the bottom ash. To further characterize the coal bottom ash before and after activation, X-ray diffraction (XRD) was employed to identify its mineral composition. The diffractograms of the coal bottom ash, both before and after activation, are shown in **Figure 2**.

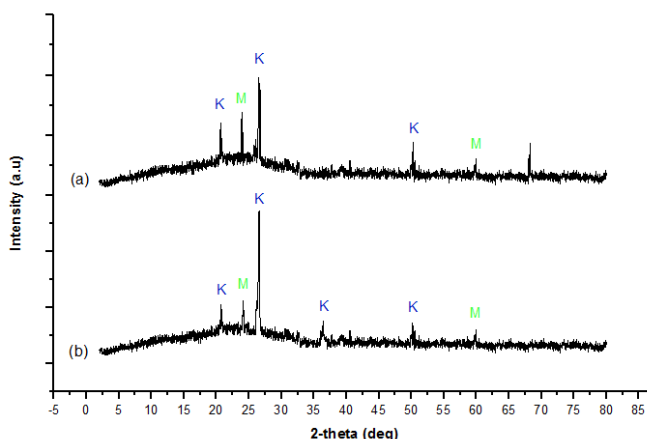


Figure 2. Diffractogram of (a) coal bottom ash before activation and (b) coal bottom ash after activation

Based on JCPDS no. 46-1045, peaks at d-spacings of 4.25, 3.33, 2.49, and 1.82 Å are attributed to quartz (SiO₂), while peaks at d-spacings of 3.69, 2.49, 2.28, and 1.54 Å are assigned to mullite (Al₂O₃), according to JCPDS no. 15-0776.

From the diffractogram data, it can be concluded that both quartz and mullite are present in the coal bottom ash before and after activation. However, quartz is more dominant than mullite in the activated bottom ash, with the quartz peak appearing more prominent. The height of the peak in an XRD diffractogram corresponds to the crystallinity of the substance, so a higher peak indicates greater crystallinity. Therefore, quartz has a higher degree of crystallinity and is the primary constituent in

the ash compared to mullite. The diffractogram also indicates that the activation process does not damage the crystallinity structure of the coal bottom ash. A peak at $2\theta = 62.28$ before activation is no longer present in the diffractogram of the activated bottom ash, likely due to the removal of free metal oxide impurities that could interfere with the adsorption process [4].

Based on **Table 1**, it can be interpreted that quartz and mullite minerals appear in the bottom ash before and after activation. Quartz mineral is more dominant than mullite mineral in the activated bottom ash. In addition, the quartz peak appears higher than the mullite peak. The higher a peak in the XRD diffractogram, the higher the crystallinity of the substance. Thus, quartz mineral has a higher degree of crystallinity and is the most dominant component compared to mullite. Based on the diffractogram, it can also be concluded that the activation process does not damage the crystallinity structure of the coal bottom ash. There is a peak detected at 2θ before activation, namely 62.28, which no longer appears in the diffractogram of the activated bottom ash. This is possibly due to the loss of free metal oxide impurities that can interfere with the adsorption process.

Table 1. Diffractogram data of bottom ash before and after activation

Sample	2θ	d-spacing (Å)	I/I ₁	Type
Coal bottom ash	20.733	4.287	28	Quartz
	23.792	3.746	27	Mullite
	26.507	3.360	100	Quartz
	49.885	2.217	17	Quartz
	59.708	1.549	11	Mullite
Activated coal bottom ash	20.741	4.279	27	Quartz
	23.945	3.713	29	Mullite
	26.516	3.358	100	Quartz
	36.362	2.469	13	Quartz
	50.093	1.819	19	Quartz
	59.892	1.543	17	Mullite

3.2. The Effect of pH Solution

The adsorption of Mg (II) ions using activated coal bottom ash is shown in **Figure 3**. The data obtained from the pH variation experiments indicate that the amount of metal ions adsorbed differs at different pH levels. The acidity (pH) of the solution can influence the adsorbent's capacity to adsorb metal ions. As shown in **Figure 3**, the amount of Mg (II) ions adsorbed increases with the pH of the adsorption solution when in contact with activated bottom ash. The optimum pH for the activated adsorbent is pH 5. The Mg (II) in solutions with low pH exists in the form of metal cations with a +2 oxidation state (M^{2+}) [5]. At pH 7, the adsorption of Mg(II) ions decreases.

The pH of the solution plays a significant role in the adsorbent's ability to bind to metal cations [6]. Under optimal conditions, the number of metal ions interacting with the adsorbent's active sites reaches its maximum capacity. This is because at this pH, the concentration

of H^+ ions decreases, while the OH^- ions are still insufficient to precipitate the metal ions [7-8].

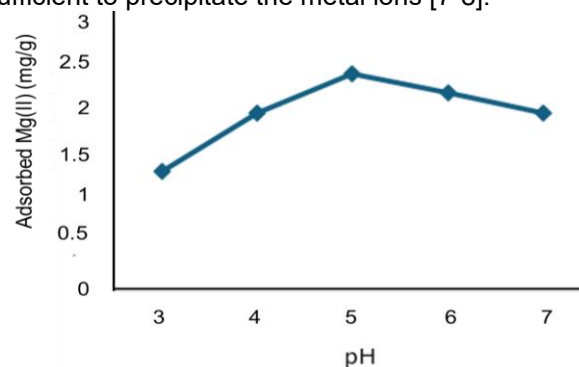


Figure 3. The impact of solution pH on the adsorption of Mg(II) ions onto activated coal bottom ash

3.3. The Effect of Adsorbent Mass Variation

The adsorption of Mg(II) metal ions using activated coal bottom ash with varying adsorbent masses is shown in **Figure 4**. From the figure, it can be observed that as the adsorbent mass increases, the amount of metal ions adsorbed also increases [9]. This rise in the amount of adsorbed metal ions indicates that the number of active sites increases with the adsorbent mass during interaction with a constant concentration [10].

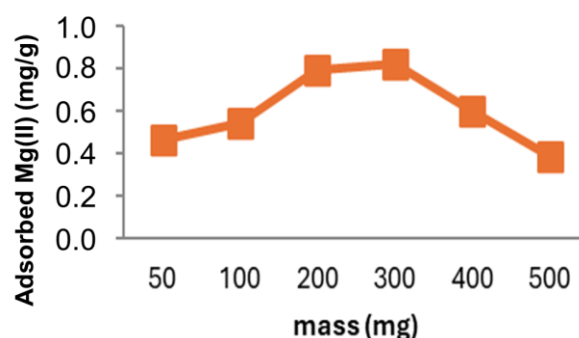


Figure 4. The influence of adsorbent mass on the adsorption of Mg(II) ions onto activated coal bottom ash

The optimal adsorbent mass for the simultaneous adsorption of Mg(II) ions using activated coal bottom ash was found to be 0.3 grams. Beyond this optimal mass, the amount of adsorbed ions tends to stabilize or decrease [11]. This is because the ion concentration in the solution has reached equilibrium, and increasing the adsorbent mass no longer affects the amount of metal ions adsorbed. The adsorption capacity of both adsorbents slightly decreases with the addition of more adsorbent, likely because the increased number of active sites may lead to interactions between them, reducing their effectiveness. Additionally, desorption may occur due to agitation during the process.

3.4. Effect of Adsorption Time Variation

The effect of interaction time on the adsorption of Mg(II) ions was investigated using activated coal bottom

ash, with a mixed solution of Mg(II) ions at a concentration of 50 ppm at the optimal pH of 5. The adsorbent mass was 0.2 g, and the interaction time was varied between 5 to 90 minutes. The remaining concentrations of metal ions after adsorption were measured using an atomic absorption spectrophotometer.

The results of the adsorption of Mg(II) ions using both activated coal bottom ash and dithizone-immobilized coal bottom ash, with varying interaction times, are shown in Figure 5. The figure indicates that the interaction time significantly influences the amount of metal ions adsorbed [12]. The amount of adsorbed ions increases as the adsorption time increases, reaching an optimum adsorption time [13].

Figure 5 show that the optimum time of Mg(II) adsorption on activated coal bottom ash is 60 minutes. This increase in the amount of adsorption is due to a longer chance of interaction between the metal ion adsorbent sites in solution [14].

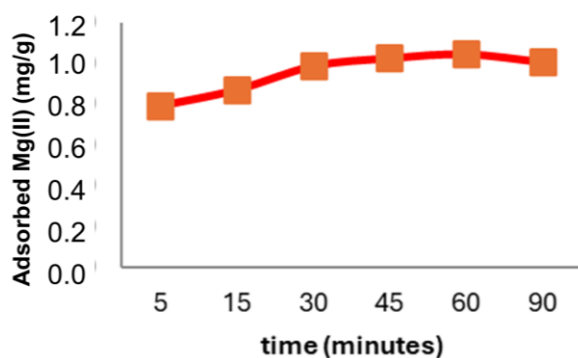


Figure 5. The impact of interaction time on the adsorption of Mg(II) ions onto activated coal bottom ash

The optimum time shows that equilibrium has been achieved in the interaction between metal ions with the active site on the adsorbent so that when equilibrium is reached the amount of adsorbed ions will be equal to the amount of dissolved metal ions. At the time of the longer interaction the adsorption tends to remain or even down due to the saturated surface condition of the adsorbent so that the adsorbent can not absorb the metal ions anymore even as the interaction time increases. The decrease in adsorption is likely due to metal loosening when stirring [15].

In the study of adsorption kinetics of Mg(II) metal ions, two kinetic models were evaluated: the pseudo-first-order and the pseudo-second-order models. These models are commonly used to understand the mechanism and rate-controlling steps of the adsorption process.

The pseudo-first-order kinetic model assumes that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. For this study, the pseudo-first-order model yielded a rate constant, $k = 0.0229 \text{ s}^{-1}$ with $R^2 = 0.5151$ (**Figure 6**). The relatively low R-value indicates a poor fit of the experimental data to this model, suggesting that the Lagergren model does

not adequately describe the adsorption behavior of Mg(II) ions [16].

The pseudo-second-order model, on the other hand, assumes that the adsorption follows second-order chemisorption, the result show that the pseudo-second-order model gave a rate constant, $k = 0.6182 \text{ M}^{-1} \text{ s}^{-1}$ with the $R^2 = 0.9983$. The high R-value (close to 1) indicates an excellent fit to the experimental data, showing that this model more accurately describes the adsorption kinetics of Mg(II) ions onto activated coal bottom ash [16].

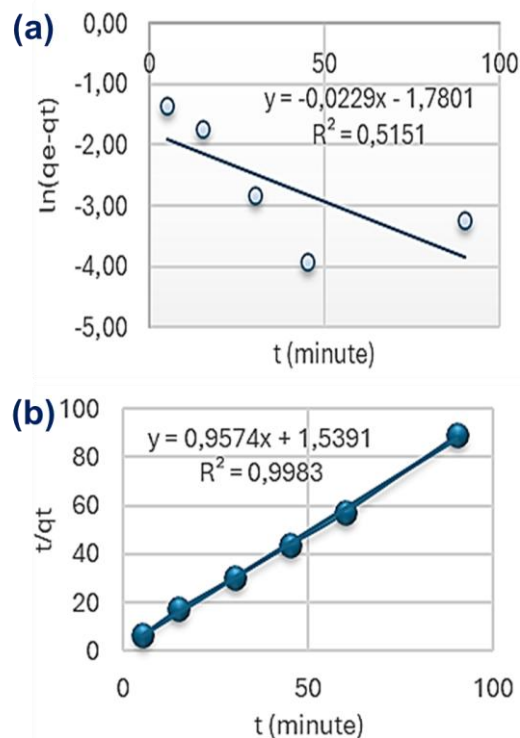


Figure 6. The linear plots of Mg(II) for Lagergren first-pseudo order (a) and Ho second-pseudo order (b)

4. CONCLUSION

This study successfully demonstrates the potential of activated coal bottom ash as an effective adsorbent for the removal of Mg(II) ions from aqueous solutions. Under optimal conditions 0.3 g of adsorbent at pH 5 and a contact time of 60 minutes the material exhibited significant adsorption performance. The kinetic analysis revealed that the adsorption process follows the Ho pseudo-second-order model, with a rate constant of $0.6182 \text{ M}^{-1} \text{ s}^{-1}$ and a high correlation coefficient ($R^2 = 0.998$), indicating that chemisorption dominates the interaction mechanism. These findings confirm that activated coal bottom ash is a promising low-cost material for the chemical adsorption of Mg(II) ion, fulfilling the objectives of evaluating both its adsorption capacity and kinetic behavior.

SUPPROTING INFORMATION

There is no supporting information in this paper. The data supporting this research's findings are

available on request from the corresponding author (DPW).

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CONFLICT OF INTEREST

There was no conflict of interest in this study.

AUTHOR CONTRIBUTIONS

DPW and CA was conducted the experiment. RB, SN, and NFPK was wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

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