Research Article

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Adsorbent made with inexpensive, local resources

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Abstract: An affordable local adsorbent was physically activated and modified to form a novel composite adsorbent. Similar processes were used to activate bentonite and limestone to create this low-cost local adsorbent. Furthermore, when compared to the inexpensive local resources, the innovative composite adsorbent showed improved adsorption capacity. Fouling brought on by sulphate-ion pollution is a significant problem in the wastewater treatment industry. In this work, a composite material known as Limestone and Bentonite composite, was developed, and its capacity to absorb sulphate ions from tainted wastewater was evaluated. Using the scanning electron microscope, X-ray diffraction, Fourier transform infrared spectroscopy, and Brunauer–Emmett–Teller theory, the chemical, elemental, and mineralogical properties, as well as the functional group interaction, of the limestone, bentonite, and LB composite were determined. The model wastewater initially included 900 mg/L of sulphate ions; however, the experiment showed that the new (LB) composite absorbed over 729 mg/L of sulphate ions. Its (LB) = 81% strong elimination effectiveness was observed. It was found that the ideal adsorption conditions were 250 rpm, 60 min, 900 mg/L, and 0.5 g/50 mL. Adsorption studies were carried out in batches. With a greater determination coefficient, the Freundlich model provides a more accurate prediction for adsorption processes, bolstering the theory that chemisorption is the actual adsorption process. These results demonstrate the novel composite adsorbent (LB)'s tremendous potential for sulphate ion absorption.

Keywords: limestone, bentonite, adsorbent, wastewater, sulphate, physical activation

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1 Introduction

The increasing concern for water pollution caused by metallic elements is a pressing issue in separation science and environmental remediation [1]. Metallic components are released into the environment from various sectors such as electroplating, metal finishing, textiles, storage batteries, mining, ceramics, and glass [2]. Metallic element ions are abundant in the organisms via which they enter food chains and cannot be broken down, leading to serious health issues in both humans and animals [3]. The toxicity of SO_4^{2-}, Cu^{2+}, and Pb^{2+} is the primary concern among the metallic elements of public concern [4–7]. Thus, it becomes vital to remove these harmful metal ions from manufacture waste water and natural water sources. Water contaminated with metallic elements has been treated using various methods such as chemical precipitation, adsorption, solvent extraction, reverse osmosis, ion exchange, filtering, and electrodialysis [8–12]. Adsorption technologies are very efficient and cost-effective due to their low price, straightforward construction, and robust operability. Numerous materials, including inorganic materials [13,14], polymers [15], activated carbon [16–18], biomaterials [19], and sorption resins [20], have been described for the adsorption of metallic elements. Despite this, many researchers are still interested in the creation of effective and significantly less expensive adsorption materials. Adsorption is a highly efficient method for removing toxins from wastewater, known

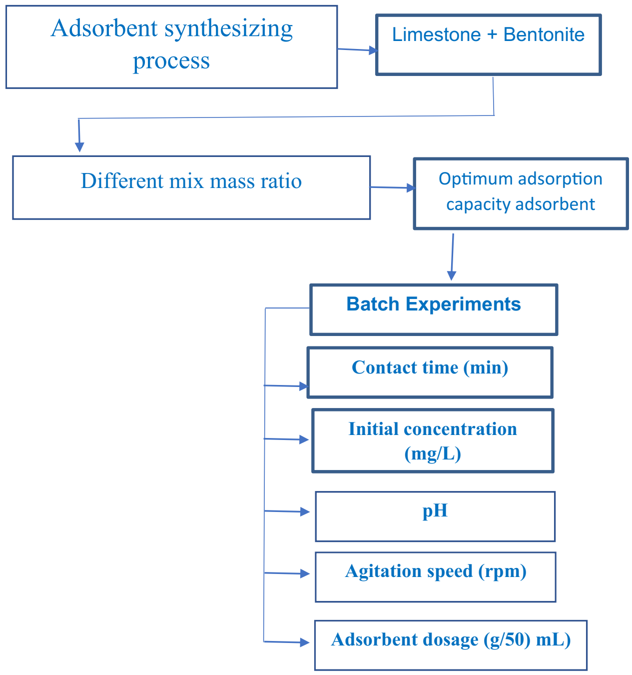

Figure 1: Procedure of the experimental work.

for its versatility, design simplicity, reusability, low cost, and eco-friendliness [21]. As shown in Figure 1 [22], adsorption is the physical adhesion of ions and molecules to the surfaces of other molecules. Hazardous contaminants have been successfully removed from wastewater using a variety of adsorbents, including biosorbents [23], activated carbon [24], biochar [25], clays and minerals [26], polymers and composites [27], and others with a high adsorption uptake capacity. This is due to their accessibility, economic viability, capacity for regeneration, eco-friendliness, and place of origin [28]. They can also be created synthetically using green materials [29]. However, the cost of using adsorbents for wastewater treatment must be reduced without compromising water treatment performance [30]. The preparation of an inexpensive and efficient adsorbent was the goal of this investigation. Using limestone and bentonite clay material as an adsorbent (BL) for the removal of sulphate ions is a smart decision because of its good efficacy and reasonable cost. Few research has examined the ability of clay minerals to extract sulphate ions from solutions, as far as we are aware. The aim of this work is to remove SO_4^{2-} from wastewater by employing waste and low-cost materials as an adsorbent. Where, clay materials like bentonite and limestone are effective adsorbents (LB) for removing sulphate ions due to their low cost and high performance, though research on their removal from liquids is limited. The project's goal is to extract SO_4^{2-} from wastewater by employing a wasteful and reasonably priced adsorbent.

2 Methodology

2.1 Flowchart

Experimental work protocol is shown in Figure 1.

2.2 Adsorbate

The sulphate solution was prepared by dissolving K_2SO_4 in distilled water, resulting in a concentration of 900 mg/L. The solution was kept at 25°C, pH adjusted using 0.1 M HCl or 0.1 M NaOH, and stock solutions were used for various concentrations (100, 200, 300, 400, 500, 700, and 900 mg/L) for experiments.

Equations used [31]:

$$W = C_i \times V\frac{M.\,\mathrm{wt}}{\mathrm{At.\,wt}}, \tag{1}$$

$$C_1 \times V_1 = C_2 \times V_2, \tag{2}$$

$$\%R = \frac{\mathrm{Co} - \mathrm{Ce}}{\mathrm{Co}} \times 100. \tag{3}$$

The symbols used in the equations above are defined in Table 1.

2.3 Adsorbent

The adsorbent composites are prepared by physical activation, crushing and forming a bentonite–water composite of limestone and bentonite by progressively adding bentonite, and sludge is then added. Sludge is added, and the materials are dried for 12 h at 105.5°C. The liquid is agitated using a magnetic stirrer for 30 min. The cure is then filtered and burned using filter sheets at 800°C for 2 h. The finished product is ground by grinding. The bentonite-to-sludge mass ratios were 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:4 [32].

Table 1: Definitions of the symbols used in Equations (1)–(3)

No	Symbol	Definition
1	W	Weight of the salt in grams,
2	V	Volume of the solution in liters
3	C_i	Required sulphate concentration in milligrams per litre
4	M	Salt's molecular weight in grams
5	At	Atomic weight of SO_4 in grams
6	C_1	Concentration of the solution (1,000 mg/L)
7	C_2	Concentration of the diluted solution
8	V_1	Volume that is needed
9	V_2	Diluted volume

2.4 Batch tests

The LB's sulphate adsorption capability was evaluated using batch adsorption studies. To achieve homogeneous mixing, the initial concentration was 900 mg/L, initial pH was 7.5, the contact time was 60 min, the agitation speed was 200 rpm, and the adsorbent dosage was 100 mg/50 mL at room temperature (25°C). The solution was filtered through 0.45 µm membrane filters, and barium chromate spectrophotometry was used to calculate sulpate content. Magnetic stirrers were used to mix 50 mL of effluent with 100 mg of adsorbent. The sulphate concentration was determined by assuming 100% sulphate dissolution in Equation (1) [33].

3 Results and discussion

Figure 2 illustrates the results of batch studies conducted to evaluate the efficacy of the adsorbent in removing sulphate from wastewater. The initial results suggested that the ideal mass ratio of LB was 1:2, resulting in an 81% efficiency.

3.1 Characterization of the material

3.1.1 Brunauer–Emmett–Teller (BET) analysis

The BET theory describes the physical adsorption of gas molecules on solid surfaces and can be used to calculate the specific surface area of a material [34]. The specific area of bentonite is 11.2959 m^2/g and limestone is 7.5571 m^2/g. The fact that composite LB had a specific surface area of 22.1282 m^2/g demonstrates that the activation process causes the specific surface area to increase to 42.1283 m^2/g. This shows that an increase in surface area leads to a higher adsorption capacity.

3.1.2 Fourier transform infrared spectroscopy (FTIR) test

Figure 3 shows the FTIR spectra of limestone, bentonite, BL before adsorption, BL after adsorption process. The samples' spectra reveal the presence of many functional groups. These spectra showed that following the alteration process, there was a decrease, broadening, disappearance, or development of new peaks. The effect of alteration was evident by the shifts in the spectra. The noticeable bands upon modification demonstrate the produced adsorbents' ability to effectively remove sulphate. The silicate characteristic bands, which are closely linked to the stretching vibrations of Si–O, are identified by the peaks seen at 1042.89, 1036.41, and 1029.58 cm^{-1}. These peaks coincide with those reported by Bulut and Tez [35] at 1,150, 1,060, and 1,030 cm^{-1}. The Si–O deformation bands are attributed to the peaks at 1036.41 and 1007.92 cm^{1}, which are more in line with the values reported at 1,033, 1,032, and 1,007 cm^{1}. The Al–OH bending vibration of kaolin clay type was attributed to the peaks ranging from 912 to 937 cm^{1}, which are more in line with the 914–936 cm^{1} range [36]. The Si–O stretching of the kaolin clay type was attributed to the peaks at 799.10, 757.78, and 797.78 cm^{-1}. These peaks matched the ones noted by Georges–IVO 2 at 796, 754, and 695 cm^{-1}.

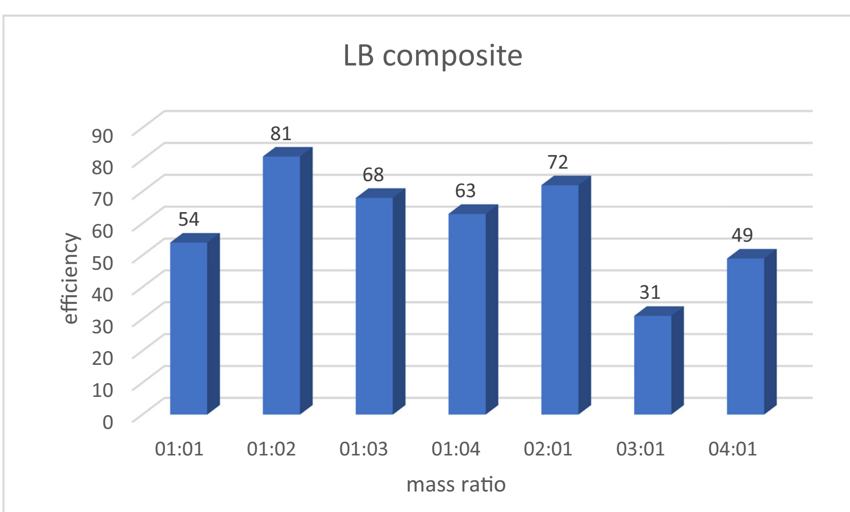

Figure 2: Removal efficiency of LB composite [33].

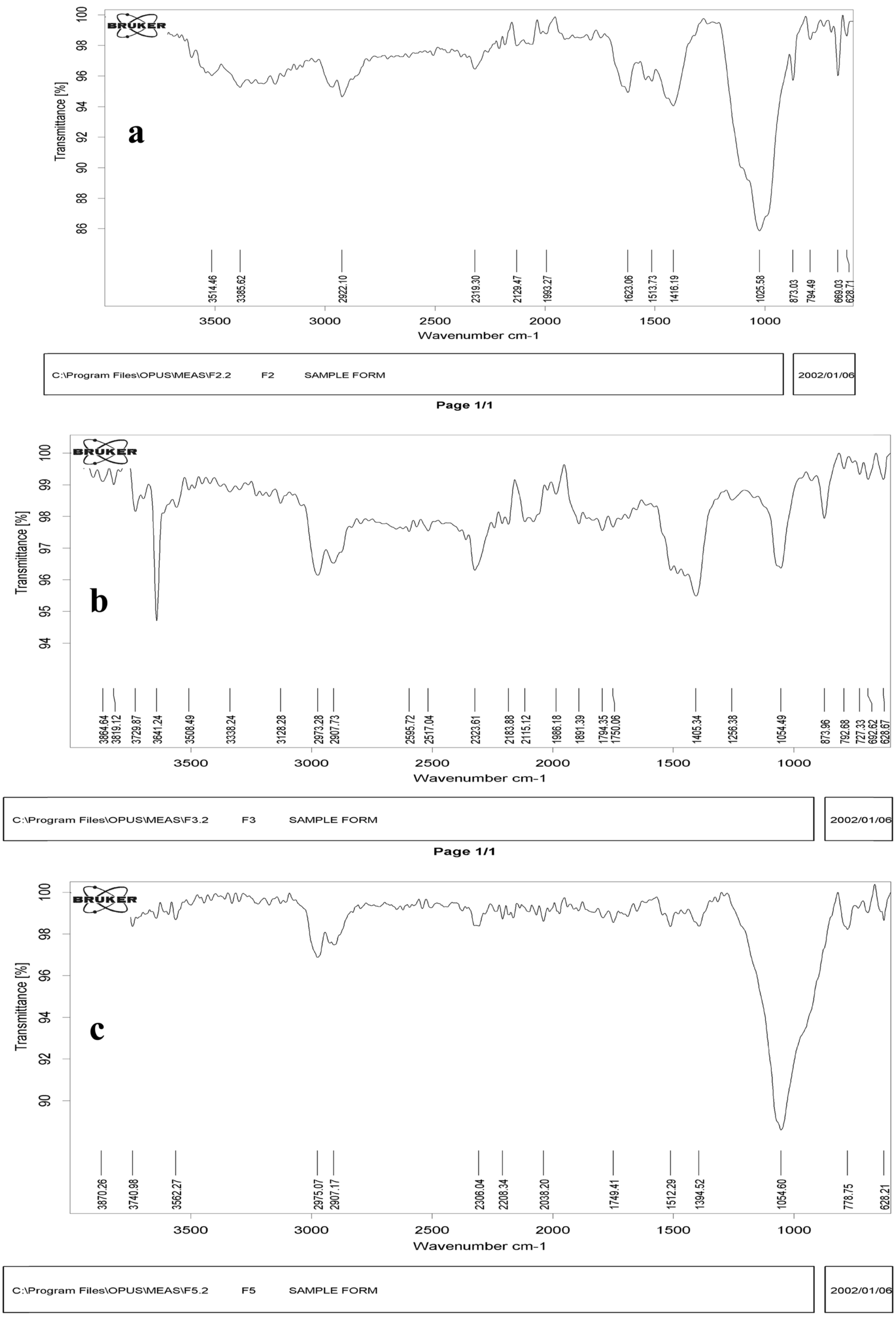

Figure 3: FTIR spectra of (a) limestone, (b) bentonite, (c) LB before, and (d) LB after sulphate adsorption.

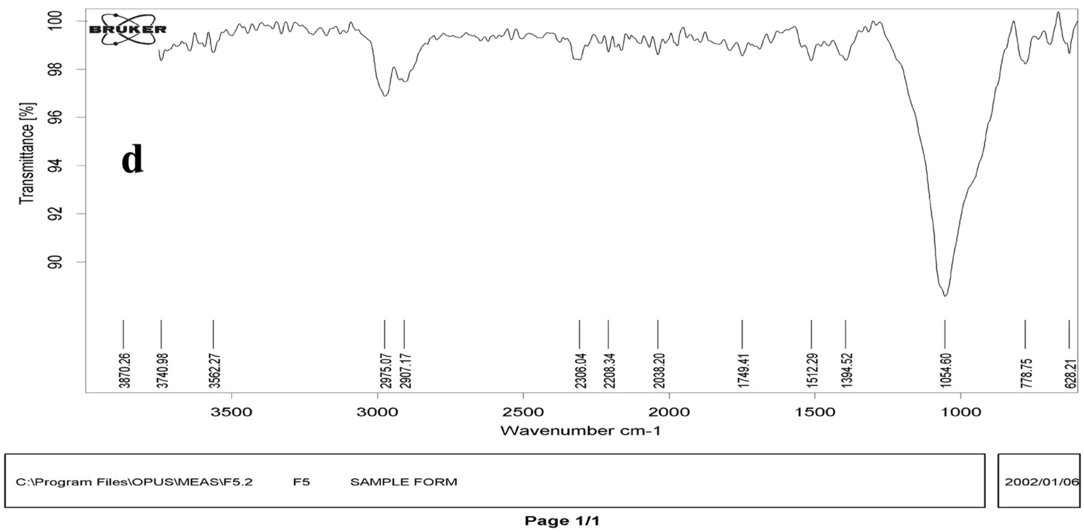

Figure 3: (*Continued*)

3.1.3 Scanning electron microscope images

The surface morphology of LB is shown in Figure 4. The LB has a compact, homogeneous pore structure with edges, sharp corners, and rough surfaces. Because of its shape and enormous surface area, LB was able to absorb additional pollution. The particles in this LB are regular and well-defined. Usually, it is lamellar in structure.

3.1.4 EDS test

The LB composite is shown in Figure 5 to incorporate elements from the S, O, and EDS spectra. The fact that the levels of S and O significantly rise after modification shows that the co-precipitation method of synthesis was successful in loading the LB composite.

3.2 Results of adsorption

This experiment's objective was to assess how effectively the adsorbent absorbed sulphate from simulated contaminated wastewater. The studies that were carried out using various methods (contact time, pH solution, starting concentration, agitation speed, and adsorbent dosage) are shown in this section.

3.2.1 Equilibrium time

The time needed to reach equilibrium is an important measurement to make during batch testing since it shows how long it will take for contaminants to re-distribute between the liquid and solid phases. The SO_4^{2-} transfer monitoring from the liquid phase to the LB composite is depicted in Figure 6 for contact durations of no more than one hour (60 min). This result was obtained with the initial conditions of pH = 7.5, 200 rpm of agitation, 0.1 g/50 mL of dosage, and 900 mg/L of adsorbate at 25°C. The LB removal percentages rise quickly due to the abundance of vacant sites accessible for interaction with sulphate molecules [37]. Nonetheless, the decline in these areas was associated with a reduction in sorption rate, especially after 180 min. This time frame is adequate to achieve "equilibrium" because no discernible change in sulphate removal occurs until 60 min, and by 180 min, the sulphate removal efficiency surpassed 90.4% [38]. Batch testing determines the time needed for contaminants to redistribute between liquid and solid phases. Monitoring SO_4^{2-} transfer from the liquid phase to the LB composite for contact times no longer than 60 min shows a quick rise in LB removal percentages due to vacant sites. However, sorption rate decreases after 180 min, reaching "equilibrium" with a sulphate removal efficiency exceeding 90.4% at 180 min [39].

3.2.2 pH of the solution

Because pH has an impact on how ions behave during adsorption, it is the primary regulator of an adsorbent's capacity to adsorb. Through protonation and deprotonation, the basic and acidic groups of the adsorbents interact with the surface structure. As protons are absorbed by the binding sites of ions, a higher pH causes an increase in ion

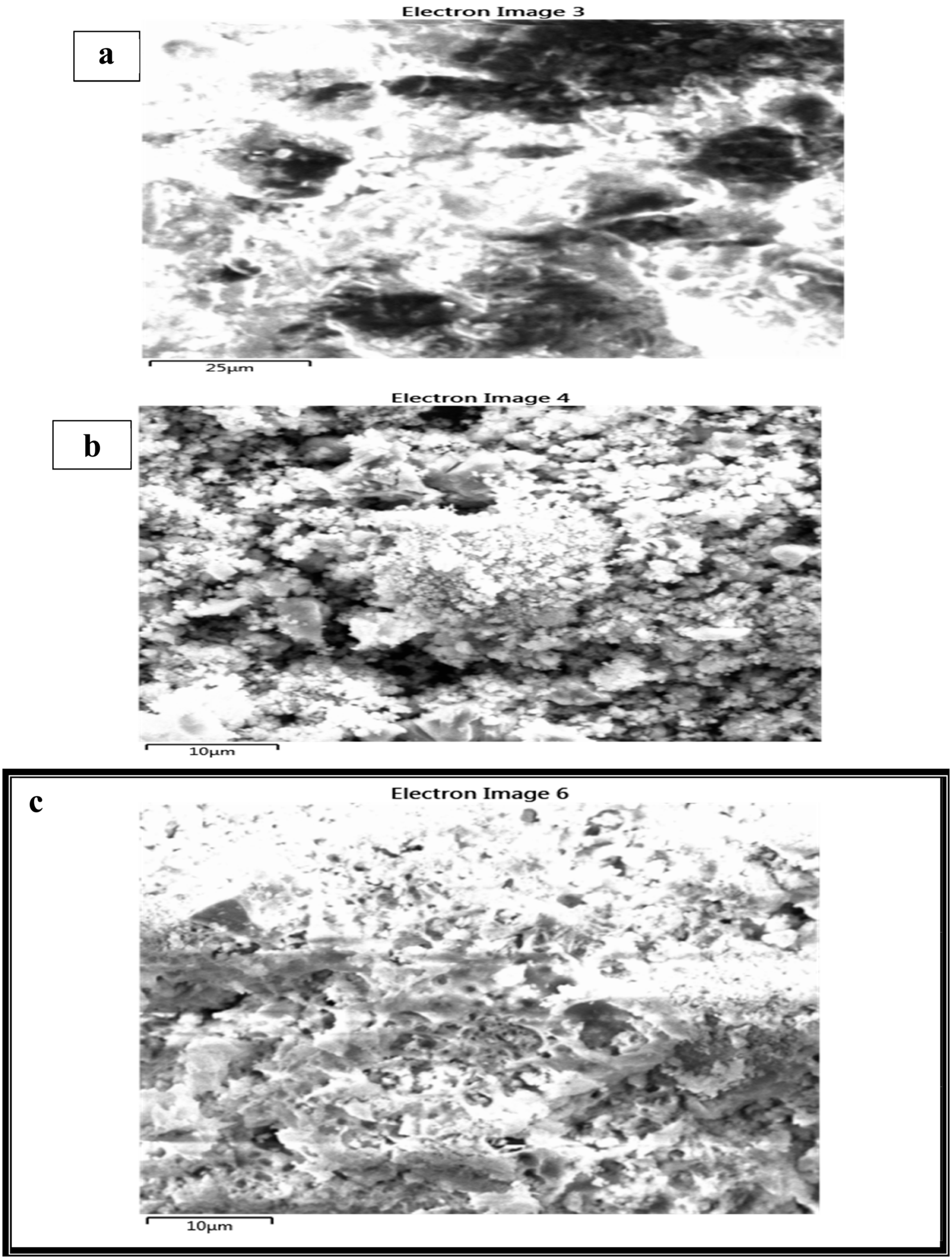

Figure 4: Images SEM for the (a) limestone, (b) bentonite, and (c) LB composite before adsorption and (d) LB composite after adsorption.

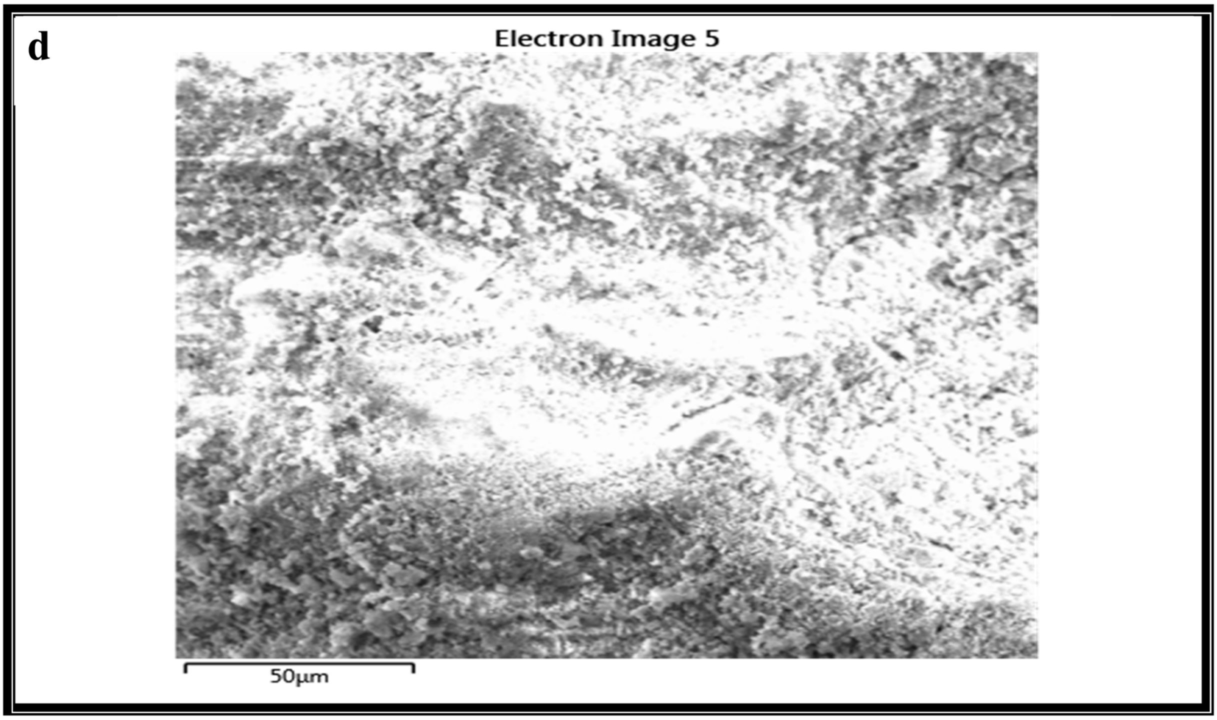

Figure 4: (*Continued*)

adsorption. The adsorbent surface plays a role in the elimination process by increasing removal efficiency through competition between pollutants and H^+ ions [35]. The results (Figure 7) are consistent with previous research, suggesting that pH plays a part in the elimination process.

3.2.3 Effect of initial SO_4^{2-} concentrations

The efficiency of sulphate removal at various ion concentrations was examined in the study. According to the findings, ion removal was more effective at lower starting concentrations but became less effective at higher concentrations. This is because ions cannot interact with the active sites of the adsorbent, which becomes less favourable as ion concentrations rise. It was also discovered that the pH had a critical influence on the elimination process. The starting ion concentration determined the percentage of elimination [40]. The results (Figure 8) are consistent with previous research, suggesting that pH plays a role in the elimination process. The decrease in the percentage of ions eliminated may result from the adsorbent's active sites' inability to adsorb additional SO_4^{2-} ions from the solution. This suggests that monolayer ions formed on the adsorbent's outer surface, as the percentage of removal was proportional to the starting ion concentration.

3.2.4 Agitation speed

The study investigates the impact of agitation speed on sulphate removal efficiency from wastewater. The results show that the removal efficiency of SO_4^{2-} increases with agitation speed, reaching 97%. This is due to improved ion diffusion on the adsorbent surface, leading to better binding between adsorbent sites and sorbate ions. At 250 rpm, the best equilibrium and higher removal efficiency are achieved due to the availability of functional groups for interaction between sorbate and adsorbent. This results (Figure 9) in faster ion removal and reduced resistance to ion transport [41]. The reason for this is that when rotational speed is increased, the degree of adsorbent aggregation decreases, increasing the total amount of adsorbent surface area and raising the ion removal percentage. Additionally, SO_4^{2-} ions encounter resistance as they move through the boundary layer from the liquid phase to the solid phase. Rotation thus accelerates the movement of ions through solutions by thinning the boundary layer and lowering the resistance to ion transport.

3.2.5 Effect of the adsorbent dosage

The study used varying adsorbent dosages in batch testing to determine their impact on sulphate adsorption.

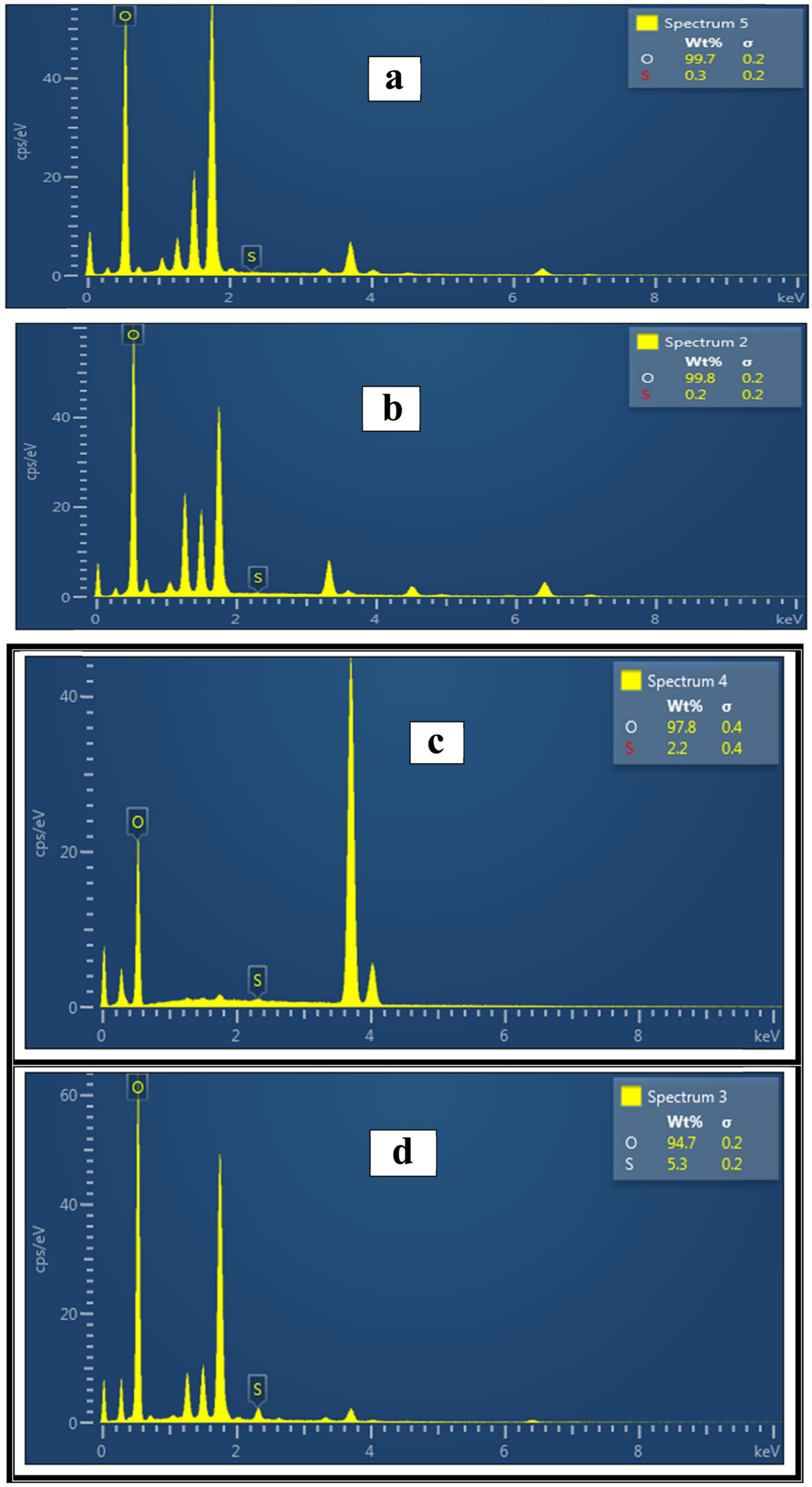

Figure 5: EDS spectrum for the (a) limestone, (b) bentonite, and (c) LB composite before adsorption and (d) LB composite after adsorption.

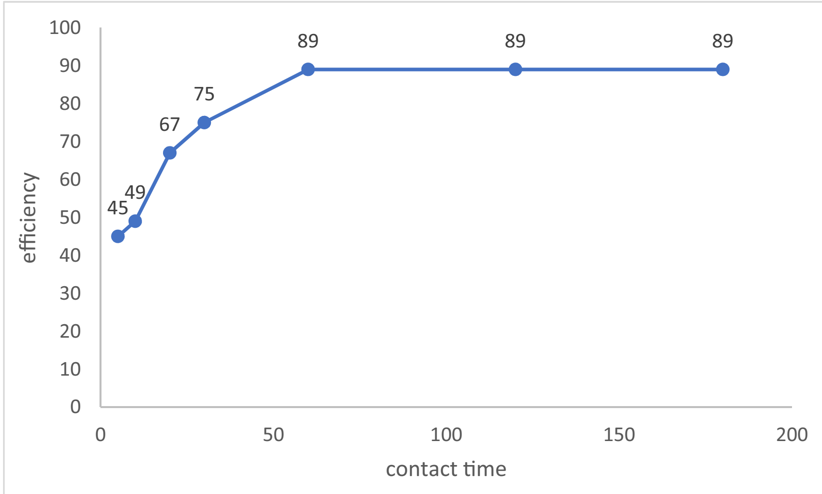

Figure 6: Sulphate removal efficiency affected by time.

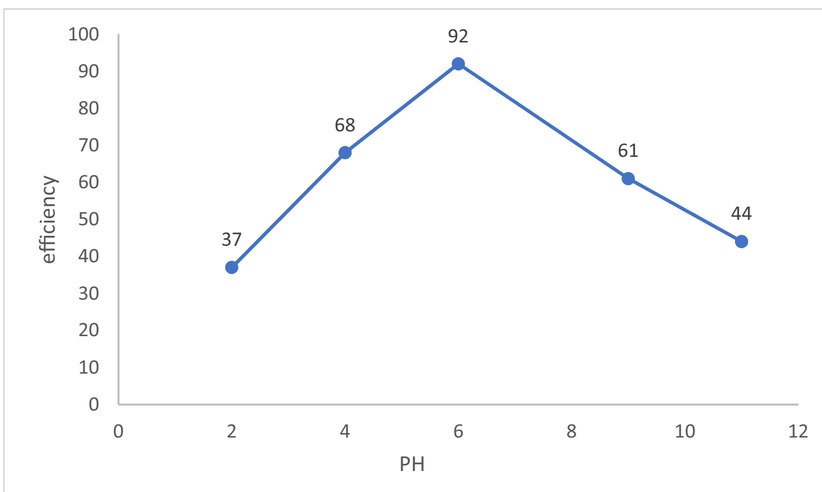

Figure 7: Sulphate removal efficiency affected by pH.

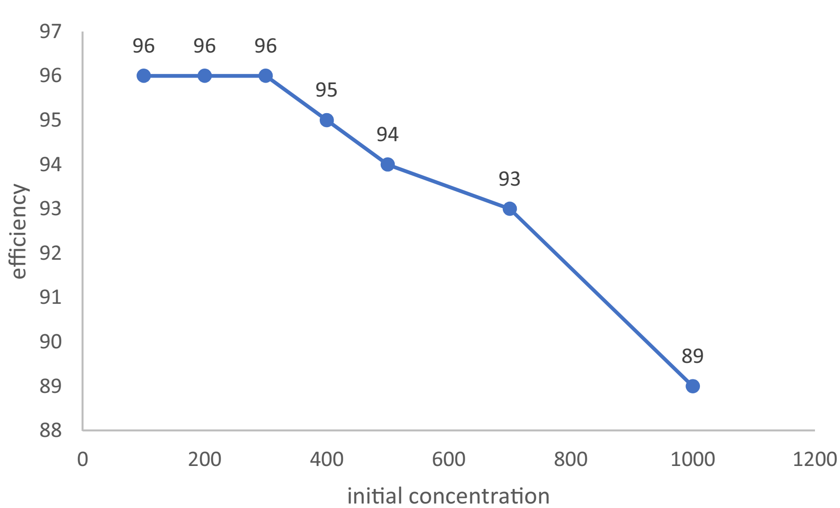

Figure 8: Sulphate removal efficiency affected by initial concentration.

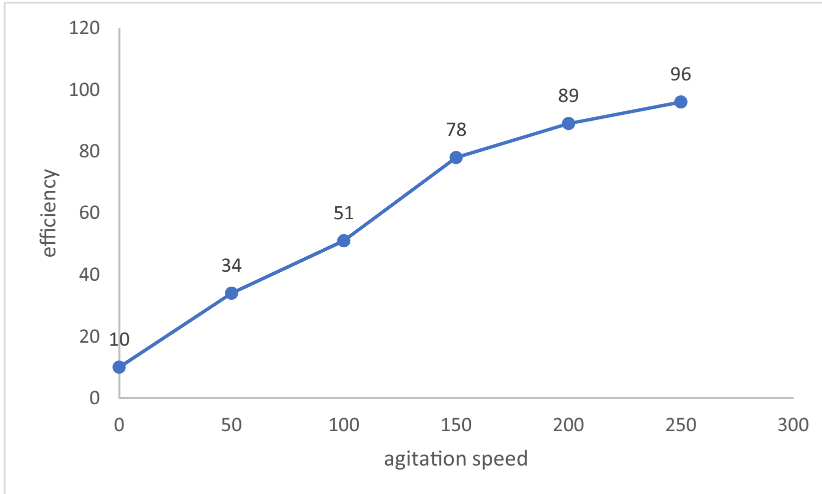

Figure 9: Sulphate removal efficiency affected by the agitation speed.

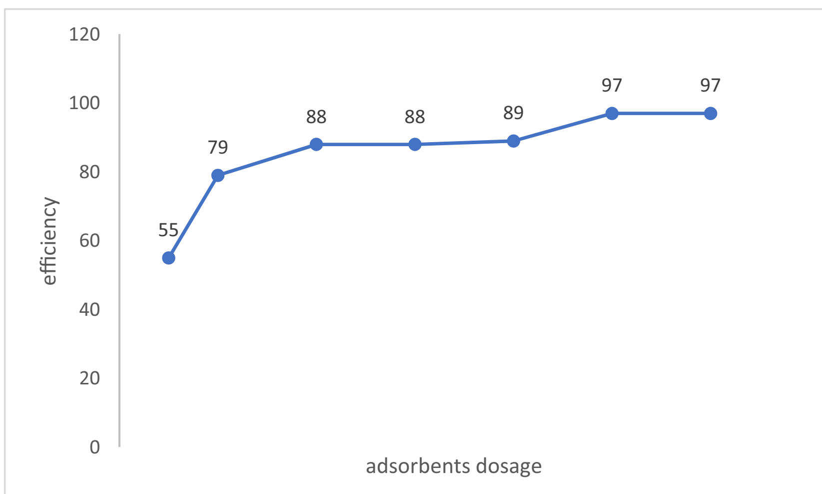

Figure 10: Sulphate removal efficiency affected by the amounts of adsorbent dosage.

Table 2: Adsorption isotherm models SO_4^{2-} on adsorbent; 25°C, pH = 6, dosage = 0.1 g/50 mL, time = 1 h, and agitation speed = 200 rpm

Isotherm	Equation No	Calculated parameters	SO_4^{2-}
Langmuir	2.2	q_{max} (mg/g)	44.4
		b (L/mg)	0.93
		R^2	0.4705
Freundlich	2.3	K_F (mg/g)	17.1
		N	1.55
		R^2	0.9798

Results (Figure 10) showed that the sulphate removal efficiency increased with increased dosages. However, the concentration of sulphate in the solution and its binding to the adsorbent remained constant after the maximum rate of sulphate removal occurred at 0.5 g of adsorbent [42].

3.3 Adsorption isotherm

The study calculates isotherms using the Langmuir and Freundlich models to fit experimental data. The results show a remarkable agreement between experimental and predicted values for SO_4^{2-} adsorption onto an adsorbent. The Freundlich model has the best fit, with a higher R^2 = 0.9798 when compared to other models. The general trend of

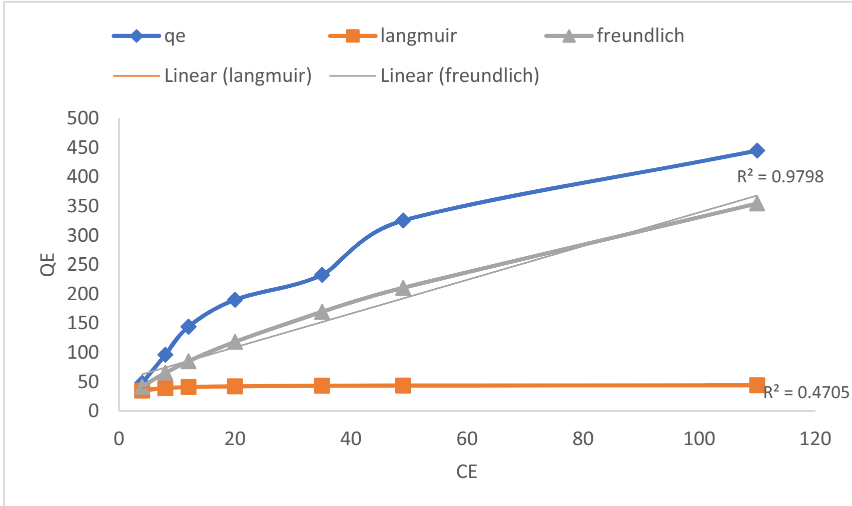

Figure 11: Adsorption isotherm models SO_4^{2-} on the adsorbent at 25°C, pH = 6, dosage = 0.1 g/50 mL, contact time = 1 h, and agitation speed = 200 rpm.

Table 3: Adsorption kinetics model coefficients for SO_4^{2-} on adsorbent; 25°C, pH = 6, dosage = 0.1 g/50 mL, time = 1 h, and agitation speed = 200 rpm

Kinetic model	Equation No	Calculated parameters	SO_4^{2-}
Pseudo-first-order	2.9	k_1 (min^{-1})	0.000167
		q_e (mg/g)	181.27
		R^2	0.8286
Pseudo-second-order	2.10	k_2 (g/mg min)	0.0003
		q_e (mg/g)	400
		R^2	0.9480
Experimental		q_e	400.5

isotherms for sulphate is favourable, as shown in Table 2 and Figure 11. Each contaminant equilibrium was determined using batch experiments.

3.4 Adsorption kinetics

The sulphate adsorption process can be modelled as a chemical or physical reaction using pseudo-first-order and pseudo-second-order kinetics models. Nonlinear regression analysis was used to examine the nonlinear forms of kinetics adsorption models. The determination coefficient (R^2) for the sulphate adsorption process was found

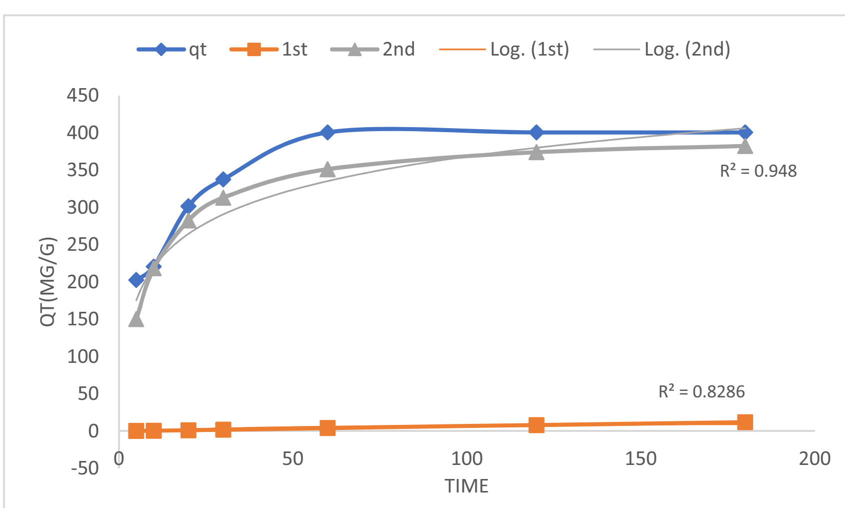

Figure 12: Adsorption kinetics models calculated using nonlinear regression analysis for Sulfate (200 rpm, 0.1 g/50 mL, C_o = 900 mg/L, 25°C, contact time = 1 h, and pH = 6).

to be higher (R = 0.948) than the pseudo-first-order kinetics model, indicating it follows a chemisorption process [43], as shown in Table 3 and Figure 12.

3.5 Adsorption mechanisms

Equilibrium, thermodynamic, and kinetic investigations were used to review the mechanism of sulphate adsorption on synthetic adsorbents. Studies using several isotherm models to describe the equilibrium of adsorption processes were conducted (Langmuir, Freundlich). It is possible to conclude that the adsorption processes on the surface of the adsorbent were homogenous, heterogeneous, or a combination of both based on the assumptions made by these models. Additionally, they can indicate whether the adsorption occurred chemically, physically, favourably, or unfavourably. The rate of the adsorption processes is mentioned in kinetic studies, which have been examined using diffusion-based models (Boyd, intra-particle diffusion, and mass-transfer models) and reaction-based models (pseudo-first-order and pseudo-second-order). The potential for instantaneous processes and the internal energy of a system can also be represented by thermodynamic parameters derived from equilibrium calculations.

4 Conclusion

Limestone and bentonite, which were used to recycle waste material, available, and without value (waste), were activated to increase their adsorption capacity, resulting in the formation of a new composite adsorbent. The researcher in this work used LB as an affordable adsorbent to solve sulphate ion contamination in wastewater treatment. The results demonstrated that LB was a more suitable adsorbent for sulphate removal due to its low cost and high efficiency. The procedure began with a concentration of 900 mg/L, pH of 7.5, a contact period of 60 min, an agitation speed of 200 rpm, and an adsorbent dosage of 100 mg/50 mL. The best mass-to-efficiency ratio, which yielded 81%, was (1:2). BET, SEM, EDX, and Fourier transform infrared spectroscopy analysis of the LB showed that the specific surface area was important for adsorption. The optimal parameters for adsorption were determined to be 60 min, 250 rpm, 900 mg/L, and 0.5 g/50 mL, with 97% efficiency. Adsorption studies were conducted in a batch mode. The Freundlich model offers a better forecast for adsorption processes, with a higher determination coefficient, supporting the hypothesis that chemisorption is the adsorption process. Because of its affordability and accessibility, LB could be used as a possible adsorbent for the removal of sulphate from wastewater.

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Data availability statement: All the data that support the findings of this study are available in the manuscript.

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