DE GRUYTER Open Engineering 2024; 14: 20220532

Research Article

Ashraf Fakhri Obeid*, Basim Khalil Nile and Maad Farouk

Sulfate removal from wastewater by using waste material as an adsorbent

https://doi.org/10.1515/eng-2022-0532
received June 29, 2023; accepted September 07, 2023

Abstract: A new composite adsorbent was created by activating bentonite, a sludge, to improve its adsorption capability. These innovative adsorbents address sulfate ion pollution in wastewater treatment. Researchers used various techniques to study the composite's surface structure, chemical, elemental, and mineralogical characteristics. The composite adsorbs over 864 mg/L of sulfate ions from wastewater with an initial concentration of 900 mg/L, demonstrating its high removal efficiency of 96%.

Keywords: composite adsorbent, physical activation, sludge, sulfate ions, wastewater

1 Introduction

Although freshwater resources are scarce globally, water is necessary for life. Half of the world's population is expected to reside in water-stressed regions by 2025 [1]. Water is necessary for human consumption, industry, and agriculture. It goes without saying that commercial and industrial activities can contaminate water [2]. The literature lists a number of toxins that can be found in groundwater, surface water, and industrial wastewater, including heavy metals [3–6], dyes [7], pesticides [8], pharmaceuticals [9], personal care products [10], hormones [11], viruses [12], radioactive elements [13], phenol-derived compounds [14], and other emerging contaminants [15]. The presence of these compounds in waters and wastewaters is dangerous for the environment and public health and is well documented in the literature [16,17]. In reality, one of our responsibilities as scientists working in the field of environmental chemical engineering is to create the materials, techniques, and technologies that will make it possible to manage, decontaminate, and reuse water. There are a number of water treatment technologies, each with benefits and cons [18]. However, adsorption is the main concern here. Adsorption is a process that involves both a solid phase (the adsorbent) and a fluid phase (in this case, water). The fluid phase contains one or more dissolved contaminants (the adsorbate). As the dissolved contaminants are transferred from the liquid phase to the adsorbent surface, water is purified [19]. Due to its advantages in terms of cost, effectiveness, simplicity of use, flexibility to use a variety of solids as adsorbent materials, and capacity to recover both the adsorbent and the adsorbate, adsorption is currently used to treat water [20–23]. It is crucial to emphasize the competitive and efficient nature of adsorption as a polishing process when pollutants are present in water at concentrations between ng/L and mg/L [24]. According to the literature from 1990 to the present, the crucial elements of being evaluated to apply adsorption for water treatment are the choice, development and characterization of the adsorbent material, the development and optimization of the adsorption mode, the mathematical modeling, the decision and development of the regeneration procedure, and the application in actual samples. Of course, the cost analysis is also quite important. Cost, however, must be taken into account separately for each of the aforementioned criteria. Adsorption charges range from 5.0 to 200 US dollars/m^3 of treated water, while prices for the majority of technologies are between 10 and 450 US dollars/m^3 of treated water [25]. About 70% of these costs are covered by the adsorbent [26]. The town and affected industries were under tremendous strain as a result of the vast amounts of sludge that were produced during wastewater treatment operations. About 25–65% of the entire operating expense for secondary wastewater treatment is toward treating and disposing of the sludge [27]. Therefore, it is important to identify a sludge disposal option that is both affordable and environmentally friendly. The

---

*** Corresponding author: Ashraf Fakhri Obeid,** Department of Civil Engineering, College of Engineering, University of Karbala, Karbala, Iraq, e-mail: ashraf.f@s.uokerbala.edu.iq
Basim Khalil Nile: Department of Civil Engineering, College of Engineering, University of Karbala, Karbala, Iraq, e-mail: dr.basimnile@uokerbala.edu.iq
Maad Farouk: Department of Civil Engineering, College of Engineering, University of Karbala, Karbala, Iraq, e-mail: maad.farooq@uokerbala.edu.iq

commercial application of adsorption has been dominated by generic adsorbent primary types such as polymeric adsorbents, molecular sieves of zeolites and carbon, activated alumina, silica gel, and activated carbon. Only a small number of adsorbents, including some zeolites, are produced naturally. The type of adsorbing surface, the pore structure, and the porosity are the features of each adsorbent [28]. The aim of this study was to prepare a low-cost and effective adsorbent. Due to its affordable price and good effectiveness, using clay material sludge and bentonite as an adsorbent (SB) for the removal of sulfate ions is a wise choice. To our knowledge, there are not many studies looking into how clay minerals can remove sulfate ions from solutions. The goal of this study is to use waste and inexpensive materials as an adsorbent to extract SO_4^{2+} from wastewater.

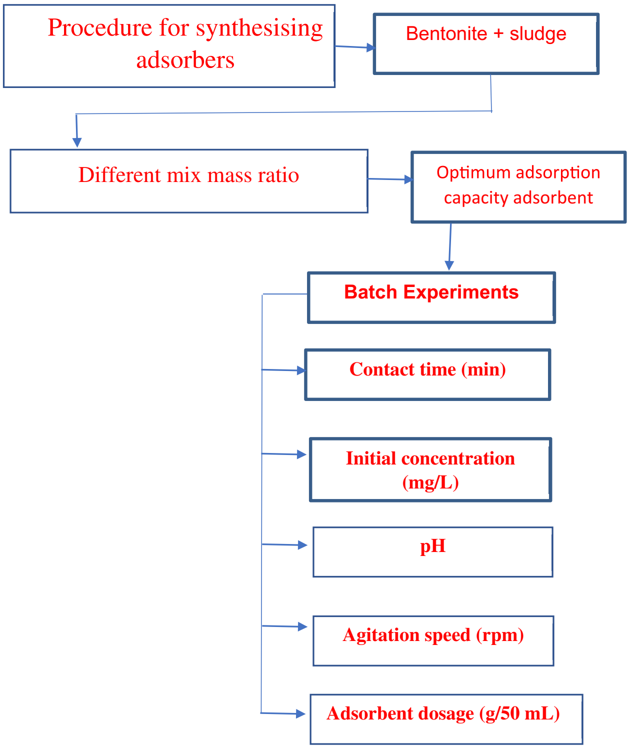
2 Materials and methods

2.1 Materials

Dewatered sludge was obtained from the wastewater treatment plant in Karbala city. The bentonite samples were collected from commercial markets. The chemical materials – potassium sulfate, sodium hydroxide, barium chloride, filter paper (Whatman 7.0 cm) – were used to filter the sample solution and distilled water from commercial markets with high purity. The chemical materials are adjusted with pH (HCl) and NaOH bases.

2.2 Preparation of adsorbent

The newly created adsorbent composites underwent physical activation to prepare them. The materials are ground, sludge and bentonite SB composite formed as bentonite is progressively added to the water, and then sludge is added with the addition of water. The materials are then dried in a drying oven for 12 h at a temperature of 105.5°C. For 30 min, the solution is stirred with a magnetic stirrer. The solution is then filtered. The filter is burned in the oven for 2 h at 800°C using filter sheets. Grinding with a grinder is the end result. The mass ratios of bentonite and sludge at 4:1, 3:1, 2:1, 1:1, 1:2, and 1:4 [29] are shown in the flowchart below.



2.3 Batch experiments

To examine the adsorption capabilities of SB for sulfate, batch adsorption tests were conducted. The procedure was carried out in its first state: Ci = 900 mg/L, contact time = 60 min, pH = 7.5, agitation speed = 200 rpm, adsorbent dosage = 0.1 g/50 mL (25°C) at room temperature to ensure uniform mixing. Following that, 0.45 m membrane filters were used to filter the solution. Barium chromate spectrophotometry was used to calculate the sulfate content. Impact of starting concentration: 50 mL of wastewater was mixed with 100 mg of adsorbent using magnetic stirrers [30]. By assuming total dissolution in equation (1), the necessary concentration of sulfate was obtained:

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

where W is the weight of the salt (mg), V is the volume of the solution (L), Ci is the required sulfate concentration (mg/L), M.wt is the salt molecular weight (g/mol), and At.wt is the SO_4 atomic weight (g/mol). To prepare the necessary concentration, the solution was diluted in accordance with

Equation (2). In addition, 0.1 moles of either HCl or NaOH, depending on the circumstance, were added to each solution to alter its pH [31].

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

where C_1 is the solution concentration = 1,000 mg/L, V_1 is the required volume of the solution (L), C_2 is the dilute concentration of the solution (mg/L), and V_2 is the dilute solution volume (L). The change in percent removal value over time can be used to calculate the efficiency of the adsorption process; this equation was used to determine the change in percent removal over time.

$$R\% = (C_o - C_e)/C_o \times 100, \tag{3}$$

where R is the removal efficiency %, C_o is the initial concentration, and C_e is the final concentration.

3 Results and discussion

3.1 Preparation results

The results of batch experiments to test how well the adsorbent removed sulfate from wastewater showed that, under the initial condition, the optimal mass ratio of SB was 1:1, with an efficiency percentage of 86%, as shown in Figure 1.

3.2 Characterization of the material

3.2.1 Brunauer–Emmett–Teller (BET) analysis

The BET theory, which describes the physical adsorption of gas molecules on solid surfaces, provides a method for calculating a material’s specific surface area [32]. The results of the mixture of bentonite and sludge were 11.2959 and 7.5571 m^2/g, respectively. The fact that the specific surface area of composite SB was 22.1282 m^2/g shows that the activation process causes the specific surface area to grow from 22.1282 to 42.1283 m^2/g. This indicates that an increase in surface area results in a good capacity for adsorption.

3.2.2 Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra of sludge, bentonite, and SB before and after adsorption show functional groups and modifications. The adsorbents effectively remove sulfate, with peaks at 1042.89, 1036.41, 1029.58, 1036.41, 1007.92, 912–937, and 799.10 cm^{-1} (Figure 2).

3.2.3 Scanning electron microscope (SEM)

In Figure 3 the morphology of surface SB is displayed. The pore structure of the SB is compact and uniform, and it has

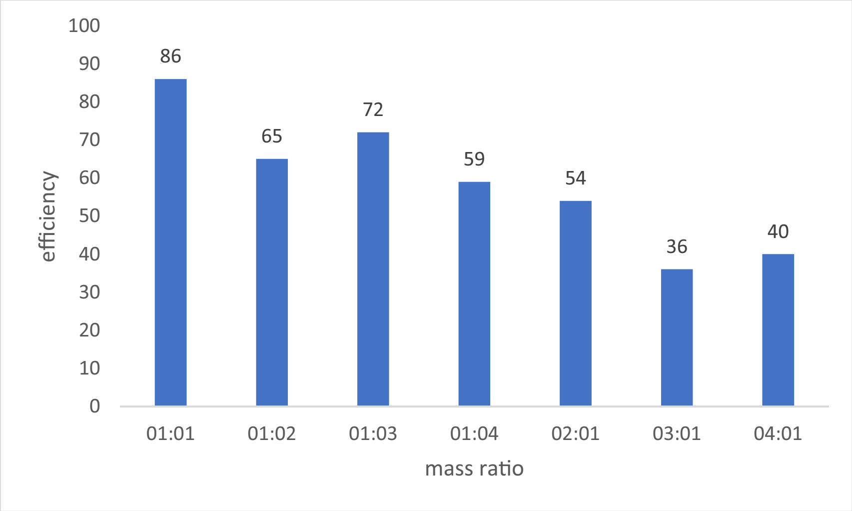


Figure 1: Removal efficiency of SB composite.

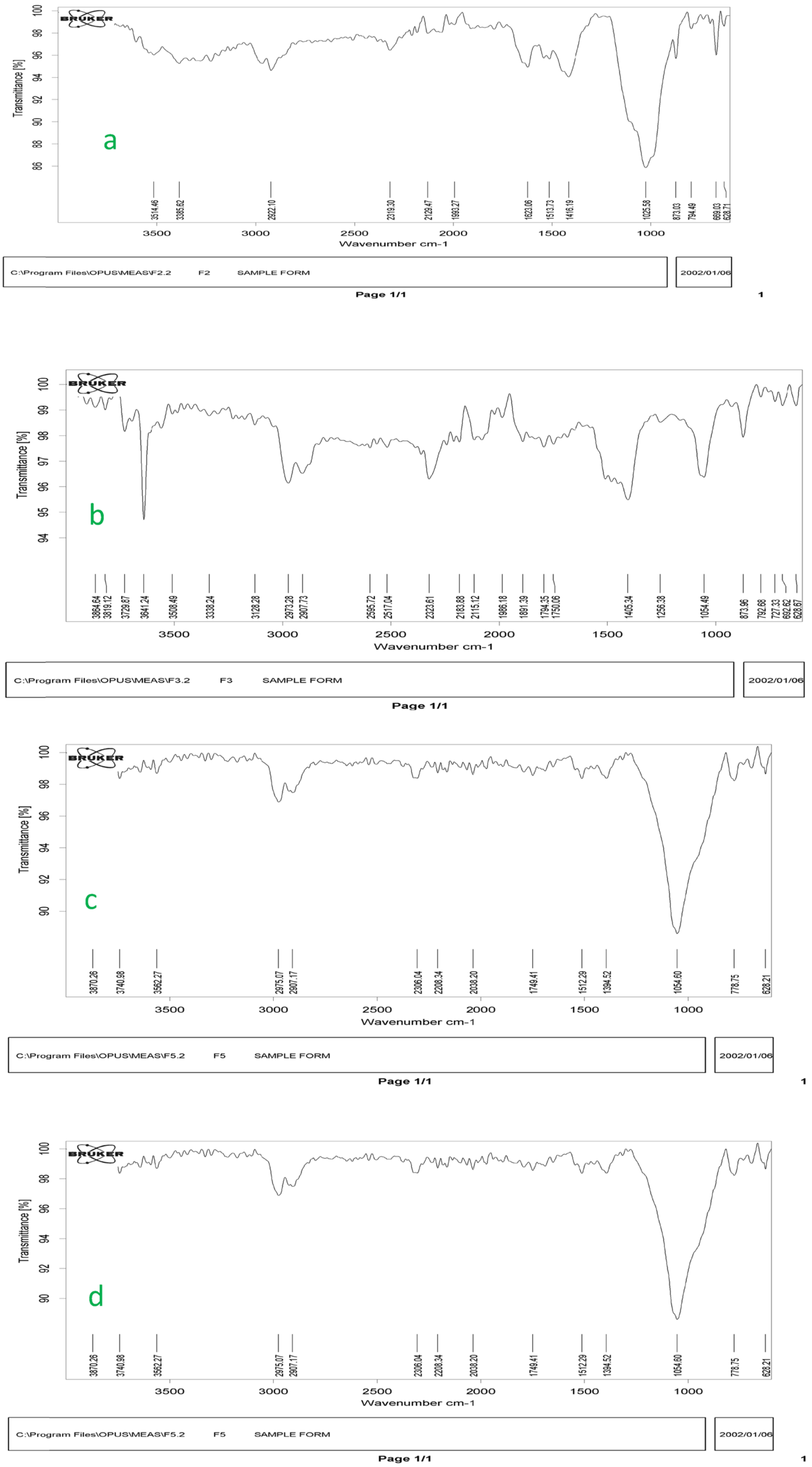


Figure 2: FT-IR spectra of materials and composite before and after adsorption: (a) sludge, (b) bentonite, (c) SB before, (d) and SB after sulfate adsorption.

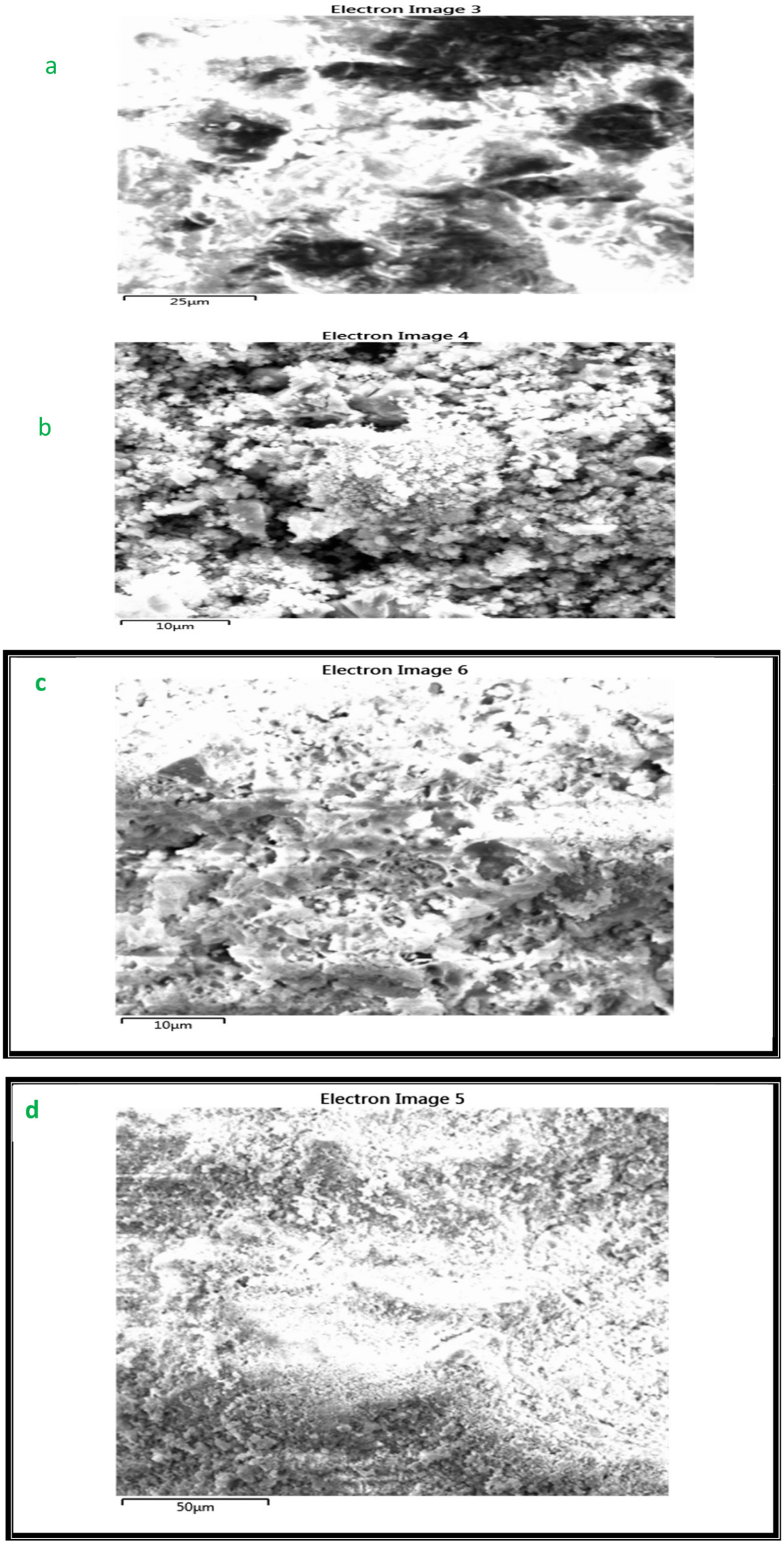


Figure 3: Images SEM for (a) sludge, (b) bentonite, and (c) SB composite before adsorption and (d) SB composite after adsorption.

edges, sharp corners, and rough surfaces. SB's structure and substantial surface area allowed it to serve as an absorbent for further pollution. The particles in this SB are clearly defined and regular. It typically has a lamellar structure.

3.2.4 Energy dispersive spectroscopy (EDS)

From Figure 4 it can be seen that the SB composite contains S and O by EDS spectrum. After modification, the contents of S and O increase dramatically, proving the successful loading of SB composite using the co-precipitation method of synthesis.

3.3 Adsorption results

The goal of this section of the experiment was to evaluate how well the adsorbent removed sulfate from simulated contaminated wastewater. This section shows that the experiments are conducted in various ways (contact time, pH solution, initial concentration, agitation speed, and adsorbent dosage).

3.3.1 Equilibrium time

Finding the amount of time needed to reach equilibrium during batch testing is essential because it shows how long it will take for contaminants to be redistributed between the liquid and solid phases. Monitoring SO_4^{+2} transfer from the liquid phase to the SB composite for contact time no longer than 1 h (60 min) is shown in Figure 5. This figure was attained at the initial conditions of pH = 7.5, 200 rpm of agitation, 0.1 g/50 mL of dosage, and 900 mg/L of cobalt at 25°C. A quick rise in the SB removal percentages is evident right away due to the ready availability of vacant sites for interacting with sulfate molecules [33]. However, a decrease in sorption rate, particularly after 180 min, was linked to the fall in these regions. Since no significant change in sulfate removal can be noticed until 60 min, this period is sufficient to reach "equilibrium" because the sulfate removal efficiency exceeded 90.4% at 180 min [34].

More than 90% was removed in 1 h. In addition, at contact times greater than 1 h, the concentrations of ions remained relatively constant. Residual ion's concentrations did not change significantly at the time up to 3 h, yet sorption experiments in other batches were conducted at 1 h.

3.3.2 pH of the solution

Due to its impact on the ionic forms of pollutants and the surface characteristics of adsorbents, solution pH is the primary factor regulating adsorbent adsorption capacity [35]. The pH value has an impact on how ions behave during adsorption because it impacts how the basic and acidic groups of the sorbent interact with its surface structure through protonation and deprotonation. Figure 6 shows that the basic and acidic sorbent groups were protonated and deprotonated, which boosted the removal efficiency (dose = 0.1 g/50 mL, Co = 900 mg/L, contact time = 1 h, T = 25°C, and agitation speed = 200 rpm), have documented a similar phenomenon of increasing the ion's adsorption when the pH of the solution has increased. The polarity a similar occurrence wherein an increase in the pH of the pH of the solution causes an increase in the ion's adsorption [36]. It was obvious from Figure 6 that when the pH value rose, the removal efficiency increased, which meant that there was competition between contaminants and H^+ ions on the adsorbent surface. The findings indicating the role of pH in the elimination process are similar to those from earlier studies.

3.3.3 Effect of initial SO_4^{2+} concentrations

Experimental testing of sulfate removal effectiveness was done at various ion concentrations at the beginning. In these tests, 0.1 g of the adsorbent per 50 mL of a solution, 200 rpm agitation for 1 h, and a pH of 6 were utilized. The starting sulfate concentrations used ranged from 100 to 1,000 mg/L. Figure 7 at mixing time = 1 h, mixing speed = 200 rpm, dose = 0.1 g/50 mL, pH = 6, and T = 25°C represents the ion's removal efficiency related to the initial ion's concentrations at equilibrium state. The outcomes demonstrate that the ion removal was greater with the lower initial concentration values. The elimination efficiency fell off as the original concentrations rose. After 100 mg/L, there was no discernible change in the ion concentration. The inability of the ions to interact with the active sites on the adsorbent is what causes this. This finding indicates that sites become energetically less favorable as ion concentrations in the solution grow [37]. The findings indicating the role of pH in the elimination process are similar to those from earlier studies. This decline in the proportion of ions removed could be brought on by an inability of the adsorbent's active sites to absorb more SO_4^{+2} ions present in the solution. As a result, the percentage of removal was dependent on the initial ion concentration, which is consistent

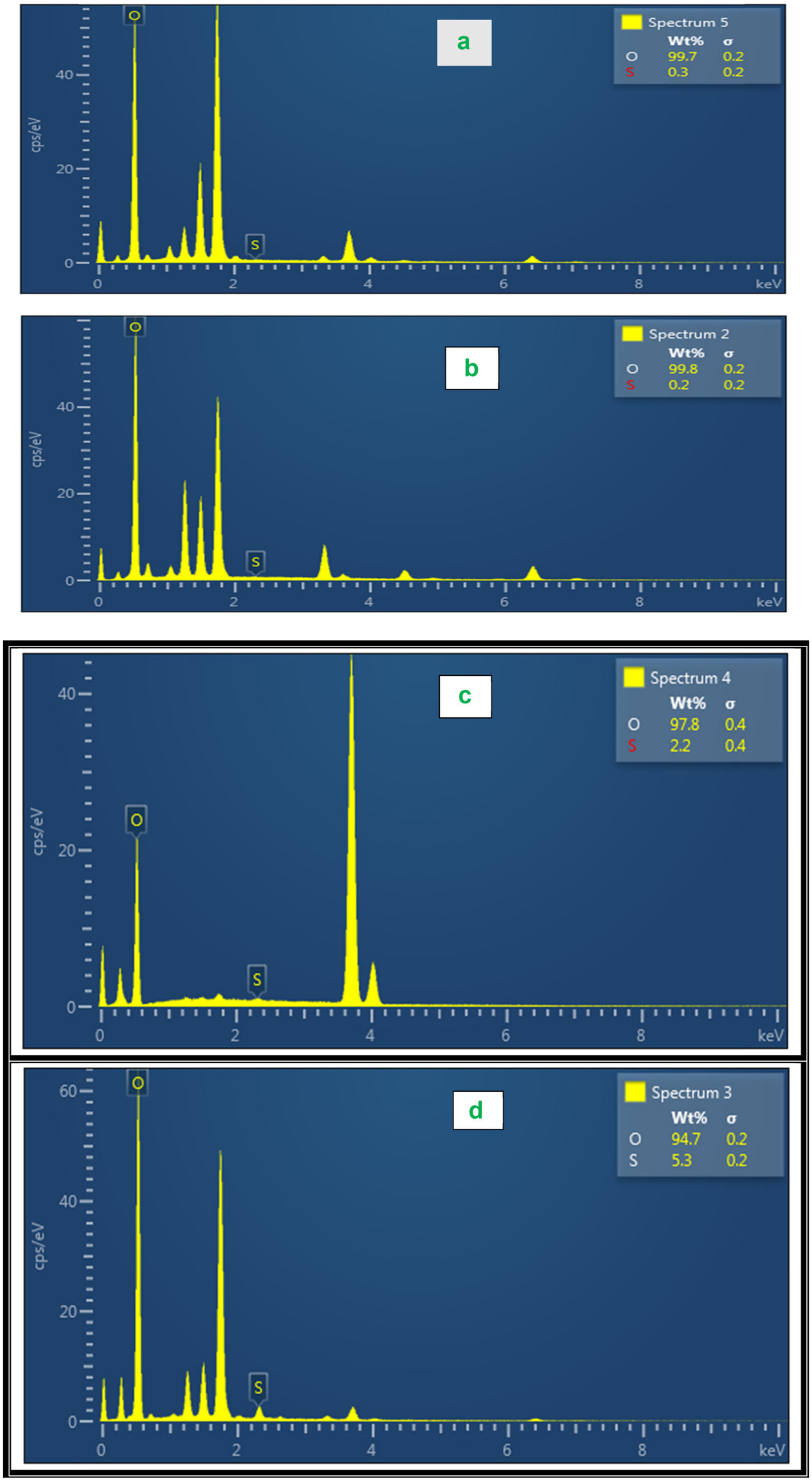


Figure 4: EDS spectrum for (a) sludge, (b) bentonite, and (c) SB composite before adsorption and (d) SB composite after adsorption.

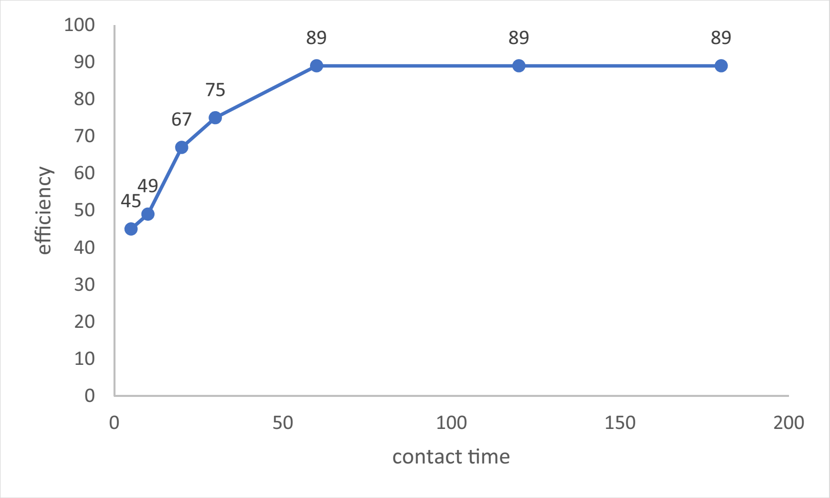


Figure 5: Sulfate removal efficiency effected by time.

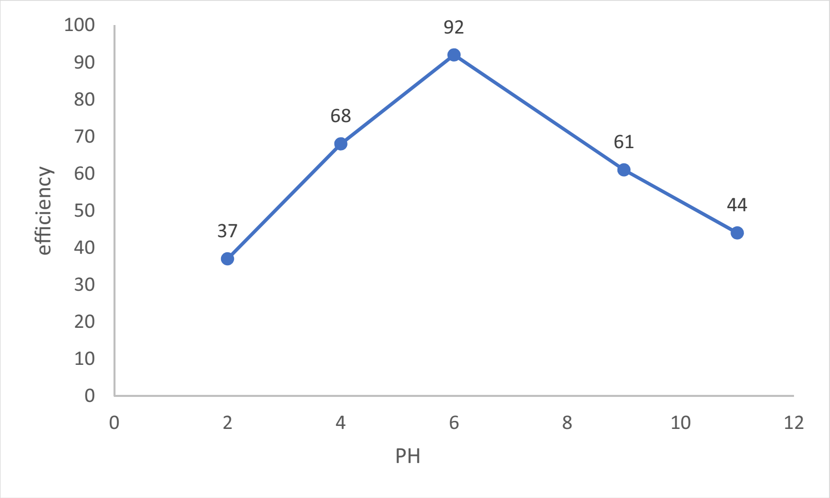


Figure 6: Sulfate removal efficiency effected by pH.

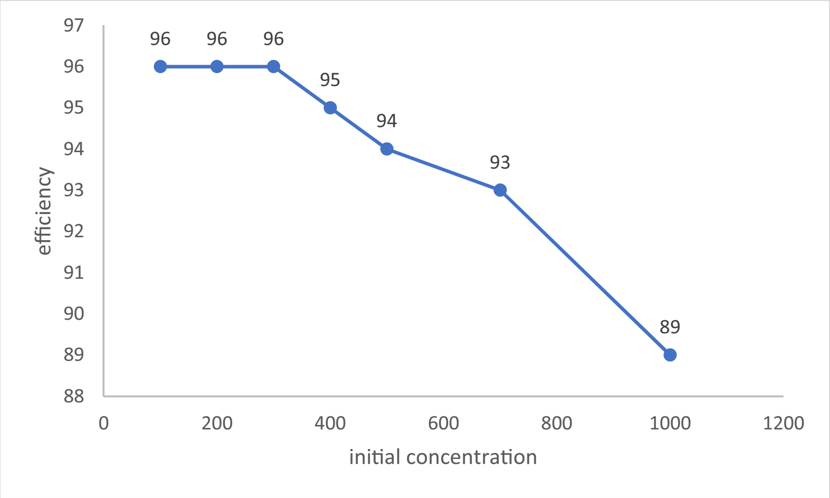


Figure 7: Sulfate removal efficiency effected by initial concentration.

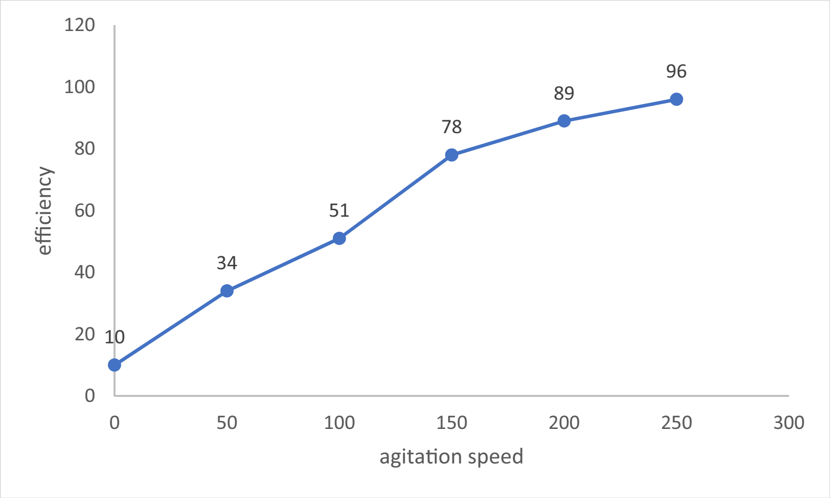


Figure 8: Sulfate removal efficiency effected by the agitation speed.

with the idea that monolayer ions formed on the adsorbent's outer surface.

3.3.4 Agitation speed

In order to study the effect of agitation speed on sulfate removal efficiency from contaminated wastewater, several experiments were carried out at different agitation speeds, ranging from 0 to 250 rpm, with contact time of 1 h, Co = 900 mg/L, dose = 0.1 g/50 mL, pH = 6, and T = 25°C. The removal efficiency of SO_4^{2+} before agitation, as shown in Figure 8, was 10%, respectively, and this efficiency increased gradually as the agitation speed increased from 0 to 250 rpm, becoming 97%. This increase is related to the fact that the ion diffusion on the adsorbent surface is improved as the agitation speed increases. So, the binding between the adsorbent sites and sorbate ions in solution is developed, and these ions are effective in transferring to the adsorbent sites [38]. As shown in Figure 8, at an agitation speed of 250 rpm best equilibrium was obtained and higher removal efficiency of SO_4^{2+} ions as all adsorbent sites at this speed for uptake sorbate ions are readily available. Also, when the required functional groups for the interaction between sorbate and adsorbent, which are located on the adsorbent surface, have greater availability, the binding capacity is improved, and the processes are rapidly carried out. This is because SO_4^{2+} ions encounter resistance as they move from the liquid phase to the solid phase through the boundary layer, and as the

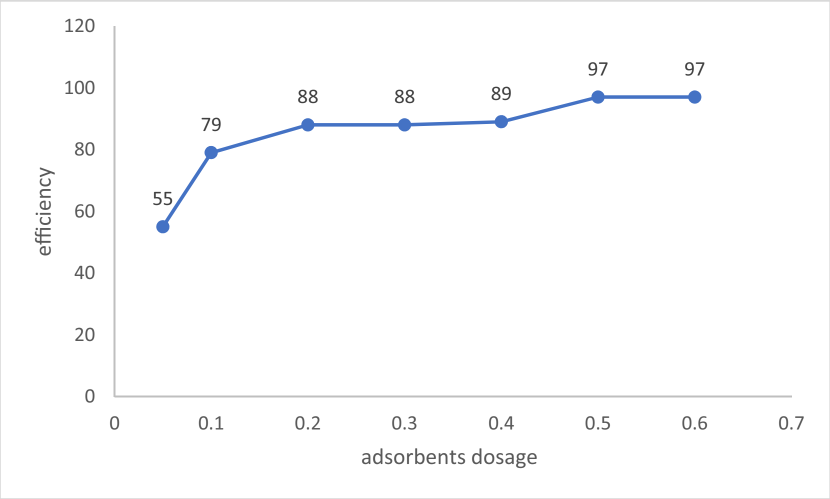


Figure 9: Sulfate removal efficiency effected by the amounts of adsorbents dosage.

rotational speed increases, the degree of adsorbent aggregation decreases, increasing the total amount of adsorbent surface area and raising the ion removal percentage. As a result, rotation causes the boundary layer to thin and the resistance to ion transport to decrease, increasing the rate at which ions move through the solutions.

3.3.5 Effect of the adsorbent dosage

Different dosages of the adsorbent, ranging from 0.05 to 0.6, were utilized with a 50 mL ion solution while maintaining the other parameters to determine how the adsorbent dosage influences the sulfate adsorption in batch testing (mixing time = 1 h, mixing speed = 250 rpm, pH = 6, Ci = 900 mg/L, and T = 25°C). Figure 9 shows different amounts of the adsorbent related to sulfate removal efficiency. The sulfate removal efficiency grew because of the increased adsorbent dosage from 0.05 to 0.5 g/50 mL with the fixing of other parameters. The result described above was expected according to the fact that, when the adsorbent dosage in a solution rises, subsequently more active sites are available. In spite of increasing adsorbent dosage, the concentration of sulfate in the solution and its binding to the adsorbent remained constant after the maximal rate of sulfate removal occurred at a dose of 0.5 g of adsorbent [39].

4 Conclusion

An adsorbent (low-cost local) was modified to create a new composite adsorbent. Physical activation is used. This inexpensive local adsorbent was similarly made by activating bentonite, a sludge. The new composite adsorbent's adsorption capability increased when compared to the low-cost LC. A major issue in the wastewater treatment sector is fouling caused by sulfate-ion pollution. In this work, scientists created an SB composite and assessed its ability to absorb sulfate ions from contaminated wastewater. The sludge, bentonite, and SB composite's surface structural morphology, chemical, elemental, and mineralogical characteristics, as well as functional group interaction, were determined using the field emission scanning electron microscope, energy dispersive X-ray spectroscopy, X-ray dispersive, FT-IR, and BTE. To ascertain the effects of solution pH, agitation speed, adsorbent dosage, contact time, and initial SO_4^{2+} concentration, batch adsorption studies were conducted for the use of the innovative SB composite in the removal of sulfate ions from the synthetically tainted wastewater. The experimental findings demonstrated that, at the ideal treatment settings of 250 rpm, pH 6, and 60 min contact time, the new SB composite adsorbed over 864 mg/L of sulfate ions from the model wastewater with an initial concentration of 900 mg/L. High removal efficiency was exhibited by SB = 96%. These findings demonstrate the new composite adsorbent's enormous potential when used to absorb sulfate ions.

Funding information: The authors declare that the manuscript was done depending on the personal effort of the author, and there is no funding effort from any side or organization.

Conflict of interest: The authors state no conflict of interest.

Data availability statement: Most datasets generated and analyzed in this study are in this submitted manuscript. The other datasets are available on reasonable request from the corresponding author with the attached information.

References

[1] World Health Organization, Geneva, Switzerland, Drinking Water. 2019. https://www.who.int/en/news-room/fact-sheets/detail/drinking-water.

[2] Ismail HK, Abd Ali LI, Alesary HF, Nile BK, Barton S. Synthesis of a poly(p-aminophenol)/starch/graphene oxide ternary nanocomposite for removal of methylene blue dye from aqueous solution. J Polym Res. 2022;29:159.

[3] Joseph L, Jun BM, Flora JRV, Park CM, Yoon Y. Removal of heavy metals from water sources in the developing world using low-cost materials: a review. Chemosphere. 2019;229:142–59.

[4] Nile BK, Faris AM. The effect of MLSS values on removal of COD and phosphorus using control method of return activated sludge concentration. J Eng Appl Sci. 2018;13:9730–4.

[5] Al Juboury MF, Abdulredha M, Nile BK. Photocatalysis and flocculation processes for recycling aquaculture effluent into nutrient-rich irrigation water. Water Supply. 2022;22(3):3103–13.

[6] Obaid H, Shahid S, Basim KN, Chelliapan S. Modeling of wastewater quality in an urban area during festival and rainy days. Water Sci Technol. 2015;72(6):1029–42.

[7] Yagub MT, Sen TK, Afroze S, Ang HM. Dye and its removal from aqueous solution by adsorption: A review. Adv Colloid Interface Sci. 2014;209:172–84.

[8] Souza RM, Seibert D, Quesada HB, Bassetti FJ, Fagundes-Klen MR, Bergamasco R. Occurrence, impacts and general aspects of pesticides in surface water: a review. Proc Saf Environ Prot. 2020;135:22–37.

[9] Carmalin SA, Lima EC. Removal of emerging contaminants from the environment by adsorption. Ecotoxicol Environ Saf. 2018;150:1–17.

[10] Yang Y, Sik Ok Y, Kim KH, Kwon EE, Tsang YF. Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in

drinking water and water/sewage treatment plants: a review. Sci Total Environ. 2017;596–597:303–20.

[11] Lee LS, Carmosini N, Sassman SA, Dion HM, Sepúlveda MS. Agricultural contributions of antimicrobials and hormones on soil and water quality. Adv Agron. 2007;93:1–68.

12] Springthorpe S, Sattar SA. Virus removal during drinking water treatment. Persp Med Virol. 2007;17:109–26.

[13] Zhang X, Gu P, Liu Y. Decontamination of radioactive wastewater: state of the art and challenges forward. Chemosphere. 2019;215:543–53.

[14] Ahmaruzzaman M. Adsorption of phenolic compounds on low-cost adsorbents: a review. Adv Colloid Interface Sci. 2008;143:48–67.

[15] Rodriguez-Narvaez OM, Peralta-Hernandez JM, Goonetilleke A, Bandala ER. Treatment technologies for emerging contaminants in water: a review. Chem Eng J. 2017;323:361–80.

[16] Taheran M, Naghdi M, Brar SK, Verma M, Surampalli RY. Emerging contaminants: here today, there tomorrow! Environ Nanotechnol Monit Manage. 2018;10:122–6.

[17] Wilkinson J, Hooda PS, Barker J, Barton S, Swinden J. Occurrence, fate and transformation of emerging contaminants in water: an overarching review of the field. Environ Pollut. 2017;231:954–70.

[18] Cheremisinoff NP. Handbook of water and wastewater treatment technologies. Elsevier, Butterworth-Heinemann; 2002. p. 576.

[19] Bonilla-Petriciolet A, Mendoza-Castillo DI, Dotto GL, Duran-Valle CJ. Adsorption in water treatment. Reference module in chemistry, molecular sciences and chemical engineering 1. 1st edn. Amsterdam: Elsevier; 2019. p. 1–21.

[20] Bonilla-Petriciolet A, Mendoza-Castillo DI, Reynel-Ávila HE. Adsorption processes for water treatment and purification. Springer International Publishing; 2017. p. 256.

[21] Ruthven DM. Principles of adsorption & adsorption processes. Wiley; 1984. p. 464.

[22] Cherkasov N. Liquid-phase adsorption: common problems and how we could do better. J Mol Liq. 2020;301:112378.

[23] Ali I, Gupta VK. Advances in water treatment by adsorption technology. Nat Protoc. 2006;1:2661–7.

[24] Cooney DO. Adsorption design for wastewater treatment. Boca Raton: Lewis Publishers; 1999.

[25] Ali I, Asim M, Khan TA. Low-cost adsorbents for the removal of organic pollutants from wastewater. J Environ Manage. 2012;113:170–83.

[26] Li W, Mu B, Yang Y. Feasibility of industrial-scale treatment of dye wastewater via bioadsorption technology. Bioresour Technol. 2019;277:157–70.

[27] Hii K, Baroutian S, Parthasarathy R, Gapes DJ, Eshtiaghi N. A review of wet air oxidation and thermal hydrolysis technologies in sludge treatment. Bioresour Technol. 2014;155:289–99.

[28] Kadhim GZ. A study of adsorption of some heavy metal on selected Iraqi surfaces. M.Sc. thesis. University of Baghdad, College of Science for Women; 2010.

[29] Huang R, Zheng D, Yang B, Wang B, Zhang Z. Preparation and characterization of CTAB-HACC bentonite and its ability to adsorb phenol from aqueous solution, China. Received 13 December 2011; accepted 24 April 2012.

[30] Nazeeh I. Removal of copper ions from simulated wastewater by applying electromagnetic-adsorption using banana peel adsorbent. M.Sc. thesis. University of Baghdad, College of Engineering; 2016.

[31] Esmail AA. Adsorption of Pb (II) ions from aqueous phase using activated carbon prepared from novel precursor. M.Sc. thesis. Al-Nahrain University, Chemical Engineering; 2016.

[32] Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure Appl Chem. 2015;87(9–10):1051–69.

[33] Alkan M, Kalay B, Doğan M, Demirbaş Ö. Removal of copper ions from aqueous solutions by kaolinite and batch design. Hazard Mater. 2008;153:867–76.

[34] Bulut Y, Tez Z. Adsorption studies on ground shells of hazelnut and almond. J Hazard Mater. 2007;149(1):35–41.

[35] Garg UK, Kaur MP, Garg VK, Sud D. Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. J Hazard Mater. 2007;140(1–2):60–8.

[36] Areco M, Hanela S, Duran J, Dos M. Biosorption of Cu(II), Zn(II), Cd (II) and Pb(II) by dead biomasses of green alga *Ulva lactuca* and the development of a sustainable matrix for adsorption implementation. J Hazard Mater. 2012;213–214:123–32.

[37] Buasri A, Yongbut P, Chaiyut N, Phattarasirichot K. Adsorption equilibrium of zinc ions from aqueous solution by using modified clinoptilolite. Chiang Mai J Sci. 2008;35(1):56–62.

[38] Anwar J, Shafique U, Salman M, Dar A, Anwar S. Removal of Pb (II) and Cd (II) from water by adsorption on peels of banana. Bioresour Technol. 2010;6:1752–5.

[39] Palaniswamy R, Veluchamy C. Biosorption of heavy metals by *Spirulina platensis* from electroplating industrial effluent. Environ Sci Indian J. 2017;13(4):139–45.