International Information and Engineering Technology Association
Advancing the World of Information and Engineering

International Journal of Environmental Impacts
Vol. 9, No. 3, September, 2024, pp. 585-592
Journal homepage: http://iieta.org/journals/ijei

Investigating the Capability of Local Adsorbent in Removing Selected Pollutants in Batch and Packed Reactors

Younis S. Tlaiaa*, Zainab A. R. Naser, Ahmed Hassan Ali

Environmental Engineering Department, College of Engineering, Mustansiriyah University, Baghdad PO Box 14150, Iraq

Corresponding Author Email: eng.younis82@uomustansiriyah.edu.iq

https://doi.org/10.18280/ijei.070319

Received: 14 July 2024
Revised: 6 September 2024
Accepted: 14 September 2024
Available online: 30 September 2024

Keywords:
bentonite, secondary wastewater, BOD_5, Cr^{6+}, phenol (pH), fecal coliforms (FC)

ABSTRACT

Bentonite is a readily available natural clay that can be modified using simple and inexpensive procedures, making it a cost-effective option for removing various organic and inorganic contaminants. In this study, the raw bentonite (RB) is modified using acid and heat treatments. The physiochemical modification of bentonite (MB) was analyzed using the Buranner-Emmett-Teller (BET) technique to determine its surface area, and Fourier transformation infrared spectroscopy (FTIR) was used for further characterization. Post modification, bentonite has a better surface area from 35.15 m^2/g for RB to 102.6 m^2/g. The porosity of MB has also increased, offering more adsorption sites and overall enhanced surface properties. Fixed bed columns filled with MB and a mixture of MB and sand (MB+S) were used to investigate MB secondary wastewater purification capacity. Filtration was completed at a flow rate of 1 mL/min (a flow velocity of 3.1 cm/h) onto MB and MB+S mixture, respectively. The results show that the maximum removal efficiency for total suspended solids (TSS), turbidity, phenol (pH), chromium Cr^{6+}, COD (Chemical Oxygen Demand), BOD_5, total coliform (TC), fecal coliforms (FC), and electrical conductivity (EC) onto MB are 100, 100, 93.67, 90.43, 93.75, 97.78, 100, 100, and 30% respectively. The efficiency for these parameters is slightly reduced in modified bentonite (MB) and sand mixtures.

1. INTRODUCTION

Reusing effluents from public wastewater treatment plants (WTP) is crucial in improving water resources management practices [1]. Treating secondary wastewater allows identifying alternative freshwater sources, partially addressing the growing water shortage in dry areas. The degree of intervention needed remains a controversial matter. Only a few nations are making fast progress toward implementing modern treatment methods that may bring wastewater to a quality similar to fresh water. Such progress is needed to protect the land and aquifers from contamination [2]. The primarily measured unit activities in wastewater treatment are TSS, TDS, BOD, COD, and pathogens. Typically, particle filtration techniques vary from using sand to employing nano-membranes. Techniques like chlorination, ozonation, UV disinfection, and membrane filtration remove pathogens [3].

The outer cell envelope macromolecules of bacterial cell surfaces are exposed to the extracellular environment and contain ionized phosphoryl and carboxylate substituents, which give them a net negative electrostatic charge. The study focused on examining the adsorption of microbes on solid surfaces that have been changed to have positive charge centers [4]. Such surfaces also remove heavy metals (anionic detergents like chromate and arsenate). Negatively charged surfaces like montmorillonite (a clay mineral) are used to remove heavy metals found in cationic forms. Additionally, it can eliminate anionic organic compounds, such as dyes and phenols [5, 6].

Bentonite is abundant naturally in massive quantities worldwide, especially in Iraq and the northern and western regions [7]. Bentonite is identified as a promising medium for water pollutant removal. However, bentonite used for wastewater treatment needs further enhancements since it has a small surface area and carries a net negative charge [8]. This study aims to modify bentonite's physico-chemical properties to increase its wastewater treatment capacity. The modification of RB was carried out using the physicochemical method via an acid-thermal activation process. The MB was used as filter media in a fixed bed filter for removing TSS, turbidity, chromium Cr^{6+}, pH, COD, BOD, TC, FC and total dissolved solid expressed as EC.

2. MATERIALS AND METHODS

2.1 Collection of wastewaters samples

Secondary effluents were acquired from the Al-Rustamiyah sewage treatment facility in Baghdad, Iraq, using the grab sampling method. The public wastewater treatment facility uptakes around 175,000 cubic meters of wastewater per day and serves a population of approximately 1,500,000 people. The wastewater treatment plant is a traditional activated sludge operation. Table 1 displays the average properties of the discharged wastewater.

Table 1. Mean effluent characteristics of Al-Rustamiyah water treatment plant

Parameter	Mean Value
BOD (mg/L)	80
pH	7.2
COD (mg/L)	150
Turbidity (NTU)	50
TSS (mg/L)	115
Chromium Cr^{6+} (mg/L)	5
pH (mg/L)	15
TC (*CFU/100mL)	105
FC (*CFU/100mL)	7.5×104
EC (mS/cm)	1

*CFU (Colony Forming Unit)

2.2 Preparation of filtration media and its properties

The clay mineral, bentonite, and quartz sand were obtained from the mining survey director (Ministry of Industry and Mining, Iraq). An energy-dispersive X-ray spectrometer (EDX; LINKISIS 300) attached to a scanning electron microscope (SEM; Cam Scan S4) was used to analyze natural bentonite Physical-chemical composition and architecture (Tables 2 and 3).

Table 2. Chemical composition of bentonite

Constituents	Composition (%)
Al_2O_3	17.12
SiO_2	60
K_2O	0.32
Fe_2O_3	2.56
MgO	2.24
CaO	1.12
Na_2O	3.11
TiO_2	0.74
Loss of ignition (LOI)	6.63
Cation exchange capacity (meq/100g)	89

Table 3. Physical characteristics of bentonite

Characteristics	Value
Bulk density	843 kg/m^3
Moisture content	6.55 %
Specific surface area	35.65 m^2/g
Particle size	700µm

An N_2 adsorption isotherm (Quantachrome Instruments, Nova 2200e) was used to measure the surface areas of RB and MB. A Fourier Transform Infrared Spectrometer (FTIR, Perkin Elmer Spectrum 100) was used to evaluate the change in spectra of the surface functional groups of MB post-modification.

This work used the acid-thermal modification of bentonite, also known as the physiochemical modification by following the methodology reported elsewhere [9] with slight modifications. The process is broken down into two distinct stages. A thermostatic shaker (SI-600R) (providing stable temperature conditions and mixing speed) was used to activate the acid. A 0.1 M HCL solution was used to treat the RB. At a ratio of 1:10, the acid-to-clay ratio was maintained. One thousand milliliters of hydrochloric acid treated one hundred grams of bentonite. Agitation was performed at 180 revolutions per minute for three hours. After adding a significant quantity of deionized water, the reaction was discontinued after three hours. An intensive washing process was performed to free samples from Cl^- ions at a pH of 5. The next step (calcination at 100°C) involved exposing the acid-activated bentonite to thermal activation for 20 min. Subsequently, the contents were allowed to cool in a desiccator. After that, samples were crushed, powdered, and sieved using a sieve (700 µm). The samples were then gathered and dehydrated in an oven (70°C) for 24 hours before use [9].

2.3 Experimental units

At first, a batch system was used to evaluate the impact of acid-thermal modification on RB removal efficiency. Phenol (C_6H_5OH) was used as an indicator to examine the modification process's success. A weight of 0.2 to 1.2 g of RB and MB was added to a 100 ml flask containing 50 mg/L phenol synthetic solution. A shaker incubator (30°C, 200 RPM) was used to stir the contents of the flasks. To guarantee that equilibrium is attained, the agitation was carried out over 24 hours [10].

Column filtration was performed in a 50 cm long column (5 cm diameter and 20 cm active layer). A 3 cm layer of gravel was used to cover the bottom of the column (Figure 1). Two experiments were carried out for each of MB and MB+S. The ratio is 4/1 (w/w) of MB to sand. Using a peristaltic pump, solutions of secondary effluents were pumped into the column (1 ml/min). Measurements of COD, BOD_5, TSS, turbidity, EC, pH, Cr^{6+}, and microbiological tests were taken for the starting solution as well as in each collected portion of 100 mL and were taken into consideration. Three technical replicates were made for each measurement, and the average was calculated.

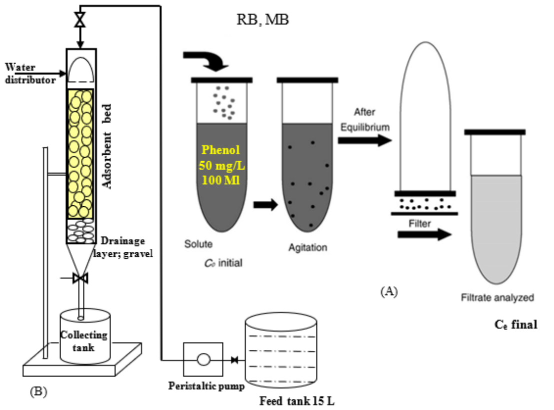

Figure 1. Schematic diagram of the experimental set up for (A) batch system and (B) continues process

2.4 Physical and chemical analysis

Utilizing a UV-visible spectrophotometer (Perkin Elmer Lambda 10), spectrophotometric analysis was performed to calculate the COD. For the BOD_5 analysis, an incubation period of five days was used. For electric conductivity (EC) measurement, an EC-pH-TDS meter (Hanna instruments, HI 9812) was used. The HACH DR-2010 Portable Data Logging Spectrophotometer measured turbidity and total suspended particles. Both TC and fecal coliform tests were carried out with the assistance of a Millipore filtering system, which consisted of a Millipore pump paired with an autoclaved funnel made of stainless steel. A sterile cellulose nitrate filter (#11406-47-can, 0.45 µm, Sartorius Stedim Biotech, Germany) was also used. After repeated dilutions, the total microbial count was measured using the conventional plate technique. A spectrophotometric analysis was conducted to measure the phenol amount in the effluent. A reading was taken at 470nm to determine the absorbance of the coloured complex of phenol with p-nitroaniline following the reaction. A standard spectrophotometric approach was used to determine the Cr^{6+}, and a spectrophotometer (model UV-160 A from Shimadzu) was utilized. The maximum wave absorbance was measured at 540 nm [11].

All these tests were done at Mustansiriyah University/College of Engineering's sanitary laboratory using conventional water and wastewater testing methodologies [11]. The percentage of removal (R%) after each test is computed using the Eq. (1):

$$Removal(\%) = \frac{C_o - C_e}{C_o}\% \tag{1}$$

where, Co and Ce are the initial and equilibrium concentrations.

3. RESULTS AND DISCUSSION

3.1 Characterization of acid-thermal modified filtration media

3.1.1 Surface area and pore size

Interestingly, MB surface area increased from 35.65 to 83.65 m^2g^{-1} after acid activation, reaching a maximum of 102.6 m^2g^{-1} when the acid and heat activation were conducted. Several factors could contribute to the increase in surface area of bentonite. One possibility is the replacement of certain cations with H^+ ions, such as K^+, Na^+, and Ca^{2+}. Another possibility is the leaching of Fe^{3+}, Al^{3+}, and Mg^{2+} from tetrahedral sites and the octahedral in bentonite when exposed to the edges of the platelets [12]. According to a study by Taher et al. [13], the particles within the dissolved octahedral sheet underwent splitting, increasing the surface area of the activated bentonite.

The characterization of RB and MB included evaluating their average pore size after modification. It was determined that the RB had an average pore size of 48.32 Å. The acid-thermal activation decreases the pore size to 40.87 Å. Removing contaminants and replacing exchangeable cations with H^+ ions (known for their small size) are the two factors responsible for this reduction in pore size [14]. Additionally, pore size reduction could have resulted from the vacant tetrahedral sites left behind after Mg^{+2}, Fe^{+3}, and Al^{+3} leaching during activation [15]. The findings also demonstrate the effectiveness of modifying natural bentonite using the acid-thermal approach.

3.1.2 FTIR of RB and MB

An analysis of the FTIR spectra of bentonite was conducted within the frequency range of 4000-400 cm^{-1} to examine the impact of acid-thermal activation on bentonite. Intensity variations of functional groups serve as an indicator of the alterations that take place during acid-thermal activation. FTIR spectra were then analyzed to examine the impact of the activation on bentonite structure (Figure 2) compared to inactivated bentonite. The FTIR spectrum showed a discernible alteration in the band morphology, indicating the successful completion of the activation process. When RB is activated, protons enter its layers and interact with its OH groups. This interaction changes the adsorption bands of the OH groups and octahedral cations. The intensity detected at 3626.16 cm^{-1} (Al-OH-Al and Al-Mg-OH) of the stretching bands faded as the acid concentration increased. The intensification of acid treatment leads to a reduction in the peaks of adsorbed water bands at wavelengths of 3425.58, 2639.22, 2835.36 cm^{-1} (H-O-H stretching), and 1643.35, 1554.63, 1413.13 cm^{-1} (H-O-H bending) as a result of adsorbed water evaporation at high temperatures during bentonite thermal activation—the variation in the bands' intensity results from the successful bentonite activation process [16, 17].

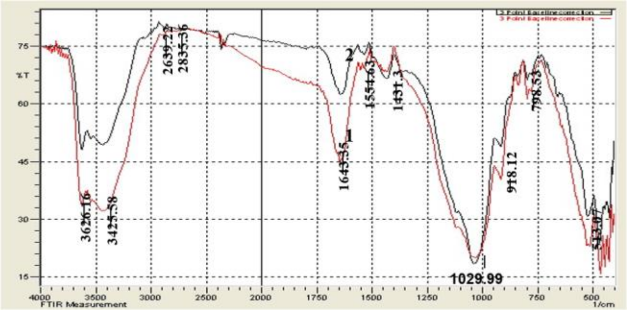

Figure 2. FTIR of (1) RB and (2) MB

Furthermore, the Si-i-Si band peak at 1029.99 cm^{-1} showed no change in intensity due to the treatment [18]. The band's is disappearance at 918.12 cm^{-1} may be attributed to the enhanced acid strength, resulting from the higher Al^{2+} ions substituting Fe^{3+} ions. The tetrahedral sheet underwent a transition with a frequency of 798.53 cm^{-1}. The formation of amorphous silica due to bentonite acid activation is evident from the increased intensity of the peak. This could potentially increase the number of adsorption sites available. The band strength at 513.07 cm^{-1}, associated with bending Al-OH-Si bonds, decreased with increasing acid quantity. This suggests that the Al^{2+} ions in the octahedral sheet of bentonite underwent partial dissolution [19].

3.2 Batch results

Phenol removal using MB was analyzed using synthetic wastewater to evaluate the influence of activation on MB pollutants removal ability. Figure 3 shows that MB achieved about 96% of phenol removal, while RB removed only 73%. The results mean that RB's thermal-acid modification improved its post-modification treatment capacity. Al-Khatib et al. [20] used Jordanian naturally occurring and acid-activated bentonite to examine the adsorption characteristics of Methylene Blue (MB) from a water-based solution. The study showed a significant increase in the efficacy of dye removal after acid treatment (from 75.8% to 99.6%). Therefore, bentonite is a potentially cost-effective adsorbent and can be used in wastewater treatment to eliminate color and dyes [20, 21]. In another study, Nasir [22] stated MB (organoclay) was prepared by adding the required quantity of hexadecyltrimethyl ammonium chloride solution (25% wt./vol.) to the desired quantity of bentonite. The particle size of local bentonite, calcium type, of 0.075mm was prepared by drying the mixed mixture in the electrical oven at 85°C for 48 hours and then ground by agate mortar and screened. The removal efficiency of MB reached 84, 88.4, and 90.6% for phenol, paranitrophenol, and salicylic acid, respectively [22].

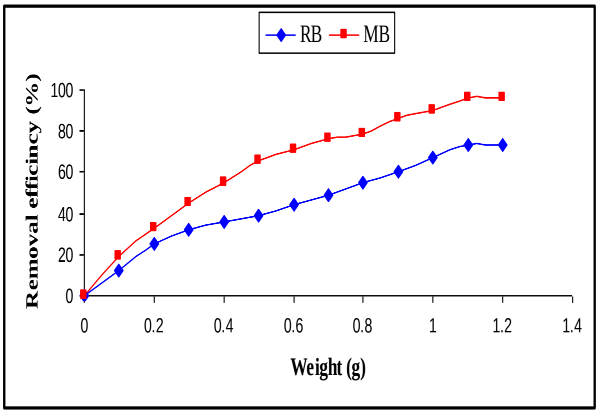

Figure 3. Removal efficiency of phenol using MB and RB

3.3 Fixed bed experiments

The results are in Figure 4 to Figure 8 show the effect of filtration using MB and mixed MB and sand (MB+S) onto several parameters using Al-Rustamiyah secondary effluents. The results shown in Figure 4 indicate a substantial decrease in TSS for all samples collected. The initial TSS concentration at time zero was 115mg/L, which was reduced to 0mg/L at 120 minutes, resulting in a removal efficiency of 100%. However, there was a slight increase in concentration afterward, possibly due to channeling that could have occurred in the filter. Consistent with this result, Figure 4 demonstrates a drop in turbidity from 50 NTU to 0, indicating a 100% removal efficiency. The experiments are repeated at the same filtration rate using MB and sand (MB+S). The turbidly and TSS are reduced to 3 and 4.3 mg/L, respectively, which indicates that the mixture reduced the efficiency from 6% to 3.7%. Filters that contained a micelle-clay complex in addition to sand were utilized by Khamis et al. [23] to evaluate the efficacy of these filters in the purification of tertiary-treated wastewater using loose ultrafiltration membranes. The turbidity and TSS were eliminated, decreasing from initial values of 14 NTU and 6 mg/L, respectively. Subsequently, there was an overall decline in the removal efficiency [23]. The use of bentonite in reducing water turbidity has been quantified, with reductions of up to 80-90% observed in municipal and industrial wastewater.

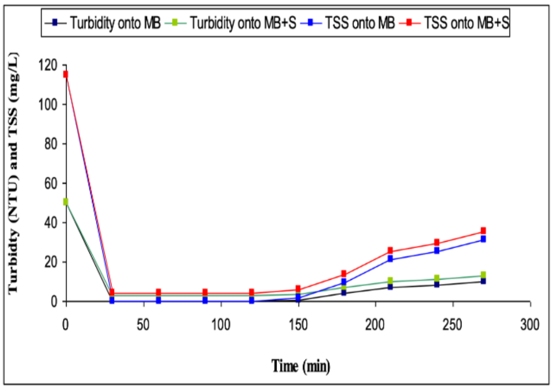

Figure 4. Variation of TSS and turbidity of different samples

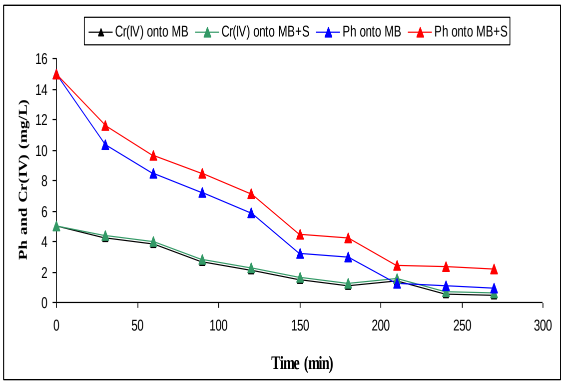

Figure 5. Variation of pH and Cr^{6+} in different samples collected from column filter

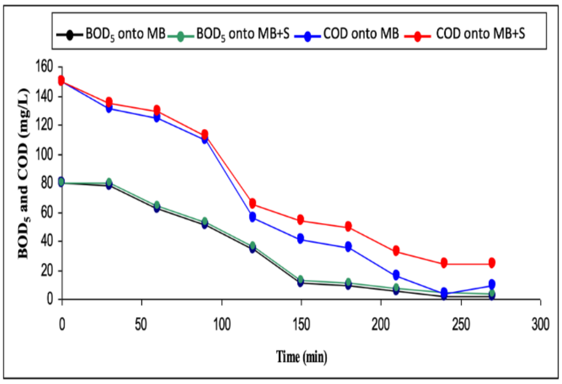

Figure 6. Analysis of the fluctuation of the COD and BOD_5 in various samples obtained from the column filter

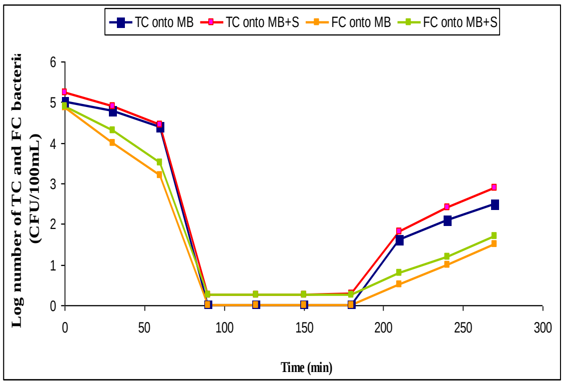

Figure 7. Variation of TC and FC bacteria in different samples collected from column filter

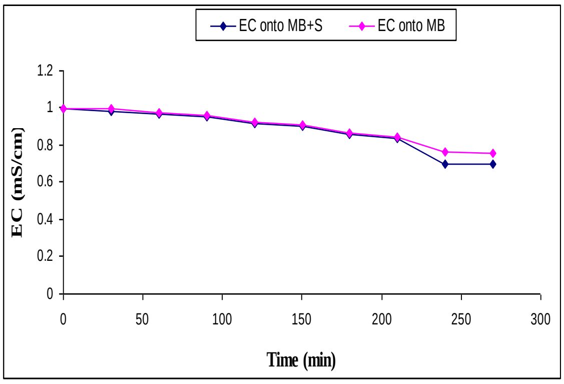

Figure 8. Variation of EC of different samples

Figure 5 shows the variation of phenol (pH) and chromium Cr^{6+} concentration from an initial value of about 15 and 5 mg/L, respectively, to final values of 0.95 and 0.475 mg/L where the removal efficiencies are 93.67 and 90.43%, respectively. This phenomenon is because, at a lower dose, metal ions compete for a limited number of adsorption sites. However, as the dose increases, the larger surface area provides more vacant sites, increasing the adsorption percentage [24]. In contrast, the removal efficiencies of the mixed media are 87.43 and 85.46%, respectively. In a batch system, Koyuncu [25] studied the removal capacity of natural bentonite towards Cr^{6+} chromium found in artificial wastewater. The results showed that 1.0 g of bentonite accomplished a 75% removal of Cr^{6+}. The adsorption percentage showed an upward trend when the adsorbent dose was increased [25]. The exceptional effectiveness of bentonite clay in removing pollutants from wastewater is attributed to its remarkable adsorption capabilities on particle surfaces. This is primarily due to silicon ions, which act as cations and are attracted to the anion particles, causing gradual flocculation [26].

Modifying bentonite surfaces is needed to enhance its adsorption capacity for specific contaminants, like heavy metals and organic pollutants. Techniques like acid activation or impregnation with other materials increase its effectiveness. The findings demonstrate the impact of filtering using the MB column on the measurements of BOD and COD (Figure 6). As the filtering process was ongoing, there was a significant decrease in both COD and BOD_5 readings. The BOD_5 reduced from 80 to 1.778 mg/L (97.78%) and COD from 150 to 9.375 mg/L (93.75%). It was determined that the more successful COD was removed by bentonite because the clay had a wide surface area, which allowed for the effective adsorption of organic materials. When bentonite is present, the elimination of COD is significantly improved [27]. While on the mixed media, the removal efficiency of BOD_5 and COD increased to 95.28 and 83.65 %, respectively. Bentonite has demonstrated a significant reduction in COD and BOD, often by more than 70%, indicating effective organic pollutant removal.

Aygun and Yilmaz [28] used RB. They treated it with ferric chloride to enhance the elimination of COD from wastewater samples obtained from the discharge point of a recycling facility in Türkiye. They found that using MB provided 84% of COD removal [28].

Figure 7 illustrates the significant decrease in the overall bacterial count, measured in colony-forming units (CFU) per mL after the MB column filtered the secondary effluent. No colonies were found in the samples after 90 to 180 min (i.e., 100 % removal efficiency for TC and FC); fewer colonies were detected afterward. MB+S reduced the total and fecal coliform to about 2600 and 2500, respectively. A study conducted by Napotnik et al. [29] examined the effectiveness of three bio-sand filters of varying sizes.

These included the Center for Affordable Water and Sanitation Technology v10 concrete filter, a 5-gallon bucket filter, and a 2-gallon bucket filter. The filters were tested with different depths of fine sand (10, 15, and 54 cm) and were evaluated for their ability to remove bacteria, protozoa, and viruses. The study also considered the impact of adding iron nails to the diffuser basin. The filters were tested over pause periods ranging from 1 to 72 hours.

Figure 8 shows the increase in the EC from 1000µS/cm (1mS/cm) to a final value of 700 µS/cm, where the removal efficiency is 30%, which is considered relatively high compared to high-cost activated carbon (46%) [30]. However, using MB+S reduced the maximum removal efficiency to 24%.

Moreover, judging by the data from Demirci et al. [31], using bentonite for wastewater treatment is efficient and economically justified.

Table 4 shows the difference between results obtained in the present study and those obtained in other studies using MB to remove several organic contaminants from contaminated water.

Table 4. Comparison of pollutant removal using different MB

	Type of modification	Contaminant Type	Removal %	References
Bentonite	Organic bentonite was synthesized by adsorbing the surfactant hexadecyltrimethylammonium (HDTMA)	Diclofenac (DCF) and cadmium (II)	Solution pH, ionic strength, and temperature affected OBHDTMA DCF sorption	[32]
Bentonite	Hexadecyl trimethyl ammonium (DK1)	Amoxicillin	Removal was 81.9% at 19 ppm and 87.5% at 2 ppm	[33]
Bentonite	the surfactant HDTMA	DCF sodium	The greatest OBHDTMA DCF sorption capacity was 388 mg/g	[34]
Bentonite	Trp-Na-bent and Fe-Na-bent were modified with L-Tryptophan and $FeCl_2$ $4H_2O$	Synthetic Estrogen	The greatest adsorption capacity was 4.20 mg/g	[35]
Bentonite	HTAB	Amoxicillin	93 %	[36]
Bentonite	Acid activation	Acid yell Acid blue Acid red	Acid yellow=71.1% Acid blue=98.4% Acid red=85.25%	[37]
Bentonite	Amoxicillin (AMX)	Cationic surfactants (CTAB &TMAB) and thermal activation	NB-CTAB=96% NB-TMAB=70% CB=94%	[38]
Bentonite	Acid activation	TSS, turbidity, pH, chromium Cr^{6+}, COD, BOD_5, TC, FC, and EC	The maximum removal efficiency for TSS, turbidity, pH, Cr^{6+}, COD, BOD_5, TC, FC, and EC onto MB are 100%, 10%, 93.67%, 90.43%, 93.75%, 97.78%, 100%, 100%, and 30%, respectively	Present work

Based on the analysis above, it was found that bentonite, a readily available natural clay, may be changed easily and cheaply to remove organic and inorganic pollutants. This study modifies RB with acid and heat. MB's porosity has improved, providing more adsorption sites and better surface characteristics. Fixed bed columns loaded with MB and MB+S were utilized to study MB secondary wastewater treatment. At 1 mL/min (3.1 cm/h), MB and MB+S mixtures were filtered. TSS, turbidity, phenol (pH), chromium Cr^{6+}, COD, BOD_5, TC, FC, and EC have maximal removal efficiencies of 100, 100, 93.67, 90.43, 93.75, 97.78, 100, 100, and 30% on MB. These characteristics are slightly less efficient in changed bentonite and sand mixes.

Our results agreed with Abdullah et al. [27] which indicated that textile effluents have been regarded as a water contamination source. Effective procedures were used to remove dyes and colorants from textile effluents. This study used modified bentonite clay (MBC) to remove textile dye reactive red 223 (RR 223). Acid treatment MBC. Under optimal settings, MBC adsorption characteristics towards RR 223 were examined using the batch method at temperatures 303-318 ±2 K. Adsorption equilibrium data were fitted in Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models, and constant values were calculated using standard graphical methods. Langmuir model fits best based on r^2 values. RL and Es adsorption feasibility were also determined. Adsorbent pHPZC was estimated by pH drift. Free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were determined for the system. Dye removal kinetics showed a pseudo-second-order rate constant. SEM imaging revealed adsorbent surface morphology. Fourier Transform Infrared Spectroscopy determined the adsorbent-adsorbate interaction forces. Desorption trials also recovered dye and regenerated adsorbent. MBC has 95.15% and 78% sorption and desorption capability.

Our results agreed with Mokokwe and Letshwenyo [38] in which stated that the adsorption of copper, iron, and nickel ions from an aqueous solution utilizing Makoro granite clay brick waste was examined through batch and fixed-bed column methods. The maximal adsorption capacities for iron, copper, and nickel are 7.60, 6.70, and 6.20 mg g^{-1} media, respectively, with an optimal duration of 60 minutes. The greatest adsorption capacities at an adsorbent dosage of 5 g L^{-1} were 10.0, 7.60, and 7.20 mg L^{-1} for iron, copper, and nickel ions, respectively. The adsorption capacities from the fixed-bed column reactor were 2.23, 2.22, and 0.74 mg g^{-1} medium. The thermodynamic parameters of enthalpy change (ΔH) were 5.21, 9.32, and 5.22 kJ mol^{-1} for copper, iron, and nickel ions, respectively, while the corresponding entropy changes (ΔS) were -0.04, -0.05, and -0.03 kJ mol^{-1} K^{-1}, respectively, indicating that the process is non-spontaneous and exothermic. The Thomas and Yoon-Nelson models produced comparable low coefficients of determination (R^2) of 0.06 and 0.07 for copper and iron ions, respectively.

Our results agreed with replacing aluminium salts as adsorbents and coagulants, bentonite and its combinations were tested for wastewater treatment via adsorption, ion exchange, and coagulation-flocculation. The optimal pH and coagulant dosage for bentonite, bentonite-zeolite, bentonite-alum, and bentonite-limestone were found. Bentonite was discovered to be a good coagulant that can absorb 90.5% COD. Bentonite-zeolite mixture removed iron (98%) and turbidity (95%) from others at the optimal dosage. Bentonite-limestone mixture had lowest zeta potential and sludge volume index. The zeta potential of treated and combined bentonite was -26.7 mV for bentonite-alum, -20.7 for RB, -19.9 for bentonite-zeolite, and -17.6 for bentonite-limestone, indicating coagulation and adsorption. However, contact time showed that mixture bentonite absorbed more than RB.

4. CONCLUSION

Therefore, acid-thermal modification of Iraqi bentonite may be feasible to improve the surface area and treatment capabilities. Conducting a broader experiment that includes using the MB and other components in sewage treatment systems will help determine the most cost-effective combination to improve the quality of water used for irrigation. The surface area of MB was increased from 35.65 to 102.6 m^2g^{-1} after the acid-thermal activation. The acid-thermal activation of RB results in a reduction in pore size from 40.87 Å to 48.32 Å. This decrease may be due to substituting exchangeable cations (K^+, Ca^{2+}, Na^+) with smaller hydrogen ions. FTIR analyses confirmed RB modification with acid-thermal activation. The variations in the intensities of functional groups serve as indicators of the alterations that occur throughout the activation process. The maximum removal efficiency for TSS, turbidity, pH, Cr^{6+}, COD, BOD_5, TC, FC, and EC onto MB are 100%, 10%, 93.67%, 90.43%, 93.75%, 97.78%, 100%, 100%, and 30%, respectively. The efficiency of these parameters was slightly lower when using MB+S.

It is advisable to conduct additional experiments, including the utilization of industrial wastewater, the competition of anions, and further characterization and modification of the media. Moreover, Bentonite is a natural material that poses no adverse effects when introduced to water. Numerous treatment facilities in the region do not utilize alum for low-turbid water; rather, water is directly transferred from sedimentation basins to filters without further treatment. This procedure exerts pressure on the filters, which are the sole components that diminish turbidity, hence requiring frequent cleanings. More investigation regarding this procedure is needed.

In contrast to chemical-based methods, it offers an environmentally acceptable, less costly, safe, effective, and economically viable technology for wastewater treatment. The recyclability of wasted natural and Na-bentonite indicated that the pollutant removal percentages were adequately high. Additional research is required to confirm the efficacy of the novel Na-bentonite as an adsorbent for the removal of methyl violet dye and to assess its capacity to absorb pollutants concurrently. In addition, the utilization of Na-bentonite in wastewater treatment before discharge is recommended and it was suggested to increase the production of this material due to its great efficacy in the treatment process.

AUTHOR CONTRIBUTIONS

Each author made contributions to the conceptualization and design of the study. Ahmed Hassan Ali, Younis Swadi Tlaiaa, and Zainab Abdul Razaq conducted material preparation, data collecting, and analysis. Ahmed Hassan Ali authored the initial draft of the manuscript, and other authors provided feedback on earlier iterations. All writers reviewed and approved the final manuscript.

ACKNOWLEDGEMENT

The authors of this study would like to express their profound gratitude to Mustansiriyah University (Iraq/Baghdad) (www.uomustansiriyah.edu.iq)/ College of Engineering/Environmental Engineering Department for their invaluable cooperation in completing this study.

CONFLICT OF INTEREST

This work does not include any instances of conflict of interest.

REFERENCES

[1] Silva, J.A. (2023). Wastewater treatment and reuse for sustainable water resources management: A systematic literature review. Sustainability, 15(14): 10940. https://doi.org/10.3390/su151410940

[2] Garcia, X., Pargament, D. (2015). Reusing wastewater to cope with water scarcity: Economic, social and environmental considerations for decision-making. Resources, Conservation and Recycling, 101(1): 154-166. https://doi.org/10.1016/j.resconrec.2015.05.015

[3] Anekwe, I.M.S., Adedeji, J., Akpasi, S.O., Kiambi, S.L. (2022). Available technologies for wastewater treatment. In Wastewater Treatment. IntechOpen, London.

[4] Olar, R., Badea, M., Chifiriuc, M.C. (2022). Metal complexes—A promising approach to target biofilm associated infections. Molecules, 27(3): 758. https://doi.org/10.3390/molecules27030758

[5] Senanu, L.D., Kranjac-Berisavljevic, G., Cobbina, S.J. (2023). The use of local materials to remove heavy metals for household-scale drinking water treatment: A review. Environmental Technology & Innovation, 29(1): 103005. https://doi.org/10.1016/j.eti.2023.103005

[6] Xanthopoulou, M., Katsoyiannis, I.A. (2023). Enhanced adsorption of chromate and arsenate ions from contaminated water with emphasis on polyethylenimine modified materials: A review. Separations, 10(8): 441. https://doi.org/10.3390/separations10080441

[7] Mohammed, I.Q. (2019). Bentonite and smectite-rich shale deposits of Iraq. Iraqi Bulletin of Geology and Mining, 1(8): 175-202.

[8] Alexander, J.A., Ahmad Zaini, M.A., Surajudeen, A., Aliyu, E.N.U., Omeiza, A.U. (2019). Surface modification of low-cost bentonite adsorbents—A review. Particulate Science and Technology, 37(5): 538-549. https://doi.org/10.1080/02726351.2018.1438548

[9] Toor, M.K. (2011), Enhancing adsorption capacity of bentonite for dye removal: Physiochemical modification and characterization. Ph.D. dissertation. School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia.

[10] Ayoob, H.W., Ridha, A.M., Jassim, A.A.A., Taieh, N.K., Homod, R.Z., Mohammed, H.I. (2024). Enhanced adsorption of phenol using graphene oxide-bentonite nanocomposites: Synthesis, characterisation, and optimisation. Journal of Molecular Liquids, 395(1): 123833. https://doi.org/10.1016/j.molliq.2023.123833

[11] Rice, E. W., Bridgewater, L., American Public Health Association (Eds.). (2012). Standard methods for the examination of water and wastewater (Vol. 10). American Public Health Association, Washington, DC.

[12] Taher, T., Rohendi, D., Mohadi, R., Lesbani, A. (2018). Thermal and acid activation (TAA) of bentonite as adsorbent for removal of methylene blue: A kinetics and thermodynamic study. Chiang Mai Journal of Science, 45(4): 1770-1781.

[13] Korichi, S., Elias, A., Mefti, A. (2009). Characterization of smectite after acid activation with microwave irradiation. Applied Clay Science, 42(3): 432-438. https://doi.org/10.1016/j.clay.2008.04.014

[14] Özcan, A.S., Özcan, A. (2004). Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. Journal of Colloid and Interface Science, 276(1): 39-46. https://doi.org/10.1016/j.jcis.2004.03.043

[15] Alabarse, F.G., Conceição, R.V., Balzaretti, N.M., Schenato, F., Xavier, A.M. (2011). In-situ FTIR analyses of bentonite under high-pressure. Applied Clay Science, 51(1): 202-208. https://doi.org/10.1016/j.clay.2010.11.017

[16] Mahramanlioglu, M., Kizilcikli, I., Bicer, I.O. (2002). Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth. Journal of Fluorine Chemistry, 115(1): 41-47. https://doi.org/10.1016/S0022-1139(02)00003-9

[17] D'Amico, D.A., Ollier, R.P., Alvarez, V.A., Schroeder, W. F., Cyras, V.P. (2014). Modification of bentonite by combination of reactions of acid-activation, silylation and ionic exchange. Applied Clay Science, 99(1): 254-260. https://doi.org/10.1016/j.clay.2014.07.002

[18] Adane, T., Hailegiorgis, S.M., Alemayehu, E. (2022). Acid-activated bentonite blended with sugarcane bagasse ash as low-cost adsorbents for removal of reactive red 198 dyes. Water Reuse, 12(2): 175-190. https://doi.org/10.2166/wrd.2022.056

[19] Al-Khatib, L., Fraige, F., Al-Hwaiti, M., Al-Khashman, O. (2012). Adsorption from aqueous solution onto natural and acid activated bentonite. American Journal of Environmental Sciences, 8(5): 510-522. https://doi.org/10.3844/ajessp.2012.510.522

[20] Fernandes, J.V., Rodrigues, A.M., Menezes, R.R., Neves, G.D.A. (2020). Adsorption of anionic dye on the acid-functionalized bentonite. Materials, 13(16): 3600. https://doi.org/10.3390/ma13163600

[21] Nasir, M.J. (2010). Competitive adsorption of multi-organic compounds onto organoclay from simulated wastewater. Ph.D. dissertation. Environmental Engineering Department, University of Baghdad, Baghdad, Iraq.

[22] Khamis, M., Karaman, R., Qurie, M., Abbadi, J., Nusseibeh, S., Manassra, A., Nir, S. (2012). Performance of micelle-clay filters for removing pollutants and bacteria from tertiary treated wastewater. Journal of Environmental Science and Engineering A, 1(1): 160-168.

[23] Tito, G.A., Chaves, L.H.G., Guerra, H.O.C., and Soares, F.A.L. (2011). Use of bentonite in the remediation of zinc-contaminated soils: Effect on bean production. Revista Brasileira de Engenharia Agrícola e Ambiental, 15(9): 917-923. https://doi.org/10.1590/S1415-43662011000900007

[24] Koyuncu, M. (2012). Adsorption of Cr (VI) from textile waste water by using natural bentonite. Institute of Integrative Omics and Applied Biotechnology Journal,

3(3): 1-4.

[25] Kawamura, S. (1991). Effectiveness of natural polyelectrolytes in water treatment. Journal AWWA, 83(10): 88-91. https://doi.org/10.1002/j.1551-8833.1991.tb07236.x

[26] Abdullah, R., Abustan, I., and Ibrahim, A.N.M. (2013). Wastewater treatment using bentonite, the combinations of bentonite-zeolite, bentonite-alum, and bentonite-limestone as adsorbent and coagulant. International Journal of Environmental Sciences, 4(3): 379-391.

[27] Aygun, A., Yilmaz, T. (2010). Improvement of coagulation-flocculation process for treatment of detergent wastewaters using coagulant aids. International Journal, 1(2): 97-101.

[28] Napotnik, J.A., Baker, D., Jellison, K.L. (2021). Influence of sand depth and pause period on microbial removal in traditional and modified biosand filters. Water Research, 189(1): 116577. https://doi.org/10.1016/j.watres.2020.116577

[29] Mortula, M., Shabani, S. (2012). Removal of TDS and BOD from synthetic industrial wastewater via adsorption. International Proceedings of Chemical, Biological and Environmental Engineering, 14: 166-170.

[30] Demırcı, Ş., ErdoĞan, B., Özcımder, R. (1998). Wastewater treatment at the petroleum refinery, Kirikkale, Turkey using some coagulants and Turkish clays as coagulant aids. Water Research, 32(11): 3495-3499. https://doi.org/10.1016/S0043-1354(98)00111-0

[31] Martinez-Costa, J.I., Leyva-Ramos, R., Padilla-Ortega, E. (2018). Sorption of diclofenac from aqueous solution on an organobentonite and adsorption of cadmium on organobentonite saturated with diclofenac. Clays and Clay Minerals, 66(6): 515-528. https://doi.org/10.1346/CCMN.2018.064119

[32] Zha, S.X., Zhou, Y., Jin, X., Chen, Z. (2013). The removal of amoxicillin from wastewater using organobentonite. Journal of Environmental Management, 129(1): 569-576. https://doi.org/10.1016/j.jenvman.2013.08.032

[33] Han, H., Rafiq, M.K., Zhou, T., Xu, R., Mašek, O., Li, X. (2019). A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. Journal of Hazardous Materials, 369(1): 780-796. https://doi.org/10.1016/j.jhazmat.2019.02.003

[34] Gallouze, H., Akretche, D.E., Daniel, C., Coelhoso, I., Crespo, J.G. (2021). Removal of synthetic estrogen from water by adsorption on modified bentonites. Environmental Engineering Science, 38(1): 4-14. https://doi.org/10.1089/ees.2020.0048

[35] Mohammed, A.K., Saadoon, S.M., Abd Ali, Z.T., Rashid, I. M., Hussin Al Sbani, N. (2024). Removal of amoxicillin from contaminated water using modified bentonite as a reactive material. Heliyon, 10(3): e24916. https://doi.org/10.1016/j.heliyon.2024.e24916

[36] Espantaleón, A.G., Nieto, J.A., Fernández, M., Marsal, A. (2003). Use of activated clays in the removal of dyes and surfactants from tannery waste waters. Applied Clay Science, 24(1): 105-110. https://doi.org/10.1016/S0169-1317(03)00153-4

[37] Naji, A.M., Abd Ali, Z.T. (2023). Evaluation of modified bentonite using chemical and physical methods for removal of amoxicillin from aqueous solutions: Batch and continuous study. Desalination and Water Treatment, 294(1): 185-201.

[38] Mokokwe, G., Letshwenyo, M.W. (2022). Investigation of clay brick waste for the removal of copper, nickel and iron from aqueous solution: Batch and fixed – bed column studies. Heliyon, 8(7): e09963. https://doi.org/10.1016/j.heliyon.2022.e09963