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Removal of Heavy Metals from Car Wash Wastewater by Using Bentonite Clay

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ABSTRACT

The contamination of water by heavy metals poses significant environmental risks, impacting ecosystems and human well-being. In response, this study investigates methods for eliminating heavy metals from car wash wastewater, focusing on adsorption techniques using the flocculation test. Recent advancements highlight the effectiveness and eco-friendly attributes of natural bentonite and modified bentonite. The primary goal is to assess the capacity of these clays in adsorbing heavy metals without the need for additional chemicals. Our findings demonstrate that modified bentonite holds promise in removing copper and zinc from car wash wastewater, achieving reductions of up to 90%, while iron reduction was around 50% with modified bentonite-zeolite. For iron reduction, raw bentonite alone proved effective, achieving 70% to 80% removal without the combination with zeolite. Additionally, we evaluate the treated water's suitability for recycling and reuse. While iron, copper, zinc, and pH levels meet recommended standards, other factors like turbidity, color, temperature, and total dissolved solids play critical roles in determining water quality for car wash applications. This study shows that turbidity, color, and total dissolved solids significantly increased due to the natural color of bentonite clay, with no chemical additives used to neutralize the color. Despite these increases, all parameters, except for color, fall within the acceptable range as per the National Water Quality Standard and the Recommended Raw Water Quality Standard. To further enhance the effectiveness of bentonite for heavy metal adsorption and gain deeper insights into its adsorption mechanisms, future research should utilize advanced characterization techniques, such as X-ray diffraction and scanning electron microscopy, to better understand the surface properties and structural changes of bentonite before and after modification, as well as following heavy metal adsorption.

Keywords: Bentonite clay; zeolite; car wash wastewater; heavy metals; iron; copper; zinc

INTRODUCTION

Water quality is under threat due to industrialization and urbanization, with car wash wastewater being a significant pollution source (Hashim et al. 2016). Discharging car wash wastewater into water systems poses significant health risks to humans and other organisms, presenting serious concerns (Tajuddin et al. 2020). Heavy metals in this wastewater, like iron, copper, and zinc pose environmental and health risks (Rosa et al. 2011). From study by Aljlil et al. 2014, copper was considered hazardous if their concentration exceeds the permissible limits both in water and for plantation. Conventional treatment methods struggle to remove these toxic metals, necessitating research for effective pollution reduction and environmental protection.

Rapid growth in car wash stations leads to environmental concerns, with heavy metals like iron, zinc, and copper in wastewater (Prabhu et al. 2018). Current chemical-based methods are expensive and introduce secondary pollutants (Ranga 2018). There is a lack of optimization in determining the ideal dosage and contact time for effective heavy metal removal from car wash wastewater, despite understanding the advantageous role of bentonite clay as an adsorption agent. Addressing this gap can enhance treatment effectiveness and resource conservation. Furthermore, as car wash water consumption rises (Edward 2002), evaluating the feasibility of recycling and reusing treated water becomes crucial for sustainable water management and cost savings.

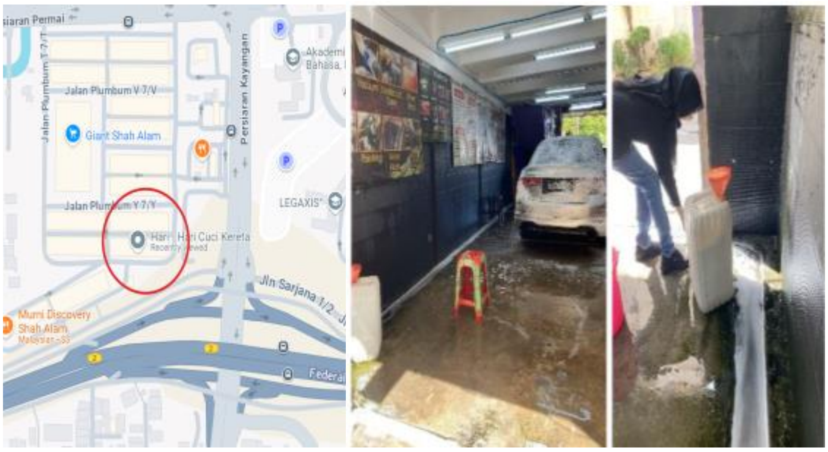
Car parts, such as engine blocks and brake drums, can release heavy metals like iron, copper, and zinc, exceeding permissible limits (Hashim et al. 2016). Sediments, including these metals, from car washing activities contributed to environmental pollution when untreated, posing risks to ecosystems and human health. It has been identified that various heavy metals in car wash wastewater, impacting humans, animals, plants, and aquatic life. Notably, iron, copper, and zinc are of concern due to their prevalence and potential environmental consequences (Ghaly et al. 2021). Iron oxide particles, zinc from galvanized coatings, and copper from brake pads and wiring are major contributors. The car wash processes release heavy metals, including cadmium, nickel, lead, iron, copper, and zinc, originating from brake parts and accumulated road dust. These metals pose threats to water quality and ecosystem health (Singh et al. 2023). However, determining heavy metal presence is challenging and costly (Talebzadeh et al. 2021). The adsorption process stands out for its cost-effectiveness and simplicity, thus various adsorbents, including silica gel, iron oxide, limestone, bauxite, activated carbon, commercial zeolites, and bentonite, has been employed (Chakraborty et al. 2022).

This study aims to evaluate the suitability of bentonite clay and bentonite-zeolite as eco-friendly options for eliminating heavy metals especially in iron, copper and zinc, and secondly, to optimize the bentonite clay dosage in the heavy metal removal process. Additionally, it seeks to investigate the possibility of reusing treated car wash wastewater, thus exploring recycling prospects in this application. As in this study, the experiment will examine how the bentonite clay and bentonite- zeolite will work without using any chemical since a lot of previous research used chemical in the adsorbent. One of the studies is from Abdullah et al. 2013, which is they use a chemical of NaCl in the zeolite and NaOH and H_2SO_4 solutions in the wastewater to adjust the pH of the wastewater.

METHODOLOGY

STUDY LOCATION AND SAMPLE COLLECTION

Wastewater samples were sourced from "Hari Hari Cuci Kereta" in Block E, Jalan Plumbum 7/Aa, Seksyen 7, 40000 Shah Alam, Selangor, Malaysia to represent car wash wastewater, as shown in Figure 1. A total of 12,000 ml was collected to ensure adequacy for flocculation experiments. Strict adherence to proper sampling techniques and sterile containers was maintained to prevent contamination. This step was pivotal in evaluating wastewater composition, pollution levels, and the effectiveness of heavy metal removal methods.



(a) (b) (c)

FIGURE 1. (a) Car wash of "Hari Hari Cuci Kereta" located in Shah Alam, Selangor; (b) Car wash activity; (c) Water sample collected from "Hari Hari Cuci Kereta".

BENTONITE CLAY AND ZEOLITE

The necessary adsorbents, bentonite clay and zeolite, were obtained through online purchasing. Bentonite clay was acquired from Multifilla Art Craft Materials (Selangor, Malaysia). On the other hand, zeolite was sourced from Agro Official Store (Penang, Malaysia). Both bentonite clay and zeolite showed in Figure 2(a) and (b) are recognized for their adsorption properties and are anticipated to play a crucial role in the removal of contaminants from the car wash wastewater (Chakraborty et al. 2022, Al-Jlil, 2010; Erdem et al. 2004).

(a) (b)

FIGURE 2. (a) Bentonite clay (Multifilla Art Craft Materials, Selangor); (b) Zeolite (Agro Official Store, Pulau Pinang)

FLOCCULATION EXPERIMENT

In this experiment, a conventional Flocculator JLT-6 Series (Velp Scientifica Srl, Italy) with six beakers and steel paddles was used. Each beaker contained 1000 ml of car wash wastewater. Sodium bentonite and zeolite with a particle size of 63 µm were selected as adsorbents in varying amounts (0 g/L, 2 g/L, 4 g/L, 6 g/L, 8 g/L, and 10 g/L). Rapid mixing at 140 rpm for 3 minutes and slow mixing at 70rpm for 5 minutes was performed, followed by a 20-minute sedimentation period. The experimental setup of the flocculation experiment is shown in FIGURE 3. Data collected were aligned with National Water Quality Standards for Malaysia (DOE 2020), to assess heavy metals like iron, copper, zinc as well as physical parameters such as turbidity, pH, total dissolved solids, color, and temperature for car wash water suitability and conservation.

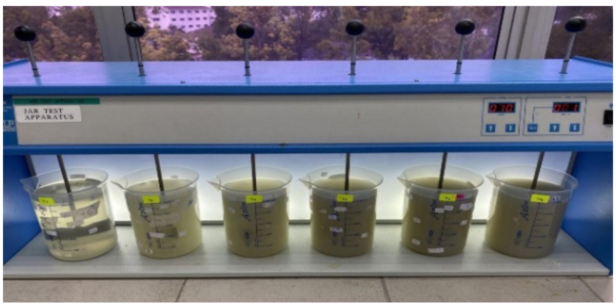


FIGURE 3. Flocculation experiments performed in Flocculator JLT-6 Series (Velp Scientifica Srl, Italy)

DETERMINATION OF HEAVY METAL IN WATER SAMPLE

In the course of conducting an experiment aimed at analyzing heavy metals, specifically Iron, Copper, and Zinc. The procedure employed in this study was derived from the Hach Water Analysis Handbook, (Hach, 2002). The color changes for each heavy metal determination were measured using the DR 2800 Spectrophotometer (Hach, Australia). For each heavy metal determination, a blank sample was prepared using treated water from the flocculation experiment, consisting of 10 ml of water in a sample square cell.

To examine the Iron (Fe) in water sample, the spectrophotometer was set to examine iron using the Fe code test: 265, ('FerroVer'). Reagent FerroVer Iron Reagent Powder Pillow (Hach, Australia) was added to each sample, followed by swirling and a 3-minute rest to induce an orange color in the presence of iron. The determination of Copper (Cu) was conducted based on Hach Method (Hach, Australia), whereby the process began with selecting option 135 for Copper, Bicin, within the 'Stored Program.' All six water samples were prepared in separate 10 ml sample square cells and treated with CuVer 1 Copper Powder Pillow (Hach, Australia) reagent. After swirling and allowing the samples to rest for 2 minutes, copper presence was indicated by a color change. The Zinc (Zn) test was performed for each of the six samples (20 ml each), whereby the sample was placed in separate mixing cylinders, and ZincoVer 5 Zinc Reagent Powder Pillow (Hach, Australia) was added. Proper mixing was essential, and an orange color indicated zinc presence, while brown or blue color may have required dilution and retesting, as mentioned in Hach Water Analysis Handbook, (Hach 2002). A blank sample was created by transferring 10 ml of solution into a square sample cell and adding 0.5 ml of cyclohexanone to the remaining solution. After shaking and resting, the sample solution was placed in a square cell and the spectrophotometer obtained the zinc concentration data by inserting the water sample in it.

DETERMINATION OF TURBIDITY IN WATER SAMPLE

Turbidity, which indicates water quality, was assessed using a Turbidimeter. Six turbidity bottles were prepared, each labeled for specific dosages. Wastewater from the flocculation test (10 ml each) was added to the bottles corresponding to dosage labels (0 g/L, 2 g/L, 4 g/L, 6 g/L, 8 g/L, and 10 g/L of the adsorbent). By referring to the guidelines established by the Environmental Protection Agency (EPA) Method (APHA 2005), the turbidity data were obtained after inserting the water sample in the Turbidimeter read in triplicates.

DETERMINATION OF PH VALUE AND TEMPERATURE IN WASTEWATER SAMPLE

The pH value is a critical factor in wastewater treatability. Using a pH meter (Mettler Toledo, USA), the pH for each sample was assessed. Since pH directly impacts car wash wastewater quality, especially concerning vehicle surfaces (Sarmadi et al. 2021), thus the determination of pH value and temperature was carried out in strict accordance with protocols by the Environmental Protection Agency (EPA) Method (APHA 2005). The pH electrode was inserted into the wastewater sample, providing pH and temperature data on the screen, which were duly recorded.

DETERMINATION OF TOTAL DISSOLVE SOLIDS IN WATER SAMPLE

Total Dissolved Solids (TDS), reflecting inorganic salts and dissolved substances in water, are vital for car wash quality. A Conductivity Meter (Model Mettler Toledo, USA) was used for TDS measurement. The instrument was activated, and 'TDS' mode was selected, and the electrode was placed in the water sample. The TDS data were shown on the screen, ensuring accurate car wash water quality. Total Dissolved Solids guidelines were adhered to according to the Environmental Protection Agency (EPA) Method (APHA 2005).

DETERMINATION OF COLOR IN WATER SAMPLE

Color analysis was essential for assessing water quality, particularly relevant for car wash wastewater. For this color analysis, the procedure was derived from the Environmental Protection Agency (EPA) Method (APHA, 2005). Triplicate reading of the samples were done using the DR 2800 Spectrophotometer. The spectrophotometer was activated and set to '125 color 465 nm'. Subsequently, the blank sample was replaced with the control sample, and the instrument provided accurate color data for the water sample, aiding in water quality assessment for car wash purposes.

RESULTS AND DISCUSSION

REDUCTION IN HEAVY METALS CONCENTRATION

DETERMINATION OF IRON (FE) IN WATER SAMPLE

Based on previous research findings, it has been observed that the use of bentonite clay leads to a reduction in heavy metal concentrations, specifically for iron, copper, and zinc (Baddor et al. 2014; Hussain et al. 2020).

While previous studies suggested that the combination of bentonite-zeolite exhibited superior efficacy in heavy metal removal (Abdullah et al. 2013), our experimental findings unveiled a nuanced outcome. Contrary to the prior research consensus, this study observed that natural bentonite, when tested individually, displayed heightened efficiency in removing iron, surpassing the combination of bentonite-zeolite as shown in Figure 4. As this study showed that natural bentonite showed more effectiveness in removing iron than the combination of bentonite-zeolite, this has been proven by Nurul et al. 2021. However, in the case of copper and zinc (Figure 5 and 6), the combination of bentonite-zeolite exhibited notably higher efficacy compared to using natural bentonite alone. These divergent outcomes across various metals indicate the complexity of interactions between adsorbents and specific heavy metals, emphasizing the need for nuanced analysis and consideration of individual metal adsorption characteristics.

The study reveals distinct optimal dosages for both bentonite and bentonite-zeolite in removing heavy metals (Figure 4). For natural bentonite, the identified optimum dosage stands at 10 g/L with 87.27% removal. In contrast, bentonite-zeolite exhibits its peak performance in iron removal at 2 g/L with 75.45%. As supported by the study of Nurul et al. 2021, it also shows the highest removal efficiency with 89% by using natural bentonite only. This disparity in optimum dosages underscores the unique characteristics and effectiveness of each adsorbent in the removal process. From the results, it has been proven that bentonite-zeolite require less than 2 g/L of dosage to make it effectively remove iron concentration, just as stated in the study by Abdullah et al. 2013, with a ratio of bentonite-zeolite being 50:50.

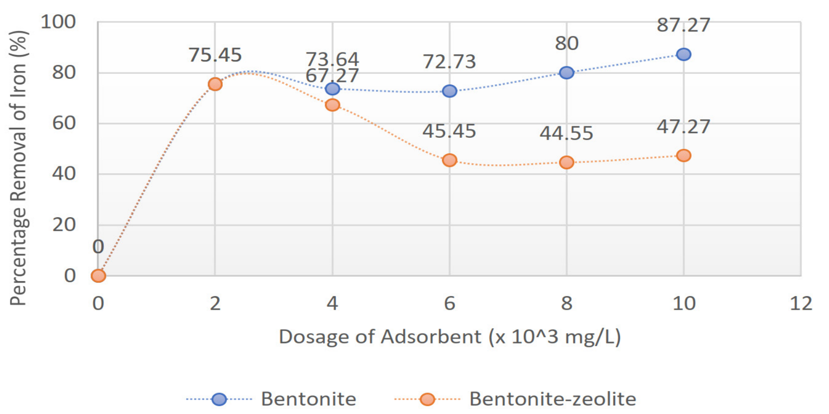


FIGURE 4. Percentage of iron removal in treated car wash wastewater at various amount of adsorbent's dosage

DETERMINATION OF COPPER (CU) IN WATER SAMPLE

Given the previous research findings showing a decrease in heavy metal concentrations with the use of bentonite clay and the suggestion that a combination of bentonite-zeolite would be more effective in removing heavy metals compared to raw bentonite (Abdullah et al. 2013; Khalil et al. 2021), it is essential to determine and compare the outcomes of copper concentration when employing bentonite-zeolite in contrast to using raw bentonite.

In analyzing the removal efficiency of copper using bentonite and bentonite-zeolite combinations at various dosages (in g/L), it was observed that the efficiency fluctuates across different dosage levels (Figure 5). At lower dosages (2-4 g/L), both bentonite and bentonite-zeolite present relatively high removal rates for copper, with bentonite reaching approximately 90.91% at 2 g/L and both adsorbents achieving promising removal rates. As supported by the study of Khalil et al. 2021, zeolite can reduce the concentration of copper by more than 90%. However, at higher dosages (6-10 g/L), there was a notable decrease in removal efficiency, particularly for bentonite, dropping to 34.09% at 6 g/L and fluctuating around the 90-100% range for bentonite-zeolite. These results also align with other studies reporting that the addition of zeolite or clay minerals such as bentonite clay can be potential materials for polluted wastewater treatment (Nguyen et al. 2022; Song et al. 2019).

The fluctuations in removal efficiency between bentonite and bentonite-zeolite for copper could be due to their physical properties, such as particle size and pore structure, as well as process factors like temperature, initial concentration, and the amount of adsorbent used (Ahmaruzzaman, 2011; Karimi et al. 2019).

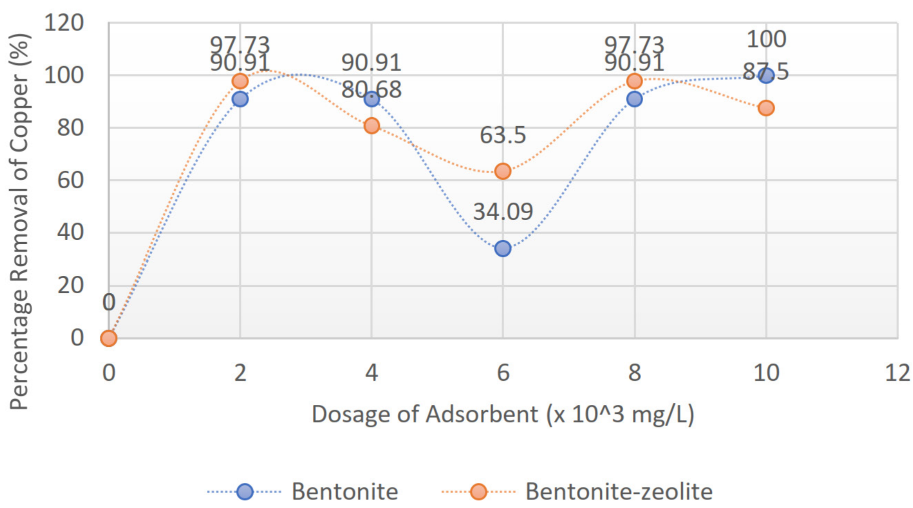


FIGURE 5. Percentage removal of copper in car wash wastewater treatment based on amount of adsorbent's dosage

DETERMINATION OF ZINC (ZN) IN WATER SAMPLE

Based on previous research, there is currently a lack of data regarding the specific impact of bentonite-zeolite on zinc concentration. In light of this, it is necessary to draw conclusions regarding the results on zinc concentration when utilizing bentonite-zeolite compared to raw bentonite. However, for raw bentonite, there is a study that shows a significant impact on reducing zinc concentration (Kumar Dehariya et al. 2018).

From our study, the result for reducing the concentration of zinc in car wash wastewater through adsorption treatment using bentonite clay and bentonite-zeolite was an increase in effectiveness with higher dosages of the adsorbents. As the amount of bentonite clay or bentonite-zeolite used in the treatment process increased, there was a corresponding increase in the reduction of zinc concentration in the wastewater, as shown in Figure 6. It was shown that by using bentonite-zeolite, there was slightly less reduction in concentration in zinc compared to raw bentonite. As shown in Figure 6, the optimum dosage for both adsorbents can be taken with 4 g/L, with 86.21% removal by using raw bentonite and 85.45% removal by using bentonite-zeolite. As reported by other studies, bentonite clay shows effective adsorption in removing zinc (Araujo et al. 2013; Chai et al. 2017). A similar situation was observed in previous works of the authors on the deposition of heavy metals and used a method called atomic absorption to see how well a natural substance called clinoptilolite (a zeolite) could soak up copper, zinc, and nickel from water, and the results discovered it could absorb a lot more of these heavy metals (Myakush et al. 2020).

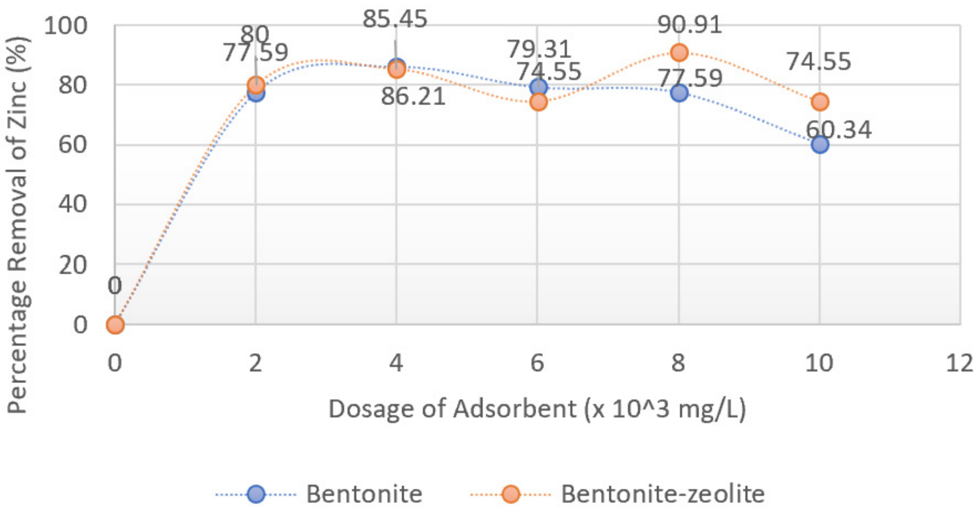


FIGURE 6. Percentage removal of zinc in car wash wastewater treatment based on amount of adsorbent's dosage

DETERMINATION OF WATER QUALITY PARAMETER (TURBIDITY, PH, TEMPERATURE, TOTAL DISSOLVE SOLID, COLOR)

In the process of treating car wash wastewater through adsorption using bentonite and bentonite-zeolite, the objective was to achieve the best possible outcome. The results were compared against the National Water Quality Standard for Malaysia, as well as the Recommended Raw Water Quality Standard. The specific parameters that were focused on were turbidity (the measure of water clarity), color, pH level (acidity or alkalinity), temperature, and total dissolved solids (TDS). By evaluating these parameters, it could be determined whether the treated wastewater met the required standards for water quality in Malaysia and adhered to the recommended standards for raw water. As observed from the reduction of heavy metals above (Figure 3, 4 and 5), it was found that the optimum dosage for both adsorbents could be taken as 2 g/L, and this study could be supported by the study by Abdullah et al. 2013, which showed that the researcher also used 2 g of bentonite clay as an adsorbent. From here, a 2 g/L dosage of adsorbent was taken to be examined the water quality parameters as shown in Table 1.

TABLE 1. Comparison between the obtain Result with

National Water Quality Standard for Malaysia and Recommended Raw Water Quality Standard

Parameter	Unit	Bentonite	Bentonite-Zeolite	National Water Quality Standard (Malaysia) Class IV-irrigation (Source: DOE, 2020b)	Recommended Raw Water Quality Standard (Source: National Standard for Drinking Water Quality, 2nd Version, 2004)
Turbidity	NTU	66.4	54.1	-	1000
Color	Pt/Co	561	586	-	300 (TCU)
pH value		6.37	6.65	5.0-9.0	5.5-9.0
Temperature	˚C	23.3	23.1	-	-
Total dissolve solid (TDS)	mg/l	80.5	82.05	4000	1500

ENHANCED REUSABILITY OF CAR WASH WASTEWATER

Based on the data collected for turbidity, color, pH, temperature, and total dissolved solids (TDS) from the treated car wash wastewater using adsorption by bentonite and bentonite-zeolite, a conclusion can be drawn regarding its suitability for recycling and reuse in car wash activities.

The turbidity parameter indicates the clarity of the water, and it was shown that the treated water meets the National Water Quality Standard for Malaysia and the Recommended Raw Water Quality Standard, suggesting that the water is clear enough for reuse in car wash activities. High turbidity levels can suggest the presence of pollutants harmful to aquatic life and health. For validation, it can be compared with previous studies that show bentonite can be applied in treating wastewater in turbidity removal (Alsaeed et al. 2022; Marey 2019).

Regarding color characteristic, which measures the visual appearance of the water, the treated water does not meet the color standards, implying that it is not an acceptable color for car wash purposes.

The pH level determines the acidity or alkalinity of the water. The treated water needs to fall within the acceptable range according to the pH standards, ensuring it is neither too acidic nor too alkaline for car wash activities. From the result obtained, the pH level was within the range and acceptable for use.

Total dissolved solids (TDS) indicate the level of dissolved contaminants in the water. In this experiment, the treated water meets the TDS standards, suggesting that it has a low concentration of dissolved solids, making it suitable for recycling in car wash activities. As mentioned from previous studies, bentonite clay has demonstrated its effectiveness in wastewater treatment and its potential for supporting recycling efforts (Baddor et al. 2014; Banerjee et al. 2022; Mateus et al. 2021). Additionally, zeolite has also shown promising outcomes in treating wastewater to a degree that allows for recycling and subsequent reuse (Abedi et al. 2019; Acosta-Herrera et al. 2021). From a recycling standpoint, solids are the first parameters to be considered. However, the critical concern lies in eliminating heavy metals due to their severe repercussions on ecosystems and human health (Sarmadi et al. 2021). Based on the evaluation of these parameters and their compliance with the relevant standards, a conclusion can be made regarding whether the treated water is suitable for recycling and reuse in car wash activities. However, the color not being within the acceptable range limit is noteworthy. Even though color may not be a crucial factor to consider when it comes to recycling and reusing the treated water, the general public may have reservations if the water's color does not appear normal. In this case, it is suggested to balance the pH value by adding chemicals. This can neutralize the color in the treated water (Abdullah et al. 2013; Alsaeed et al. 2022). Additionally, previous studies have shown that using chemicals like Alum as a coagulant can result in a 97% reduction in turbidity, while using waste hydrogen peroxide resulted in an 83% reduction in turbidity (Bhatti et al. 2011; Veit et al. 2020).

CONCLUSION

In conclusion, the evaluation of various water quality parameters, including turbidity, pH, temperature, and total dissolved solids (TDS), indicates that the treated car wash wastewater using adsorption by bentonite and bentonite-zeolite is generally suitable for recycling and reuse in car wash activities. However, the parameter of color presents a unique consideration.

While color may not be a pivotal factor in terms of the water's functionality for car washing, it is worth noting that public perception and acceptance can be influenced by the visual appearance of the water. In light of these findings, it is advisable to consider both the technical suitability of the treated water and public perception. From a technical perspective, the treated water appears to meet the essential criteria for car wash activities. However, in practice, it may be beneficial to address the color issue, as customer satisfaction and perception are key factors in the success of car wash businesses. Therefore, while the treated water can indeed be reused for car washing, it may be advisable to explore methods to improve its visual appearance to meet customer expectations and enhance the overall user experience (Akpor et al. 2015).

Lastly, this study highlights the need for additional chemical support to optimize car wash wastewater treatment. While natural bentonite can be used directly for cleaning polluted water from heavy metals, it is possible to increase its adsorption capacity by modifying its chemical composition (Zhumagaliyeva et al. 2021). The results demonstrate that the utilization of raw natural bentonite and bentonite-zeolite without chemical additives is effective, particularly for removing heavy metals like iron, copper, and zinc. Thus, this approach stands as a viable and necessary method for wastewater treatment. To further enhance our understanding and optimize the use of bentonite in heavy metal adsorption, future studies should explore advanced characterization techniques, such as X-ray diffraction and scanning electron microscopy. These methods can provide valuable insights into the surface properties and structural changes of bentonite before and after modification, as well as after heavy metal adsorption, thereby improving its efficiency in practical applications.

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DECLARATION OF COMPETING INTEREST

None.

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