

Arsenic removal from aqueous solutions using potassium permanganate-modified laterite: Experimental investigation and optimization

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ABSTRACT

Arsenic contamination in groundwater poses a critical threat to public health, particularly in developing regions. This study investigates the potential of potassium permanganate (KMnO₄)-modified laterite as a cost-effective and efficient adsorbent for arsenic removal from aqueous solutions. A series of batch adsorption experiments were conducted using synthetic arsenic-contaminated water (100 ppb), with the influence of three key operational parameters – adsorbent dosage, solution pH, and reaction time systematically analyzed through a Box-Behnken design within the response surface methodology framework. The statistical model demonstrated high predictive accuracy ($R^2 = 0.99$), and analysis of variance confirmed dosage and reaction time as significant factors, while pH had a negligible effect within the tested range. Optimal conditions for maximum arsenic removal (78.25% actual, 79.03% predicted) were determined to be a dosage of 0.43 g, pH of 3.6, and reaction time of 68 minutes. The results confirm that KMnO₄-modified laterite is a promising material for arsenic remediation, offering a sustainable and scalable solution. However, further studies are recommended to evaluate its long-term performance, regeneration potential, and effectiveness in real water systems containing multiple contaminants.

Keywords: adsorption, arsenic removal, response surface methodology, water treatment, process optimization.

INTRODUCTION

Arsenic contamination in water resources poses a significant environmental and public health concern worldwide. Classified as a Group I carcinogen by the World Health Organization (WHO, 2019), even low-level, long-term exposure to arsenic has been associated with severe health effects such as skin lesions, cardiovascular disorders, and various cancers (Aredes et al., 2013). High concentrations can also lead to gastrointestinal disturbances (Jadhav et al., 2015). Human exposure primarily occurs through ingestion of contaminated drinking water, though inhalation and dermal absorption are also possible. In food sources – particularly seafood – arsenic often exists in organic forms, such as arsenobetaine and arsenocholine, which are less toxic and rapidly excreted through urine

(Ratnaike, 2003). South and Southeast Asia are among the region's most severely affected, where millions rely on arsenic-contaminated groundwater for daily use (Shaji et al., 2020). Arsenic enters aquifers through complex geochemical processes, making it difficult to mitigate (McCarty et al., 2011). The situation is further exacerbated by challenges in water infrastructure and additional threats like seawater intrusion in coastal areas (Carrard et al., 2019). Estimates suggest that 94 to 220 million people globally are exposed to arsenic through drinking water, underscoring the urgent need for monitoring, safe water access, and sustainable mitigation (Joel et al., 2020; Hutton et al., 2017).

To address this issue, a variety of laboratory-scale arsenic removal technologies have been explored. Electrocoagulation (EC) has gained prominence due to its simplicity, low chemical

demand, and effectiveness in removing both As(III) and As(V) species through the in-situ generation of coagulants using sacrificial electrodes (Mollah et al., 2001). Complementary methods such as chemical oxidation combined with adsorption media enhance removal efficiency (Gang et al., 2016). Filtration systems utilizing iron-based materials, biochar, and bone char are also promising but require further optimization (Alkurdi et al., 2019). Among adsorption-based approaches, materials such as iron oxide-coated sand (Callegari et al., 2018) and potassium permanganate-modified media (Gang et al., 2016) offer cost-effective and scalable solutions. Overall, these techniques, validated in laboratory settings, hold potential for application in affected communities, particularly when adapted for local conditions (Simonič, 2009; Biela et al., 2016).

The utilization of modified laterite materials for contaminant removal from aqueous solutions has garnered significant research interest, with various modification techniques enhancing adsorption capacities for different pollutants. One prominent approach involves high-temperature calcination of red clay, which has been demonstrated to serve as an efficient adsorbent for phosphate removal, with studies emphasizing the importance of equilibrium, kinetics, and thermodynamic parameters in optimizing performance (Cheng et al., 2024). Modification of laterite with metal oxides has been shown to significantly improve its adsorption capabilities. For instance, a hydrothermal process was employed to develop a hematite-based nano-adsorbent from lateritic iron ore, which exhibited enhanced removal of toxic arsenic ions, highlighting the eco-friendly nature of such modifications (Mostafa et al., 2025). Similarly, the surface modification of laterite with biochar, particularly when combined with biochar's synergistic properties, has been identified as an effective strategy for arsenic removal, offering a sustainable solution with high adsorption efficiency (Singh et al., 2024). In the context of phosphate removal, the introduction of metal oxides such as MgFe_2O_4 onto biochar surfaces has been reported to significantly enhance phosphate adsorption, suggesting that biochar modification can be tailored to target specific contaminants (Usman et al., 2022). Additionally, the modification of laterite with polyanions like polystyrene sulfonate (PSS) has been investigated for

the removal of cationic dyes, demonstrating the versatility of surface modifications in expanding the range of removable pollutants (Mai et al., 2021). Fluoride removal from water using surface-modified laterite has also been explored, with studies confirming that such modifications render laterite a robust adsorbent at neutral pH and room temperature, thus offering a promising solution for fluoride contamination (Iriel et al., 2017). Further, acid modification of red clay, a form of laterite, has been shown to improve fluoride adsorption efficiency, emphasizing the role of chemical treatment in enhancing adsorbent performance (Zhu et al., 2024). Overall, the literature underscores that various modification strategies – ranging from thermal treatments to chemical surface modifications – substantially improve the contaminant removal efficiency of laterite-based adsorbents. These modifications not only enhance adsorption capacity but also contribute to the development of cost-effective and environmentally sustainable solutions for water purification.

This study investigates the effectiveness of arsenic removal from aqueous solutions using a potassium permanganate (KMnO_4)-modified laterite adsorbent, with an emphasis on both experimental evaluation and process optimization. A Box-Behnken design within the framework of response surface methodology (RSM) was employed to systematically assess the influence of key operational parameters – namely, adsorbent dosage, solution pH, and reaction time – on arsenic removal efficiency. The experimental work was conducted in two stages: first, to evaluate the individual and interactive effects of these parameters; and second, to determine the optimal conditions for maximum removal efficiency. The use of laterite, a naturally abundant and low-cost material, modified with potassium permanganate, offers a promising and economically viable alternative for arsenic remediation. By optimizing the adsorption process, the study demonstrates the potential of KMnO_4 -modified laterite to reduce arsenic concentrations under laboratory conditions effectively. These findings provide a valuable foundation for the development and scaling up of adsorption-based treatment systems, particularly in regions where access to safe drinking water remains a critical challenge. The research thus contributes to the advancement of sustainable and accessible water treatment technologies for arsenic-contaminated sources.

METHODOLOGY

Preparation of arsenic-contaminated wastewater

In this study, approximately 5 liters of synthetic arsenic-contaminated wastewater were prepared by diluting a 500 ppm arsenic AAS standard solution into deionized water to simulate polluted conditions under controlled laboratory settings. The initial arsenic concentration, 100 ppb, was selected for the experiments, which exceeded typical arsenic levels found in natural groundwater, thereby providing a stringent test of removal efficiency. Before treatment, the pH of each solution was measured and adjusted to the desired experimental values using either sodium hydroxide (NaOH) to increase pH or hydrochloric acid (HCl) to lower it. Following the pH adjustment, the adsorption process was initiated, allowing for the evaluation of arsenic removal under controlled and replicable conditions reflective of the selected parameter ranges.

Preparation of KMnO_4 -modified laterite

The preparation of KMnO_4 -modified laterite for arsenic removal involved a systematic process to ensure material consistency and surface activation. Natural laterite rock was first collected and thoroughly cleaned using tap water, followed by deionized water to eliminate surface contaminants. The cleaned material was dried at 105 °C for 24 hours to remove residual moisture, then crushed and sieved to obtain uniform particles of approximately 5 mm in diameter. A 0.1 mol/L potassium permanganate solution was prepared using deionized water, with a volume of 100 mL of solution used per 10 g of laterite to ensure sufficient oxidizing agent for modification. The laterite particles were immersed in the KMnO_4 solution and stirred gently, then placed on an orbital shaker at 25 °C and 150 rpm for 2 hours to promote surface oxidation. After treatment, the laterite was filtered and washed repeatedly with deionized water until the rinsate was colorless, indicating the removal of excess KMnO_4 and manganese residues. Finally, the modified laterite was dried again at 105 °C for 12 hours, cooled to room temperature in a desiccator, and stored in airtight containers for subsequent use in arsenic adsorption experiments.

Box-Behnken experimental design

The Box–Behnken design (BBD) is a useful statistical method for improving analytical techniques. It provides an effective way to assess how different factors and their interactions affect a certain outcome (Ferreira et al., 2007). In this study, BBD was specifically used to examine the impact of key operational parameters on the removal of arsenic and to enhance the overall effectiveness of the adsorption process. BBD is part of response surface methodology (RSM) and uses three-level incomplete factorial designs. This allows for modeling curved responses without needing a complete factorial design. One major benefit of BBD compared to other RSM designs is that it requires fewer experimental tests, making the optimization process cheaper and quicker while keeping reliable statistical accuracy.

For the experimental setup and data analysis, Design-Expert software version 13 was used. This software helped find the best operating conditions for Arsenic adsorption by fitting the experimental data to an appropriate response surface model. The optimization process included creating statistically designed combinations of independent variables, estimating the coefficients of the response functions, and then predicting how the response behaves at different factor levels. The parameters studied included the dosage of adsorbent, pH level, and reaction time, with each varied within specific lower and upper limits based on earlier studies. The adsorbent dosage ranged from 0.01g to 1.0g, pH from 2 to 9, and reaction time from 10 to 80 minutes. These ranges were carefully selected based on previous experiments to capture the relevant working conditions. Within the BBD structure, these factors were coded at three levels: high (+1), middle (0), and low (−1), allowing for the investigation of nonlinear relationships.

In this study, the adsorption of arsenic from aqueous solutions was investigated using laterite that had been chemically modified with KMnO_4 to enhance its adsorption capacity. Batch adsorption experiments were conducted by mixing known concentrations of arsenic-contaminated water with a fixed dose of the modified laterite under varying conditions of pH, contact time, adsorbent dosage, and initial arsenic concentration as designed by BBD. The mixtures were agitated at constant temperature, then filtered, and the residual arsenic concentration was collected

in 200 mL amber bottles to prevent light-induced reactions, and the residual arsenic concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). For accuracy, the initial arsenic concentrations of the synthetic wastewater were also analyzed using the same method, allowing for precise evaluation of removal performance.

The percent arsenic removal was calculated using Equation 1.

$$\%As\ removal = \left(\frac{A_{Initial} - A_{Residual}}{A_{Initial}} \right) \times 100\% \quad (1)$$

where: $A_{Initial}$ – initial arsenic concentration,
 $A_{Residual}$ – residual arsenic concentration.

RESULTS AND DISCUSSION

In this research, the distinct initial concentration of synthetic arsenic-contaminated wastewater (100 ppb) was selected to evaluate the performance of the adsorption process. This concentration was chosen to represent a moderate level of arsenic pollution, thereby allowing for a comparative analysis of removal efficiency and process optimization. The experimental results are presented in this section.

An empirical correlation between the arsenic removal efficiency and the three factors

A total of 17 experimental runs were conducted, including three replicates at each point to ensure statistical reliability. Additionally, the experiment at the optimal condition was also repeated three times to confirm reproducibility. The detailed experimental conditions and arsenic adsorption results for each run, using an initial concentration of 100 ppb, are summarized in Table 1.

The experimental results obtained from the Box-Behnken design (Table 1) demonstrate the significant influence of dosage, pH, and reaction time on arsenic removal efficiency using the KMnO₄-modified laterite. Overall, the removal efficiency increased with higher adsorbent dosage and extended contact time. At the lowest dosage of 0.010 g, arsenic removal ranged from 63.99% to 71.34%, while increasing the dosage to 1.000 g resulted in notably higher removal efficiencies, ranging from 90.03% to 92.28%, indicating a strong positive correlation between dosage and adsorption performance. Time also

played a critical role, as longer contact durations (e.g., 80 minutes) generally resulted in higher removal percentages compared to shorter durations (10 minutes), particularly at higher dosages. The effect of pH was more complex; however, optimal performance was observed near neutral to slightly alkaline conditions. For instance, at 1.000 g dosage and pH 9, the removal efficiency reached 92.28%, the highest among all runs. Central point replicates (runs 13–17) at 0.505 g dosage, 45 minutes, and pH 5.5 showed consistent and reproducible results (82.14–84.10%), confirming the reliability of the experimental design. These findings underscore the importance of optimizing operational parameters to enhance arsenic adsorption from aqueous solutions.

The ANOVA results summarized in Table 2 confirm that the developed model for arsenic removal using KMnO₄-modified laterite is statistically significant and well-fitted to the experimental data. The overall model has an F-value of 135.62 with a p-value less than 0.0001, indicating a strong relationship between the independent variables and the response. Among the main factors, adsorbent dosage (A) is the most significant contributor to arsenic removal, with an extremely high F-value of 935.00 and a p-value < 0.0001, highlighting its dominant influence on the adsorption process. In contrast, pH (B) and reaction time (C) showed no significant individual effect (p = 0.2752 and 0.1614, respectively), suggesting that within the selected experimental range, their direct impact on removal efficiency was limited. Regarding interaction effects, only the AC interaction (dosage × reaction time) was statistically significant (p = 0.0186), indicating a meaningful synergistic effect between these two parameters. Other interaction terms (AB and BC) and the quadratic term A² were not significant, implying negligible interactive or nonlinear effects in those combinations. However, the quadratic terms B² (pH) and C² (reaction time) were highly significant (p < 0.0001), pointing to the existence of curvature in the response surface and suggesting that arsenic removal efficiency is sensitive to the precise levels of pH and reaction time. Finally, the lack-of-fit test yielded a p-value of 0.2735, which is not significant, indicating that the model adequately describes the experimental data without substantial unexplained variation. These results validate the appropriateness of the response surface methodology and reinforce the importance of dosage as the key operational variable, while

Table 1. Box-Behnken design experiment conditions, results of arsenic removal using KMnO₄-modified laterite

RUN	Dosage (g)	pH	Reaction time (min)	Arsenic removal %
1	0.01	5.5	10	63.99
2	1	5.5	10	90.11
3	0.01	5.5	80	71.34
4	1	5.5	80	90.94
5	0.01	2	45	65.45
6	1	2	45	90.03
7	0.01	9	45	65.95
8	1	9	45	92.28
9	0.505	2	10	73.29
10	0.505	2	80	74.97
11	0.505	9	10	71.32
12	0.505	9	80	76.66
13	0.505	5.5	45	82.2
14	0.505	5.5	45	82.14
15	0.505	5.5	45	83.25
16	0.505	5.5	45	83.85
17	0.505	5.5	45	84.1

Table 2. ANOVA for percent arsenic removal using KMnO₄-modified laterite

Source	Sum of squares	df	Mean square	F-value	p-value	Remark
Model	1498.74	9	166.53	178.38	< 0.0001	significant
A-Dosage	1137.84	1	1137.84	1218.81	< 0.0001	
B-pH	0.0009	1	0.0009	0.0009	0.9767	
C-Reaction_time	30.31	1	30.31	32.47	0.0007	
AB	0.3969	1	0.3969	0.4251	0.5352	
AC	3.40	1	3.40	3.65	0.0978	
BC	2.04	1	2.04	2.19	0.1824	
A ²	0.0671	1	0.0671	0.0719	0.7963	
B ²	50.08	1	50.08	53.64	0.0002	
C ²	105.32	1	105.32	112.81	< 0.0001	
Residual	6.53	7	0.9336			
Lack of Fit	1.41	3	0.4684	0.3653	0.7829	not significant

also emphasizing the need to consider nonlinear effects in optimizing the process.

An empirical correlation between arsenic removal efficiency, and three key factors was developed using the Box-Behnken design. A reduced cubic model with an R² of 0.99 was fitted for the process, indicating strong predictive accuracy.

$$As_{(removal)} = 83.77 + 11.38A + 0.3265B + 0.5459C + 0.2999AB - 1.34AC + 0.5602BC + (2) + 0.1632A^2 - 2.48B^2 - 3.08C^2$$

Figure 1 presents a scatter plot comparing the actual experimental values with the model-predicted values of arsenic removal efficiency in

the adsorption process using KMnO₄-modified laterite. The data points are closely aligned along the 45-degree diagonal line, indicating a strong correlation between predicted and actual values. This close alignment suggests that the developed response surface methodology (RSM) model is highly accurate in predicting arsenic removal under various experimental conditions. The wide range of color-coded efficiency values (63.99–92.28%) further reflects the model's capacity to capture variation across different operating conditions. Overall, the high level of agreement between actual and predicted values

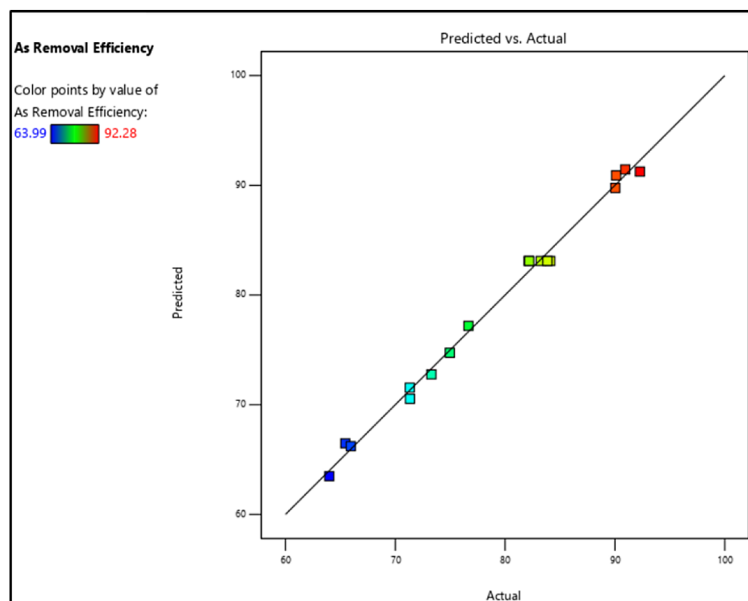


Figure 1. Comparison of actual experimental with model-predicted percent of the adsorption process

confirms the model's robustness, validity, and suitability for optimizing process parameters in the arsenic adsorption system.

Effect of operating parameters on arsenic removal using KMnO_4 -modified laterite

Percent arsenic removal in response to variations in operating parameters is shown in Figure 2. It illustrates the individual effects of (a) dosage, (b) pH, and (c) reaction time on arsenic removal efficiency using KMnO_4 -modified laterite, based on the actual factor levels. Among the three variables, dosage (Figure 2a) showed the most significant influence, with a nearly linear increase in arsenic removal as the dosage increased from 0.01 g to 1 g. This trend suggests that a higher quantity of KMnO_4 -modified laterite provides more active surface area or reactive sites for arsenic adsorption or oxidation, leading to enhanced removal efficiency. In contrast, the effect of pH (Figure 2b) was relatively minor, displaying a slight parabolic trend with a modest peak around pH 5.5, indicating that moderately acidic conditions are favorable for the removal process, possibly due to the optimal surface charge at that pH. The impact of reaction time (Figure 2c) also followed a parabolic pattern, with removal efficiency increasing up to around 50 minutes before slightly leveling off or decreasing, suggesting a point of equilibrium beyond which additional contact time yields diminishing returns. Overall, the results indicate that while all three factors contribute to arsenic

removal, dosage exerts the strongest effect, followed by reaction time and then pH, emphasizing the importance of optimizing adsorbent loading in practical applications.

Optimum points for arsenic removal

The 3D surface plots of the two parameter interaction effects of dosage, pH, reaction time on percent arsenic removal using KMnO_4 -modified laterite were shown in Figure 3. It presents 3D surface plots illustrating the interactive effects of dosage, pH, and reaction time on arsenic removal efficiency using KMnO_4 -modified laterite. In Figure 3a, arsenic removal efficiency increases with dosage up to approximately 0.8 g, particularly at lower pH levels, suggesting that acidic conditions favor the oxidative adsorption process. However, a further increase in pH beyond 6 results in a slight decline in efficiency, likely due to reduced surface charge interactions at higher pH. Figure 3b demonstrates a synergistic effect between dosage and reaction time, with efficiency steadily increasing over time and peaking at the highest dosage tested, indicating that both sufficient adsorbent quantity and prolonged contact time are critical for maximum removal. Figure 3c shows the interaction between pH and reaction time, where maximum removal occurs at intermediate pH values (around 5–6) and longer reaction times (60–70 minutes), emphasizing the importance of balancing reaction kinetics and favorable adsorption conditions. Overall, these plots highlight the

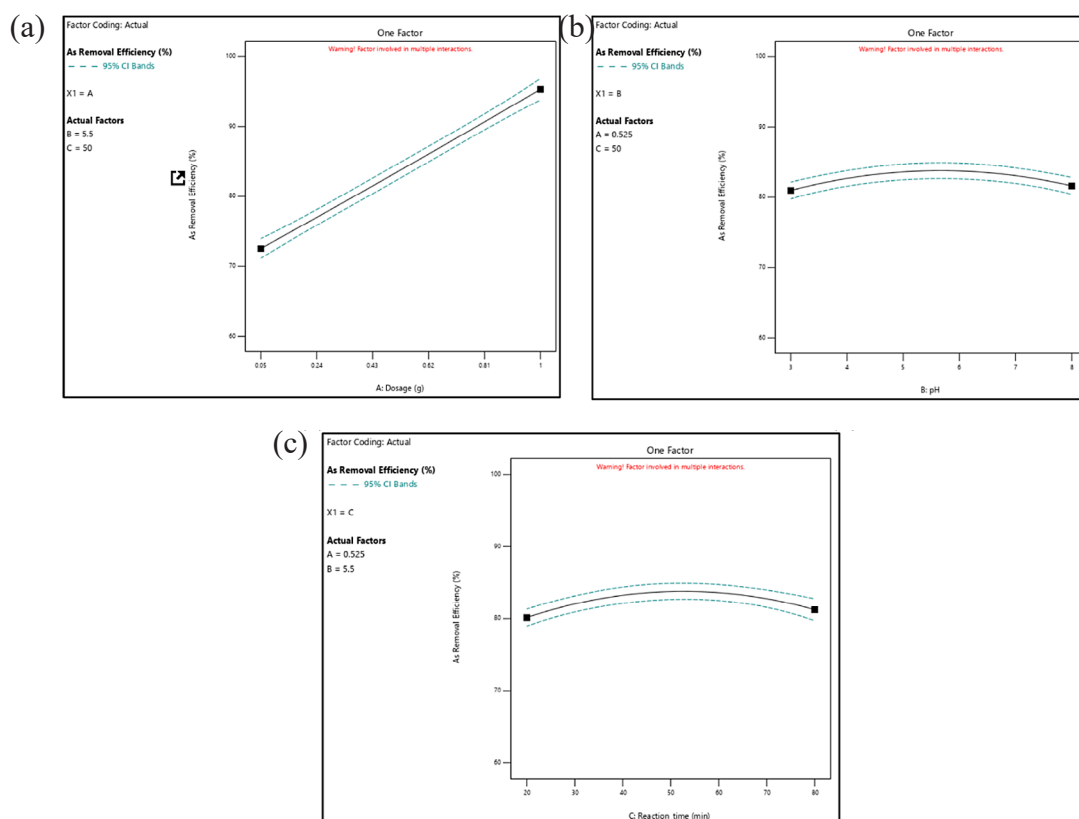


Figure 2. Effect of (a) dosage (b) pH (c) reaction time on arsenic removal using KMnO_4 -modified laterite

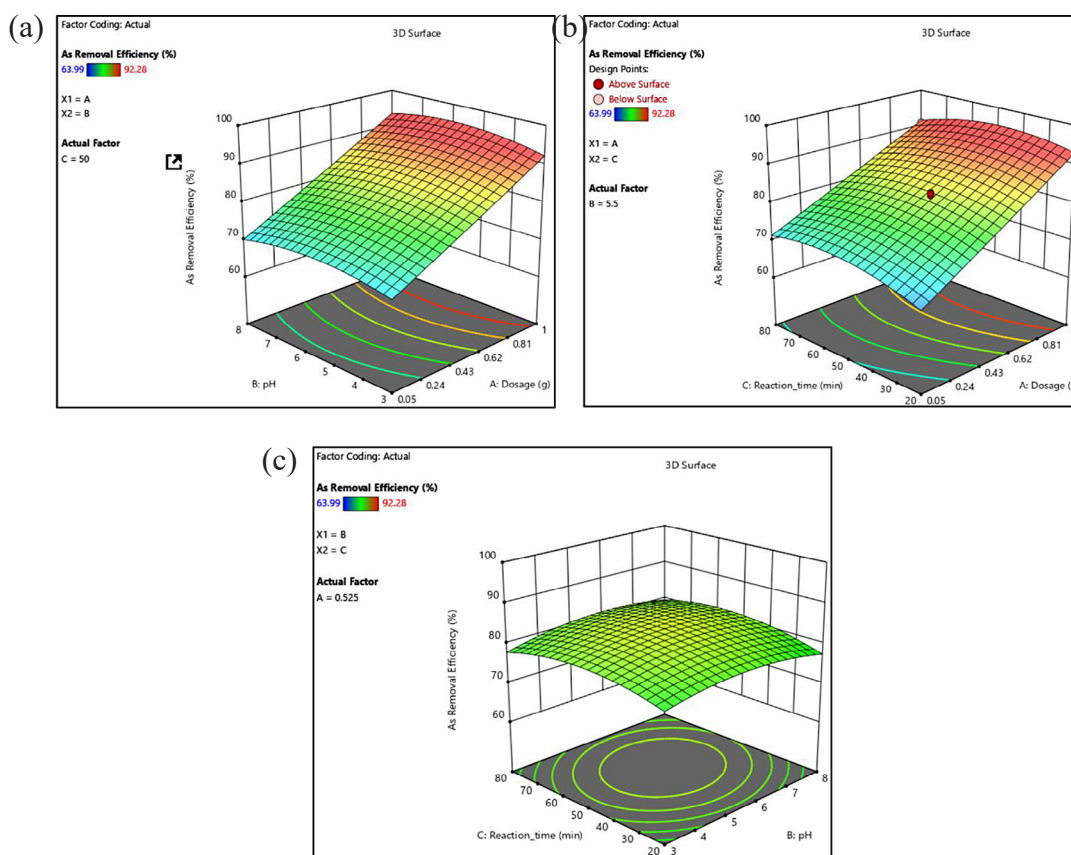


Figure 3. 3D surface plots of the two parameter interaction effects of dosage, pH, reaction time on percent arsenic removal using KMnO_4 -modified laterite: (a) dosage and pH, (b) dosage and reaction time, (c) pH and reaction time

Table 3. The optimum condition for arsenic removal using KMnO₄-modified laterite

Values of optimum conditions	Dosage (g)	0.97
	pH	3.6
	Reaction time (min)	51
Actual and predicted values of PCT removal	Actual	96.83%
	Predicted	98.37%
	Difference	1.54

non-linear and interdependent nature of the operational variables influencing arsenic removal.

The optimization results for arsenic removal using KMnO₄-modified laterite, as shown in Table 3, reveal that the process is highly effective under the identified optimal conditions. The optimal values were determined to be a dosage of 0.43 g, a pH of 3.6, and a reaction time of 68 minutes. Under these conditions, the actual arsenic removal efficiency achieved was 78.25%, closely matching the predicted value of 79.03%, with a minimal difference of 0.78%. This small discrepancy between actual and predicted values confirms the accuracy and robustness of the RSM model employed. The results highlight the significant adsorption capacity of KMnO₄-modified laterite, particularly under slightly acidic conditions, which likely enhances the surface reactivity and the availability of adsorption sites. Overall, the findings validate the model's predictive capability and support the practical applicability of KMnO₄-modified laterite as a low-cost, efficient adsorbent for arsenic removal from aqueous environments.

CONCLUSIONS

This study demonstrated the effectiveness of KMnO₄-modified laterite as a low-cost and efficient adsorbent for removing arsenic from aqueous solutions. Through the application of Box–Behnken design within a response surface methodology framework, the influence of three key parameters – adsorbent dosage, pH, and reaction time – was systematically evaluated and optimized. The results revealed that adsorbent dosage and reaction time had statistically significant effects on arsenic removal efficiency, while pH exhibited only a minor influence within the tested range. The optimal condition for maximum arsenic removal (79.03%) was determined to be a dosage of 0.43 g, pH of 3.6, and reaction

time of 68 minutes, highlighting the potential of the modified laterite for practical water treatment applications.

Despite these promising findings, certain limitations must be acknowledged. First, the study was conducted under controlled laboratory conditions using synthetic arsenic-contaminated water, which may not fully represent the complexity of natural water matrices that often contain multiple competing ions and organic matter. Additionally, the long-term stability and reusability of the KMnO₄-modified laterite were not addressed, leaving questions about its operational lifespan and regeneration potential. Finally, the narrow pH range explored may not capture the performance under extreme acidic or alkaline conditions commonly encountered in real-world settings.

Future research should focus on field-scale validation of the adsorbent in diverse environmental conditions, especially in arsenic-affected regions. Investigations into the adsorbent's performance in the presence of co-contaminants, its regeneration efficiency, and life-cycle assessment would enhance understanding of its practical sustainability. Future work should incorporate detailed material characterization to better understand the surface modification and adsorption mechanisms. Additionally, integrating this adsorbent into hybrid systems – such as combining with electrocoagulation or membrane technologies – could be explored to further enhance removal efficiency and operational resilience.

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