

RESEARCH ARTICLE



Analysis of Antimony Removal with Modified Activated Carbon Using Response Surface Methodology

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ABSTRACT

Antimony (Sb) is a metal compound that can cause health problems when it accumulates in the food chain and becomes toxic to the ecosystem. Industrial activities have driven Sb contamination of water, including surface water. At the same time, some drinking water treatment plants (DWTP) use surface water as raw water, which requires adequate treatment. An invention of cheap and accessible technology is needed for developing countries such as Indonesia; hence, this study presents research on modified activated carbon with iron sulfate and manganese sulfate to create a better adsorbent from commercial granular activated carbon (GAC). The independent variables in this study included the type of adsorbent (GAC and GACMF), acidity level, and dosage. Response surface methodology was implemented for the analysis. According to the study, it was found that the optimum state of non-modified GAC for Sb removal appears at pH 3 and a dosage of 0.03 g L⁻¹. In contrast, the presence of modified GAC was more effective for Sb removal with an optimum pH of 6 and a dosage of 0.057 g L⁻¹ for GACMF. This research suggests that GACMF is preferable for DWTP because the optimization shows that GACMF is optimized in a neutral state; therefore, additional chemicals are unnecessary to achieve a neutral acidity state.

Introduction

Antimony (Sb) is a metal element found in the earth's crust in relatively small amounts [1]. A high Sb concentration in the ecosystem is toxic and potentially causes health problems for the public when it accumulates in the food chain. Sb is toxic and carcinogenic to humans, and long-term exposure to Sb can cause health problems. Therefore, their presence in water requires more attention [2–7]. Although the carcinogenicity of Sb is not explicitly stated, some studies have found that patients with cancer have a higher Sb content in their bodies than healthy people [8]. Generally, the number of antimony compounds in water is low unless water is contaminated with mining waste [9]. Sb production fluctuated globally between 2016 and 2020; however, there was a significant increase in its production capacity from 2017 to 2019 [10]. The presence of Sb in water is promoted by several industrial processes that use Sb for production, such as paint, dyeing, ceramics, semiconductors, electronics, plastics, glass, and flame-retardant products [8,10–13]. These activities could lead to Sb contamination in the environment, including in water.

In 2022, pre-experiment sampling showed that drinking water from a DWTP in Surabaya consists of 0.48 mg L⁻¹ of Sb. This amount of Sb has exceeded the regulations stated in Indonesia, which only allows Sb up to 0.02 mg L⁻¹ in drinking water [14]. Another test was conducted using wastewater from the ceramic industry which contained 0.53 mg L⁻¹ of Sb. In terms of wastewater, there are no regulated standards for Sb in ceramic industry wastewater. The exclusive directive addressing the concentration of Sb in wastewater, with a specific focus on the accumulator battery industry, is outlined in the Regulation of the Governor of East Java [15]

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concerning Wastewater Quality Standards. As stipulated in this regulation, the permissible limit for Sb in wastewater is strictly limited to 0.2 mg L⁻¹.

The abundance of industrial activities in Surabaya has resulted in restrictions on the availability of clean water. Consequently, many citizens depend on local water treatment plants as their primary source of clean water. This dependency is supported by data from *Informasi Kinerja Pengelolaan Lingkungan Hidup Daerah* (IKPLHD) in Surabaya City [16], indicating that Surabaya citizens rely on local water treatment plants to meet their daily clean water needs. The Surabaya water treatment plant uses water from Kali Surabaya for treatment, and multiple industries discharge wastewater into the same river [17,18]. Additionally, the lack of monitoring exacerbates this situation because it makes it challenging to detect the presence of Sb [19].

Various studies on Sb removal technologies have been conducted in recent years to limit the spread of contamination. These technologies include electrochemical methods, extraction, coagulation-flocculation, adsorption, membrane separation, and ion exchange. Various studies have revealed that iron-modified carbon-based adsorbents are widely used for the treatment of clean water and wastewater [5,12,16,20–22]. Efforts to modify adsorbents are necessary to enhance their ability to capture metals. A previous study on modified activated carbon using manganese (II) sulfate and iron (II) sulfate confirmed its ability to remove Arsen (V) in water [23]. This study aimed to explore the removal of Sb using a similar method, as the similarity of antimony (Sb) and arsen (As) makes it possible to implement removal technology for Sb removal [5,24].

Materials and Methods

Data Collection

This study used a purely experimental design to minimize the presence of confounding variables. A pretest-posttest control group design was implemented to determine the differences before and after sample treatment. Sb removal was carried out using activated carbon modified with manganese (II) sulfate and iron (II) sulfate. Granular activated carbon (GAC) was modified with a manganese sulfate solution followed by an iron sulfate solution (known as GACMF). The types of adsorbents, GAC and GACMF, were tested in this study, and the observed variables were the acidity and dosage. This study was conducted at the Energy Conservation and Pollution Prevention Laboratory at Chemical Engineering, Gadjah Mada University.

The samples were sent to Jasa Tirta I Solo (a government-based environmental laboratory accredited by the National Accreditation Committee). The analysis was performed according to the American Public Health Association (APHA) 3120, using iCAP-7000 ICP-OES for inductively coupled plasma (ICP) analysis with a detection capability of up to 0.001 ppm. The collected data were statistically analyzed by response surface methodology (RSM) using Design Expert 13.

Materials and Tools

Samples of the antimony solution were prepared using potassium antimony (III) oxide tartrate hydrate (K₂(SbO)₂C₈H₄O₁₀·H₂O; Merck, Italy). Modification was performed using manganese (II) sulfate monohydrate (MnSO₄·H₂O from Merck, Germany) and iron (II) sulfate heptahydrate (FeSO₄·7H₂O, Merck, Ukraine). The pH (buffer solution) was adjusted using 65% nitric acid (HNO₃; Merck for analysis, Germany) and sodium hydroxide (NaOH; Merck for analysis). Distilled and Double-distilled water were purchased from a local store, with no specific description. Finally, the adsorbent (granular activated carbon) was purchased from a retail store, and no specifications were included in the package.

Preparation of Modified GAC

The GAC was modified with manganese sulfate and iron sulfate. First, GAC (5 g) was immersed in manganese sulfate solution (50 ml of 0.5 M) at room temperature for 24 h in a shaking bath at 150 rpm. The adsorbent was heated in an oven at 80 °C for 24 h. The dried GAC was rinsed three times with double-deionized water (DDW) before another 24 h heated procedure; for the second layer of GACMF, impregnated GACM was placed into 50 ml of iron sulfate (0.5 M) and run using a shaking incubator at 150 rpm for 24 h at room temperature. Finally, the adsorbent was separated from the solution and heated in an oven for 24 h. The final product of modified GACMF was prepared for use.

Data Analysis

Data analysis was performed using the response surface method (RSM) to determine the optimum state and formulation for Sb removal. The experimental design was adopted using a central composite design (CCD), as this research merely consisted of two independent variables or two-level factors [25]. These factors

included pH (X1) and adsorbent dosage (X2), with Y (response) representing the percentage removal of Sb. The range and level of each variable are presented in Table 1. In this study, the range was determined by specifying values of -1.141 , -1 , 0 , $+1$, and $+1.141$. The range that appears at 1.141 is part of the star point, indicating the highest and lowest values of the factor beyond the predefined values of -1 and $+1$.

Table 1. Independent variables and the levels of central composite design (CCD).

Independent variables	Symbol	Range & levels				
		-1.141	-1	0	1	1.141
pH	X1	3.17	4	6	8	8.83
Dosage (g L ⁻¹)	X2	0.009	0.016	0.033	0.050	0.057

The Sb removal procedure was completed in 13 runs with a certain amount of adsorbent (Table 2) that was submerged in 250 ml Sb solution (10 ppm) and run using a shaking incubator at 150 rpm for 24 h at room temperature. Subsequently, the samples were stored in a sample bottle and sent to Jasa Tirta I Solo for Sb analysis.

Table 2. The Sb removal toward pH and dosage.

StdOrder	Run order	Coded		Actual		Y	
		X1	X2	X1	X2	R% GAC	R% GACMF
1	7	-1	-1	4	0.017	10.83	3.07
2	8	1	-1	8	0.017	1.98	6.05
3	4	-1	1	4	0.050	9.44	10.19
4	5	1	1	8	0.050	1.39	10.33
5	11	-1.414	0	3.17	0.034	14.37	2.19
6	1	1.414	0	8.83	0.034	3.78	9.25
7	12	0	-1.414	6	0.010	5.72	7.54
8	6	0	1.414	6	0.057	3.31	25.01
9	3	0	0	6	0.034	1.69	6.85
10	13	0	0	6	0.034	2.04	8.4
11	9	0	0	6	0.034	3.77	8.98
12	2	0	0	6	0.034	2.55	14.24
13	10	0	0	6	0.034	2.25	11.13

X1: pH, X2: Dosage (g L⁻¹); Y: Sb Removal (%).

Results and Discussion

This section is structured into several subsections, each of which addresses the key aspects of the study. The first subsection focuses on adsorbent characterization and examines the properties of the materials used in this study. The evaluation was restricted to GAC before removal and GACMF after Sb removal to observe the presence of Sb after absorption. Next, a discussion of the statistical analysis and variables (pH and dosage) in Sb removal is provided to explore how different factors affect the efficacy of the removal process. Finally, a comparative analysis was conducted using RSM to obtain a better understanding of the optimization.

Adsorbent Characterization

The characterization is being investigated for non-modified adsorbents before they are used for Sb removal and the modified GAC adsorbent with the highest percentage of removal from the given variable after its application for Sb removal. According to this study, GACMF with experiment code P3D5 (pH 6 and dosage 0.057 g L⁻¹) had the best removal of 25.01%. Therefore, this state has become a requirement for characterization tests. The characterization tests were divided into several assessments, including the surface area test using the Brunauer-Emmett-Teller (BET) method, the functional group test using Fourier-transform infrared spectroscopy (FTIR), and the characterization of the surface adsorbent using scanning electron microscopy (SEM)-EDX-Mapping.

There were noticeable differences between the GAC and GACMF groups. In terms of color, GAC tended to be dark black, whereas GACMF had an orange layer that covered the surface, as the last treatment given to GACMF was submerged with iron (Figure 1). According to SEM analysis, unmodified GAC tends to be smooth, whereas GACMF has a coarser surface porosity. This finding suggests that the modification procedure successfully increased the porosity of the adsorbent (Figure 2).

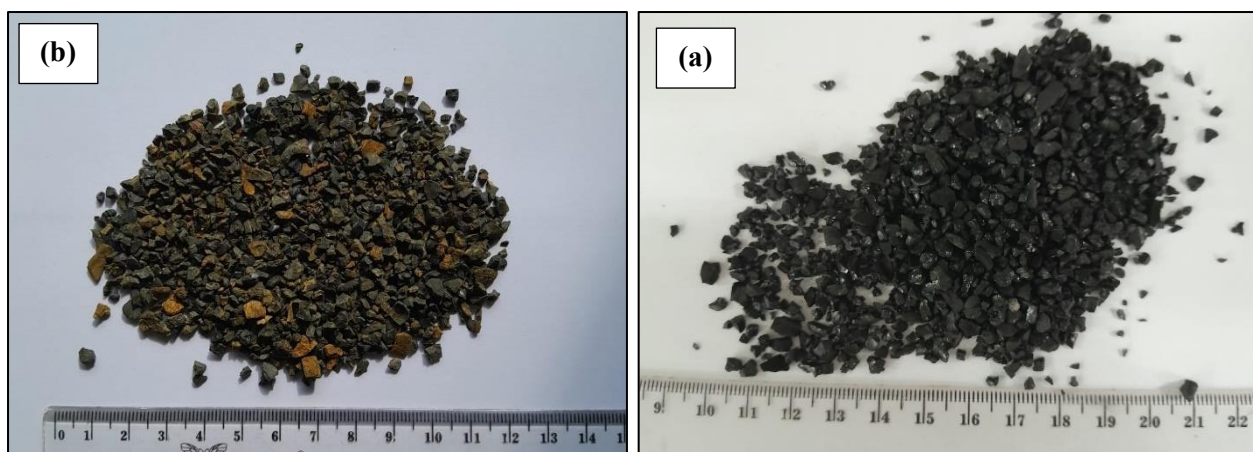


Figure 1. Comparison of (a) GAC and (b) GACMF.

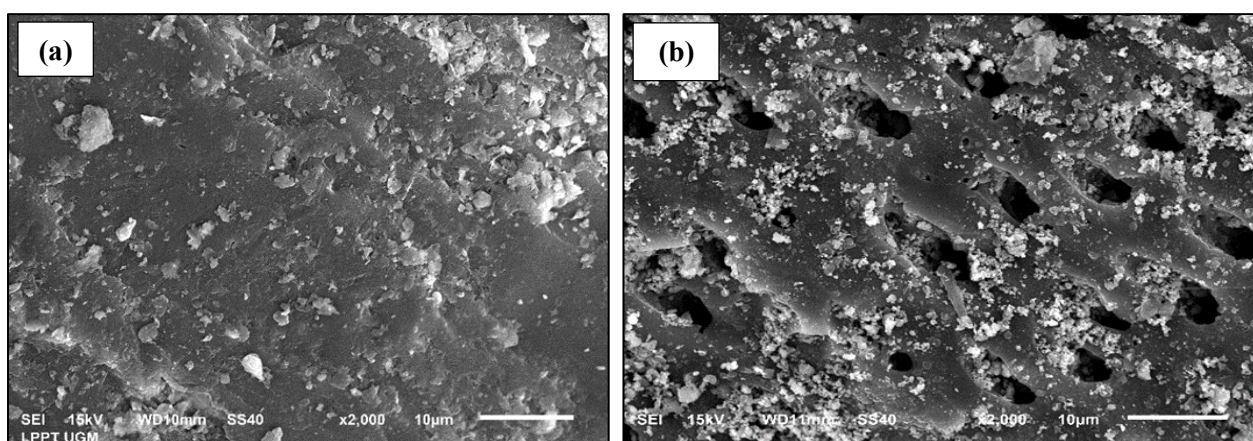


Figure 2. The surface of (a) GAC* and (b) GACMF** using SEM (*Before Sb adsorption; **after Sb adsorption).

The BET test showed that the surface area and total pore volume of GACMF decreased after modification (Table 3). Before treatment, the surface area of GAC was $177.153 \text{ m}^2 \text{ g}^{-1}$, which decreased to $6.403 \text{ m}^2 \text{ g}^{-1}$ after modification. Moreover, the value of the total pore volume also represents its depletion as a non-modified GAC, which was $1.01\text{E-}01 \text{ cm}^3 \text{ g}^{-1}$, eventually decreasing to $1.46\text{E-}02 \text{ cm}^3 \text{ g}^{-1}$. In terms of the mean pore radius, the value presented a slight depression of 0.183 \AA after the treatment.

Table 3. Surface Area Characterization of GAC and GACMF according to BET analysis.

Parameter	Value	
	GAC*	GACMF**
BET surface area ($\text{m}^2 \text{ g}^{-1}$)	177.153	6.403
Total Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	1.01E-01	1.46E-02
Mean pore Radius (\AA)	20.106	19.923

*Before Sb adsorption; **after Sb adsorption.

The enhancement of Fe triggered the clogging of pores and caused a reduction in pore volume and pore size [23]. This is highlighted by the Energy Dispersive X-Ray Spectroscopy (EDS) test that recognized the accumulation of Fe, which expanded from 0.66% to 13.84% after the modification (Table 4), and SEM-Mapping, which showed the presence of Fe before and after treatment (Figure 3). Depletion of the surface area and pore size would eventually affect Sb removal efficiency [22]. Fe is effective in Sb (III) removal because it dominates the Sb (III) adsorption process. Adsorption is mainly attributed to the interaction between the positively charged antimony species and negatively charged surface functional groups on the iron-based adsorbent [24].

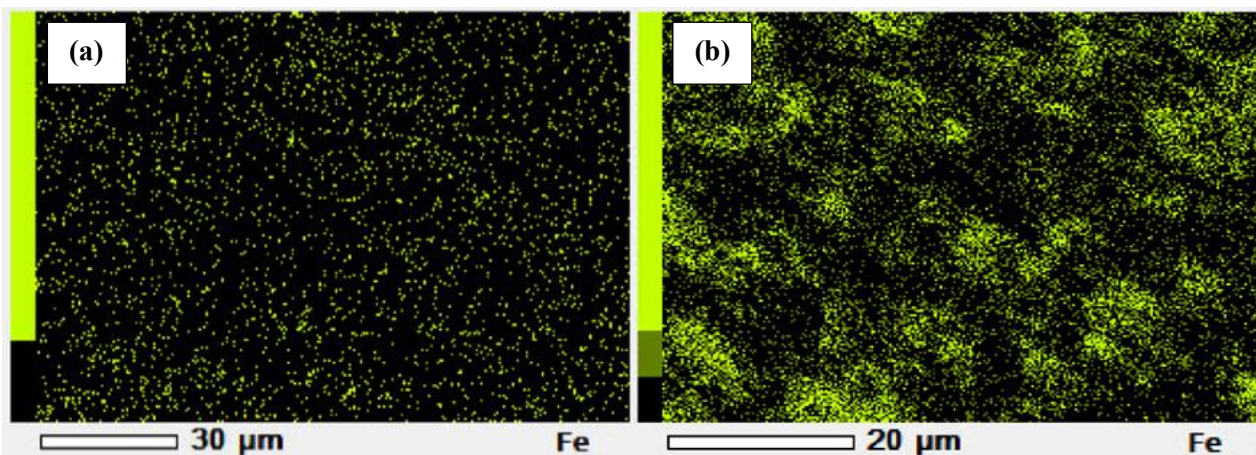


Figure 3. Fe mapping on the surfaces of (a) GAC and (b) GACMF.

Table 4. Chemical composition of GAC and GACMF according to EDS analysis.

GAC*			GACMF**		
Element	Mass (%)	Atomic (%)	Element	Mass (%)	Atomic (%)
C	54.55	61.39	C	58.32	73.18
N	18.41	17.76	O	23.25	21.91
O	22.18	18.73	Al	0.47	0.26
Al	1.56	0.78	Si	0.28	0.15
Si	1.98	0.95	K	0.46	0.18
K	0.32	0.11	Fe	13.84	3.74
Ca	0.35	0.12	Cu	1.51	0.36
Fe	0.66	0.16	Sb	1.86	0.23
Total	100.01	100	Total	99.99	100.01

*Before Sb adsorption; **after Sb adsorption

The EDS test determined that GACMF contained Sb at 1.86% of its total mass (Table 4). The presence of Sb was also confirmed by SEM mapping, which revealed Sb (green dots) on the surface of GACMF (Figure 4). SEM-Mapping and the FTIR test discovered the functional group of Sb from the adsorbent. This indicates that the use of the adsorbent (GACMF) was effective for Sb removal from water. Hence, various studies about iron-based adsorbents have been acknowledged as one of the most studied modified adsorbents and are considered favorable on a large scale [13].

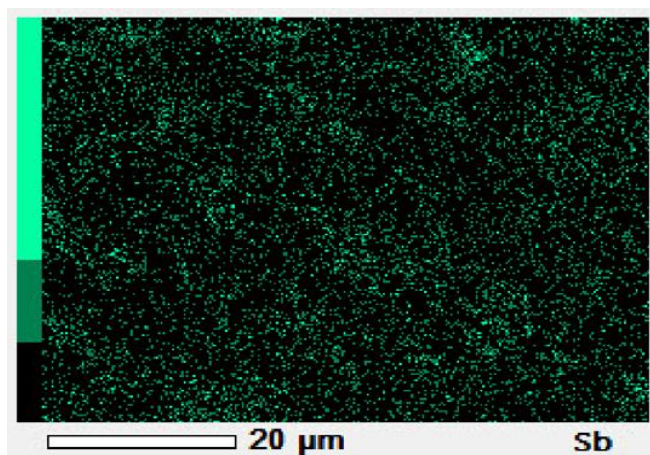


Figure 4. Sb mapping on the surface of GACMF after adsorption.

Although GACMF was modified using manganese, EDS analysis did not detect the presence of manganese. Roh et al. [23] stated that manganese could not be seen as iron oxide had entirely covered manganese oxide in the second layering procedure. However, the presence of Mn functional groups was still recognized by

FTIR examination. As the oxidation of Sb (III) to Sb (V) is dominated by Mn, Mn plays a crucial role in Sb adsorption [26,27]. A comprehensive examination of the characteristics of GAC after Sb adsorption is necessary to obtain a meticulous comparative analysis between GAC and modified GAC (GACMF). Through EDX analysis, another metal-Copper (Cu), was detected at 0.36% in terms of atomic percentage, which was higher than that of Sb. This finding may prove the additional ability of GACMF to absorb other metals. Nevertheless, further studies on Cu inside water before and after treatment are needed to confirm whether GACMF is capable of adsorbing Cu from water.

Statistical Analysis

The model needs to be evaluated through statistical analysis (ANOVA). The lack-of-fit values for GAC and GACMF appear to be insignificant (P-value >0.05), indicating that the obtained model fits the data (accounting for 0.4166 and 0.2316, respectively). Based on these data, it can be observed that the influence of variables on Sb removal varies among the adsorbents. In GAC, the dosage did not exert a significant effect, consistent with the value of the dosage square model and the 2-way interaction between the pH and dosage. In contrast, the modified GAC showed a significant result regarding dosage variation, with a P-value of 0.0084.

The value of R-squared (R^2) determines the percentage of total variance in the model, where a high value (closer to 1) represents a good fit for the model [28]. In this experiment, the R^2 of 0.9763 from the GAC was the best compared to that of the modified GAC. A low R^2 value indicates an insufficient correlation between the dependent and independent variables [29]. In addition to R^2 , Myers and Montgomery [30] stated that the best model was achieved using the maximum values for adjusted R^2 and predicted R^2 . Regarding predicted R^2 , non-modified GAC had a higher value than GACMF (accounting for 0.9005 in GAC), indicating that non-modified GAC appears to be sufficiently accurate to predict new outcomes.

The Influence of Variable Toward Removal

Generally, the adsorption capacity of an adsorbent is affected by several factors such as pH, dosage, time, and temperature. Studies have shown that the influence of pH and dosage varies between unmodified and modified GAC. In non-modified GAC, higher acidity provides better efficiency for Sb removal, whereas in modified GAC, the best efficiency should occur in a neutral state [22,27].

Effect of pH

As previous studies have shown that the effects of pH and dosage differ between non-modified and modified GAC, this study also found a similar result. The data showed that with higher acidity (pH 3), unmodified GAC exhibited the best performance (up to 14.37%) in removing Sb (III). Under the same conditions, only 2.19% of the Sb (III) was removed using GACMF. However, as acidity was reduced (pH 6), the modified GAC exhibited the highest removal percentage (25.01%). Previously, two different ferric-oxide-based adsorbents were compared, and it was found that samples in a neutral state (pH 7.6–7.7) had the best removal efficiency [31].

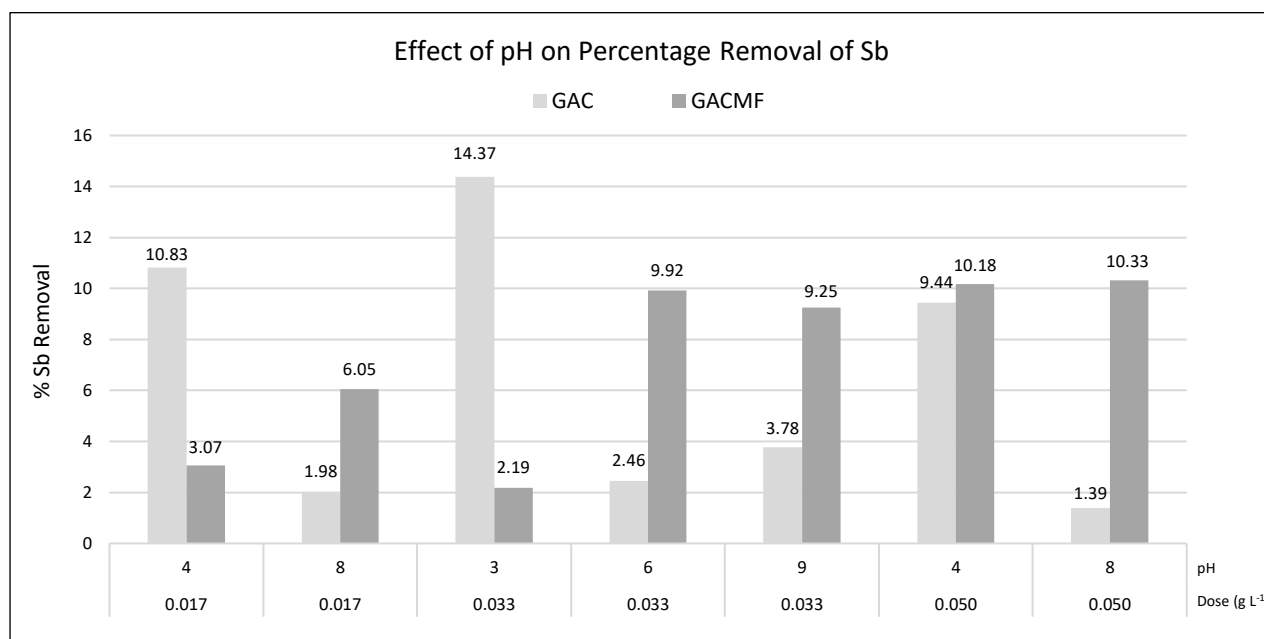


Figure 5. Effect of pH on Removal Percentage of Sb.

A similar result was obtained in this study, as the modified GAC had a better removal efficiency than the non-modified GAC under neutral to alkaline conditions. This study found that GACMF could remove up to 10.33% of Sb at pH 8 (Figure 5). A study on Sb (III) removal using modified GAC with ferric chloride (FeCl_3) found that pH had an immense effect, whereas the best acidity level for modified GAC ranged from 5 to 9 [22]. Pintor et al. [32] stated that pH affects the speciation of antimony and the surface charge of the adsorbent which affects the interactions between Sb compounds and the absorption site.

Effect of Adsorbent Dosage

In terms of adsorbent dosage, this study showed that an additional dosage led to a lower Sb removal capability of the unmodified GAC. Under acidic conditions, 0.017 g L^{-1} of unmodified GAC reduced the Sb content by 10.83%. However, when the dosage was tripled (0.05 g L^{-1}), the removal percentage decreased to 9.44% (Figure 6). In a previous study, Yu et al. [22] stated that increasing the dosage of non-modified GAC did not significantly affect removal effectiveness. By contrast, this study discovered that an increase in the adsorbent eventually increased the removal efficiency of the modified adsorbent. In GACMF, Sb removal improved after the extra dosage was added through acidic, neutral, and alkaline states. In contrast, the highest dosage (0.057 g L^{-1}) represented the best removal with 25.01% at pH 6.

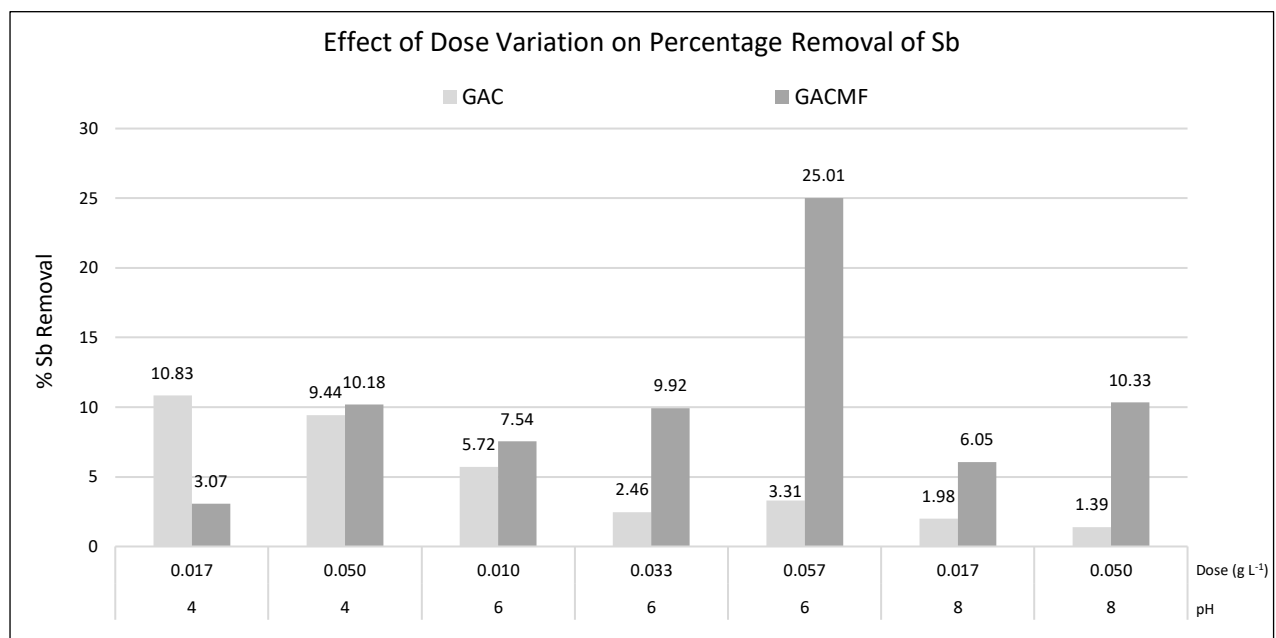


Figure 6. Effect of dosage variation on the Sb removal percentage.

Optimization using Response Surface Methodology

Data analysis from the Environmental Laboratory of Jasa Tirta Solo showed that each treatment in the experimental group affected the percentage removal value. However, the influences of the pH, dosage, and type of GAC are variables that cannot be explicitly shown in the data. Therefore, further data processing using statistical methods with RSM is needed to determine the interpretation of the data obtained. The contour plot of the unmodified GAC shows that Sb removal increased to its peak when the acid concentration was increased, and the dosage was inclined. The highest percentage of Sb removal accounted for more than 14% when the acidity level reached three, and the dosage was 0.034 g L^{-1} (Figure 7). Under the same conditions, the modified GAC showed the opposite result, as Sb removal was the least effective removal percentage, less than 4%. According to the data, the best state for modified GAC occurs at pH 6, with an adsorbent dosage of 0.057 g L^{-1} (removal percentage of more than 25%).

The correlation between the dosage and Sb removal in the unmodified GAC showed that as the dosage increased, the removal percentage declined. This finding is contrary to that of a previous study, which discovered that adding dosage slightly increased the removal percentage, although it did not significantly affect the Sb removal effectiveness [22]. A possible explanation for this finding is that, in this design experiment, the highest dosage was only 0.057 mg L^{-1} . Yu et al. [22] used exactly 1 mg L^{-1} of adsorbent (17.5 times greater). In non-modified GAC, an additional dosage represents a better removal of GACMF. Similar to

the results of this study, the contour plot of GACFM revealed that a higher dosage resulted in better Sb removal. With respect to the acidity level, the best removal percentage of GACMF occurred in a neutral atmosphere at pH 6.

Although non-modified GAC represents the best removal with the least amount of adsorbent, non-modified GAC is not considered desirable for DWTP because the peak would only be achieved at higher acidity (pH 3). Instead, the highest point of GACMF for Sb removal occurs at pH 6, which makes it favorable because additional chemicals are considered unnecessary; thus, it is environmentally and economically friendly. Nonetheless, the utilization of non-modified GAC would offer benefits for treating water near Sb mining areas because the area has a higher acidity level. A previous study by Eppinger et al. [32] reported that one of the surface waters of the Kanstishna Hills antimony mining site, Alaska, had an acidity level of 2.7–5.8.

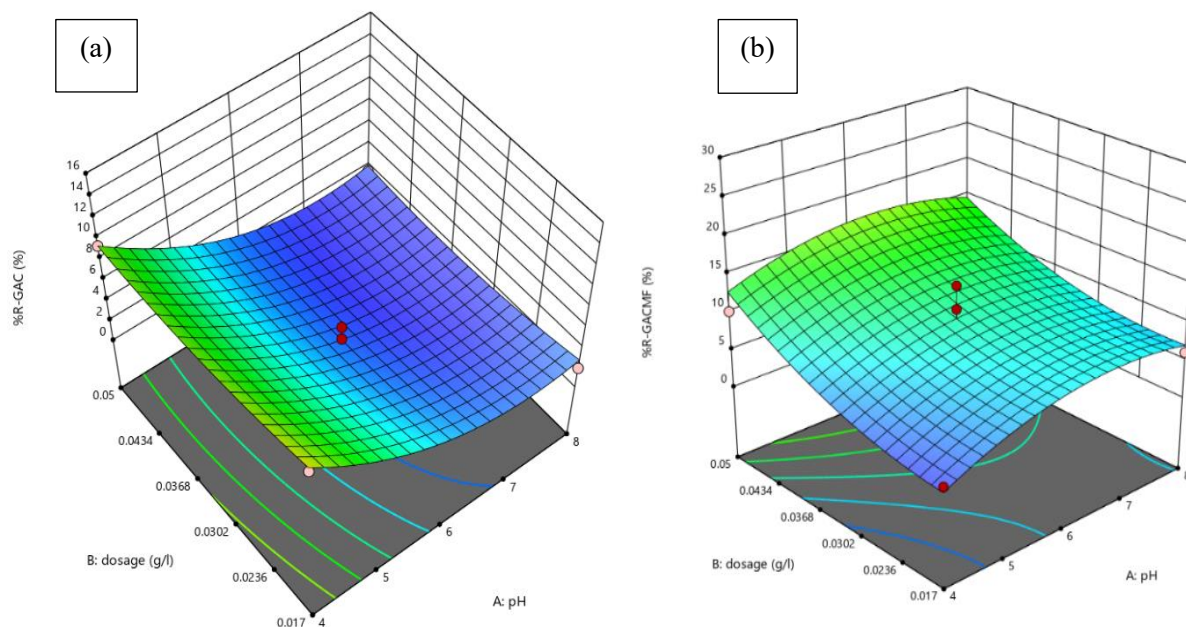


Figure 7. Surface plot for Sb removal percentage vs. dosage and pH of (a) GAC and (b) GACMF.

The Removal Comparison of GAC and GACMF

The variations in pH and dosage represent the different Sb removal efficiencies for each adsorbent (GAC and GACMF). According to the research, this experiment concluded that non-modified GAC had the best efficiency at pH 3 and a dosage of 0.034 g L^{-1} , whereas modified GAC had the greatest removal capacity in a neutral state (pH 6) and the highest dosage value (0.057 g L^{-1}). Statistical analysis using RSM revealed that the optimum state of GAC was higher acidity (pH 4) and the lowest dosage value (0.017). In contrast, there was consistency between the raw data and optimization in GACMF, which showed the highest removal in the same state at both (pH 6 and dosage 0.05 g L^{-1}).

From the raw data, unmodified GAC can remove up to 14.37% of Sb (III). The Sb removal capacity of the modified GAC was 25.01%. Ilavsky [31] found that adsorbents modified with iron oxides have more effective removal capabilities than unmodified GAC. In that study, Ilavsky compared two trademarks, Bayoxide E33 and Granulated Ferric hydroxide (GEH), and found that GEH is three times more effective in antimony reduction, where GEH has an adsorption ability of $85.04 \mu\text{g g}^{-1}$. In contrast, the adsorption capacity of Bayoxide E33 is only $27.78 \mu\text{g g}^{-1}$. A modified adsorbent using Fe was developed by Pintor et al. [33], who modified raw cork granules with FeCl_3 . Studies have found that Sb (III) adsorption on modified raw cork granulates is three times more effective than that on unmodified raw cork granulates. This finding is similar to that of Yu et al. [22], who stated that the reduction in antimony levels by modifying GAC with FeCl_3 was three and a half times higher than that of unmodified GAC.

In addition to ferric oxide, manganese oxide (MO) modification has been applied to reduce antimony metal levels. Wan et al. [27] have researched modified biochar (BC) using Potassium Permanganate (KMnO_4), which acts as the MO. X-ray photoelectron spectroscopy (XPS) analysis showed that biochar modified with MO can

absorb Sb (III) up to 53.3% Sb (III). Studies on the combination of modified GAC using Fe and Mn conducted by Bai et al. [24] found that Fe-Mn binary oxides (FMBO) can oxidize Sb (III), where MO plays a vital role in the oxidation of Sb (III) to Sb (V), while iron dominates in the adsorption process of Sb (III).

Conclusions

This research showed that based on this experiment, modified GAC has proven more effective for Sb (III) removal than non-modified GAC. Among the two types of adsorbents, it is clear that GACMF has better removal ability than GAC, as the optimization analysis showed that GACMF is ideal in a neutral state (pH 6) and makes it more favorable for implementation in a DWTP. In addition, it was confirmed that the removal efficiency increased with increasing dosage. Further analysis using produced water from local DWTP might be helpful in the future, as the observation could be a representative comparison of the effectiveness of GACMF for Sb removal so that it can be more realistic to implement it in drinking water treatment plants.

Author Contributions

JT: Experimental Design, Methodology, Data Collection and Treatment, Writing, Editing; **AP:** Conceptualization, Review & Editing, Supervision; **PA:** Review & Editing, Supervision.

Conflicts of interest

The are no conflicts to declare.

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