

Efficacy of Activated Cow Bone Ash for the Removal of Heavy Metals in Bilge Wastewater

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Abstract— This study evaluated the effectiveness of activated cow bone ash (ACBA) in removing heavy metals from bilge wastewater. Bilge wastewater is the contaminated water that collects in the lowest part of a ship's hull and typically contains oily residues, machine grease, and heavy metals, which can cause environmental pollution if not properly treated. Five dosage levels of activated cow bone ash (8 g/L, 9 g/L, 10 g/L, 11 g/L, and 12 g/L) were prepared in triplicate and tested through batch adsorption experiments. The treated samples were evaluated for heavy metal removal efficiency and statistical significance. Initial analysis of the bilge wastewater detected cadmium (Cd) at 0.009 mg/L, while lead (Pb) was below the method detection limit (MDL). Therefore, only cadmium removal was included in the evaluation. The results showed that cadmium removal efficiency ranged from 94% to 97% across all dosage levels. The highest and most consistent removal efficiency of 97% was obtained at dosages of 9 g/L to 11 g/L. Most treated samples had cadmium concentrations below the method detection limit, indicating effective adsorption. However, the Kruskal-Wallis test ($H = 7.125$, $p = 0.129$) showed no significant difference among the different dosage levels. The findings suggest that activated cow bone ash is an effective and low-cost adsorbent for removing cadmium from bilge wastewater. Future studies are recommended to optimize adsorption parameters such as pH, contact time, agitation speed, temperature, particle size, and adsorbent dosage. It is also recommended to use wastewater with higher heavy metal concentrations and compare activated cow bone ash with other animal bone-derived adsorbents to further evaluate its adsorption performance.

Keywords— Activated cow bone ash; bilge wastewater; heavy metal removal; adsorption; potassium hydroxide activation; wastewater treatment; low-cost adsorbent.

I. INTRODUCTION

Heavy metal contamination of water sources has become a significant global environmental issue, posing serious risks to aquatic ecosystems and human health. Increasing levels of heavy metal pollution are mainly driven by industrialization, climate change, and urbanization. Common sources include mining waste, landfill leachates, municipal and industrial wastewater, and urban runoff. Heavy metals are toxic, potentially carcinogenic, and capable of bioaccumulating in living organisms, where they may damage vital organs such as the brain, liver, kidneys, and lungs even at low levels of exposure [1].

In the Philippines, heavy metal pollution has also been recognized as an environmental concern, particularly in marine and coastal waters. Studies conducted in Manila Bay detected lead (Pb), cadmium (Cd), and mercury (Hg) in water samples, with several concentrations exceeding the allowable

limits established by the Department of Environment and Natural Resources (DENR). Cadmium and mercury concentrations were found to be higher during the dry season, whereas lead concentrations increased during the wet season, reflecting the continuous discharge of pollutants from industrial and maritime activities [2].

One of the major contributors to marine contamination is bilge wastewater, a type of wastewater generated aboard ships. Bilge wastewater is a complex mixture containing oils, organic hydrocarbons, surfactants, heavy metals, and other contaminants that can pollute seawater, threaten aquatic organisms, and degrade water quality [3].

Among the available wastewater treatment methods, adsorption has been widely recognized as an effective technique for removing contaminants such as heavy metals, dyes, organic pollutants, nutrients, and pathogens. Activated carbon is one of the most used adsorbents because of its high surface area, well-developed porosity, and strong adsorption capacity. However, its practical application is often limited by high production costs, low selectivity toward specific contaminants, and challenges associated with regeneration and reuse. These limitations have encouraged the exploration of alternative adsorbent materials. Natural adsorbents such as clay, zeolite, and biomass, together with synthetic and hybrid materials including metal oxides, polymers, and carbon-based nanomaterials, have demonstrated promising adsorption performance due to their high efficiency, selectivity, stability, reusability, and relatively low cost [4].

This study was conducted to determine the potential of activated cow bone ash as an alternative adsorbent for the removal of Cd and Pb from bilge water.

II. METHODOLOGY

A. Preparation of Cow Bone Ash Adsorbent

A total of 3 kg of fresh cow bones was purchased from a local market and thoroughly washed with tap water to remove dirt, blood, and adhering tissue residues. The bones were then boiled in water for 30 minutes to facilitate the removal of the remaining flesh and connective tissues, after which they were allowed to cool to room temperature and manually scraped clean. The cleaned bones were sun-dried for seven (7) days, with periodic turning to ensure uniform drying, and subsequently oven-dried at 110°C for 2 hours to eliminate residual moisture and increase brittleness. The dried bones were crushed into smaller pieces using a hammer while

covered with a waste sack to prevent fragments from scattering and were further pulverized using a mortar and pestle to obtain a fine powder. The resulting powder was sieved through a 150- μ m mesh sieve to produce a uniform particle size before being transferred into clean, airtight containers and stored at room temperature until the activation process. The prepared cow bone ash used for the activation process is shown in Fig. 1



Fig. 1. Prepared Cow Bone Ash

B. Activation of Cow Bone Ash

The prepared cow bone ash was chemically activated with potassium hydroxide (KOH). A 1:2 solid-to-liquid ratio (w/v) of cow bone ash to KOH solution was used during the activation process to ensure adequate contact between the adsorbent and the activating solution. The cow bone ash was immersed in the KOH solution and maintained at room temperature for 12 hours to facilitate the activation of the bone powder. After the soaking period, the mixture was filtered through cheesecloth to separate the activated cow bone ash from the excess activating solution. The retained material was gently pressed to remove excess liquid and subsequently sundried for one (1) day to remove the remaining moisture before thermal activation.

Thermal activation of the dried cow bone ash was accomplished by heating it in a lab oven at a steady 200°C for 2 hours. After thermal treatment, the activated cow bone ash was allowed to cool naturally to room temperature for 30 minutes before further handling. The activated material was then stored into airtight containers until used in the adsorption experiments. The prepared activated cow bone ash was stored under ambient conditions until it was used in the adsorption experiments for the removal of heavy metals from bilge wastewater. This activated cow bone ash served as the adsorbent throughout the study and was used in all experimental treatments during the batch adsorption process. The activated cow bone ash (ACBA) obtained after chemical and thermal activation is shown in Fig. 2.



Fig. 2. Activated cow bone ash (ACBA)

C. Batch Adsorption and Heavy Metal Analysis

Batch adsorption experiments were carried out to evaluate the effectiveness of activated cow bone ash (ACBA) in removing heavy metals from bilge wastewater. Five adsorbent dosages (8.0, 9.0, 10.0, 11.0, and 12.0 g/L) were tested to determine the effect of different ACBA dosages on treatment performance. Each dosage was tested in two (2) replicate trials, resulting in a total of ten (10) treated samples.

Five (5) glass jars, each containing 1 L of bilge wastewater, were placed in a jar test apparatus and labeled according to the assigned ACBA dosages (8.0, 9.0, 10.0, 11.0, and 12.0 g/L). The corresponding amount of ACBA was added to each jar. The samples were mixed at 100 rpm for 30 min and then left undisturbed for 3 h at room temperature (25 °C).

After the contact period, the treated wastewater samples were filtered using Whatman filter paper to remove suspended solids and transferred into clean, labeled 1-L polyethylene terephthalate (PET) bottles. The samples were stored at temperatures below 8 °C and transported to the laboratory for heavy metal analysis. The raw bilge wastewater and the treated samples were analyzed to determine the concentrations of cadmium (Cd) and lead (Pb). The raw bilge wastewater served as the baseline for evaluating the treatment performance of activated cow bone ash (ACBA) at dosages of 8.0, 9.0, 10.0, 11.0, and 12.0 g/L. The laboratory results were used to compare the effectiveness of each ACBA dosage, and the dosage that achieved the lowest heavy metal concentration was identified as the optimum dosage.

D. Statistical Analysis

Descriptive statistics were used to summarize the removal efficiency of cadmium (Cd) and lead (Pb) at different dosages (8 g/L, 9 g/L, 10 g/L, 11 g/L, and 12 g/L) across the experimental trials. The Shapiro-Wilk test was used to assess the normality of the data, while Levene's test was applied to evaluate the homogeneity of variances among treatment groups. One-way analysis of variance (ANOVA) was used to determine whether there are statistically significant differences

in removal efficiency among the different dosages ($p < 0.05$), provided that the assumptions of normality and homogeneity of variance are satisfied. If significant differences were observed, post hoc tests were conducted to identify which specific dosage groups differed from each other. Graphical tools, such as line graphs, were used to present trends in removal efficiency with increasing adsorbent dosage and to evaluate consistency across trials. If the assumptions required for ANOVA are not met, the Kruskal–Wallis test was used as a non-parametric alternative to compare differences among dosage groups.

III. RESULTS AND DISCUSSION

A. Raw Bilge Wastewater Heavy Metal Concentration

Table 1 shows that cadmium (Cd) was present in the raw bilge wastewater at a concentration of 0.009 mg/L, while lead (Pb) was below the method detection limit (MDL). These results describe the condition of the wastewater before any treatment was applied. Knowing the initial concentration of heavy metals is very important because it serves as the baseline for the study. This baseline allows for a clear comparison of the extent of contamination reduction after treatment with activated cow bone ash. Without this initial data, it would be difficult to determine whether the treatment method is effective. Thus, these results provide an important reference point for evaluating the performance of the treatment process in removing heavy metals from bilge wastewater.

TABLE 1. Initial Concentration of Heavy Metals in Raw Bilge Wastewater

Heavy Metals	Test Method	Concentration (mg/L)
Cadmium	Direct Flame Atomic Absorption Spectrophotometric Method, SMEWW ¹ 3111 B., 24 th Ed., 2023	0.009
Lead		<MDL

The raw bilge wastewater contained 0.009 mg/L of cadmium (Cd), while lead (Pb) was below the method detection limit (MDL) of 0.003 mg/L. Previous studies reported higher concentrations of heavy metals in raw bilge water, with Pb and Cd concentrations reaching 0.3 mg/L and 0.1 mg/L, respectively [5]. The lower concentrations observed in the present study may be attributed to differences in ship operations and wastewater characteristics. According to the Department of Environment and Natural Resources (DENR) Administrative Order No. 2016-08, the allowable limit for Cd in Class SB marine waters is 0.006 mg/L. The measured Cd concentration (0.009 mg/L) exceeded this limit, indicating that treatment is required before discharge. In contrast, Pb was below the MDL, indicating that its concentration was within the allowable limit.

Jar Testing

Figure 3 shows the jar testing setup used during the adsorption experiment using different dosages of activated cow bone ash. Five beakers containing wastewater samples

were placed in the jar test apparatus and mixed simultaneously at a constant speed to ensure uniform dispersion of the adsorbent. Different dosages of activated cow bone ash (8 g, 9 g, 10 g, 11 g, and 12 g) were added to each sample to evaluate their effectiveness in the treatment process.

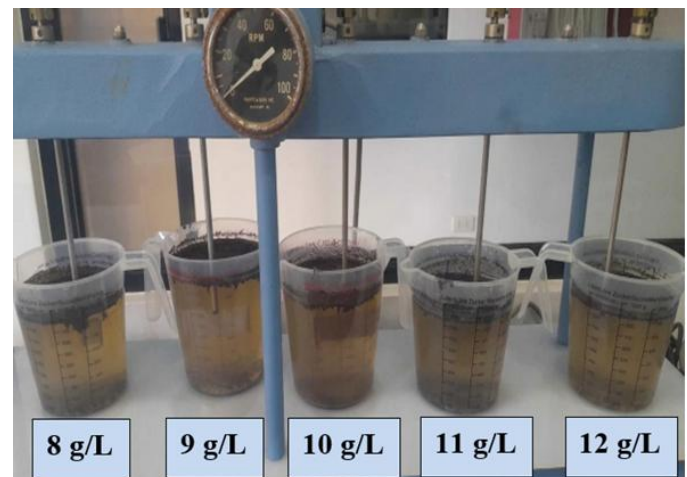


Fig. 3. Jar Test of Bilge Wastewater Using Different ACBA Dosages

A. Activated Cow Bone Ash (ACBA) Adsorption Observation

The adsorption performance of activated cow bone ash (ACBA) was evaluated at different dosages (8 g, 9 g, 10 g, 11 g, and 12 g) using a jar test. During the process, the ACBA remained as solid particles and spread throughout the wastewater, making the solution appear brown in all samples. The mixture remained turbid, and the particles were visibly moving in the water. As stirring continued, the ACBA particles became more evenly distributed in the solution.

B. Cadmium Concentration in Treated Bilge Wastewater

Table 2 presents the effluent test results for cadmium at different ACBA dosages. The cadmium analysis using the Direct Flame Atomic Absorption Spectrophotometric Method (SMEWW 3111 B, 24th Edition, 2023) showed that most values were below the method detection limit (MDL = 0.0004 mg/L), indicating very low cadmium concentrations in the treated wastewater. Only the 8 g and 12 g dosages showed detectable cadmium concentrations of 0.0004 mg/L and 0.0005 mg/L, respectively, while the remaining treatments were reported as below MDL.

TABLE 2. Effluent Test Results for Cadmium at Each Dosage

Trial	Test Method	RESULT				
		8g	9g	10g	11g	12g
1	Direct Flame Atomic Absorption Spectrophotometric Method	0.0004	<MDL	<MDL	<MDL	0.0004
2	SMEWW ¹ 3111 B., 24 th Ed., 2023	<MDL	<MDL	<MDL	<MDL	0.0005

In Trial 1, cadmium concentrations for the 9 g, 10 g, and 11 g samples were below the MDL, while the 8 g and 12 g samples recorded 0.0004 mg/L. In Trial 2, most samples from 8 g to 11 g were below the MDL, while the 12 g sample showed 0.0005 mg/L. Overall, the results indicate that

cadmium levels in the effluent were very low across all treatments.

Since several results were reported below the method detection limit (MDL), a substitution method was applied for data analysis. We replaced values that were below the MDL with half of the MDL (MDL/2), which is a common practice for handling left-censored environmental data. Results below the method detection limit (MDL) are frequently encountered in environmental and occupational studies and are commonly addressed using simple imputation methods such as MDL/2 or MDL/ $\sqrt{2}$ [6].

C. Cadmium Removal Efficiency

Table 3 presents the removal efficiency of cadmium at different dosages of activated cow bone ash (ACBA) for two trials. The table shows the percentage of cadmium removed from the wastewater after treatment using different amounts of adsorbent. The results were used to evaluate the effectiveness of ACBA in reducing cadmium concentration and to identify the dosage with the highest removal efficiency

TABLE 3. Removal Efficiency for Cadmium

Trial	8	9	10	11	12
1 (mg/L)	95%	97%	97%	97%	95%
2 (mg/L)	97%	97%	97%	97%	94%

The removal of cadmium using cow bone ash (CBA) is affected by several factors, particularly the amount of adsorbent used. Increasing the adsorbent dosage generally improves heavy metal removal by increasing the availability of active sites and pore space for adsorption. However, after reaching the optimum dosage, the removal efficiency may no longer increase or may show only minimal improvement because of the saturation of available adsorption sites[7].

In both trials, a similar trend was observed. In Trial 1, the removal efficiency was 95% at 8 g/L, increased to 97% at 9 g/L, and remained at 97% from 10 g/L to 11 g/L before slightly decreasing to 95% at 12 g/L. In Trial 2, the removal efficiency was 97% at 8 g/L and remained at 97% from 9 g/L to 11 g/L before slightly decreasing to 94% at 12 g/L. These results indicate that the adsorption process was highly effective across all dosages, with only slight variations in removal efficiency. The findings also suggest that the optimum dosage was reached within the tested range, where further increases in adsorbent dosage did not result in significant improvement in Cd removal. The slight decrease in removal efficiency at the highest dosage may be attributed to particle aggregation, which can reduce the effective surface area and limit access to adsorption sites.

Figure 4 shows the removal efficiency of cadmium using activated cow bone ash (ACBA) at different dosage levels for two experimental trials. The figure illustrates the percentage of cadmium removed from the wastewater after treatment at dosages of 8 g/L, 9 g/L, 10 g/L, 11 g/L, and 12 g/L. The graphical presentation was used to compare the removal efficiency obtained at each dosage level for both trials conducted in the study.

From 9 to 11 g/L, the removal efficiency remained relatively constant at approximately 97% in both trials. This stable trend indicates that the adsorption process had likely reached its effective capacity, where most of the active sites on the adsorbent surface were already occupied by metal ions,

resulting in minimal improvement in removal efficiency [8]. At 12 g/L, the removal efficiency slightly decreased to approximately 94–95%. This decline may be attributed to the excessive amount of adsorbent, which can promote particle aggregation. Particle aggregation reduces the effective surface area and blocks some active adsorption sites, thereby limiting the interaction between cadmium ions and the adsorbent [9]. As a result, the overall removal efficiency slightly decreased despite the higher adsorbent dosage.

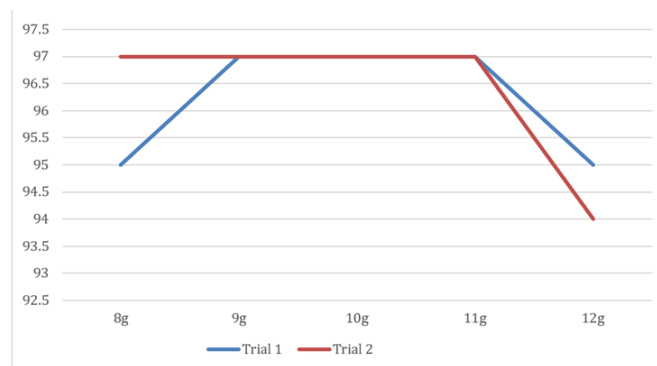


Fig. 4. Removal Efficiency for Cadmium

D. Cadmium Removal Performance and Statistical Analysis

Table 4 presents the mean cadmium concentration at different dosages of activated cow bone ash (ACBA) for two trials. The table shows the cadmium concentrations obtained after treatment and the corresponding mean values for each dosage level.

TABLE 4. Mean Cadmium Concentration (mg/L) at Different ACBA Dosages

Dosage (g)	Trial 1 (mg/L)	Trial 2 (mg/L)	Mean (mg/L)
8	0.0004	0.0002	0.0003
9	0.0002	0.0002	0.0002
10	0.0002	0.0002	0.0002
11	0.0002	0.0002	0.0002
12	0.0004	0.0005	0.00045

At 8 g/L, the mean cadmium concentration (0.0003 mg/L) was relatively higher, indicating lower adsorption performance at this dosage level. At 9–11 g/L, the mean concentration decreased and remained constant at 0.0002 mg/L, indicating more consistent cadmium removal within this dosage range. The similar results obtained at 9 g/L, 10 g/L, and 11 g/L suggest that increasing the dosage beyond this range did not significantly improve adsorption performance. At 12 g/L, the mean concentration increased to 0.00045 mg/L, indicating a decrease in cadmium removal efficiency at the highest dosage tested.

To verify the assumptions required for a one-way ANOVA, the Shapiro–Wilk test was used to assess the normality of the data. The results indicated that the data followed a normal distribution ($W = 0.872$, $p = 0.105$). However, homogeneity of variance, evaluated using Levene's test, showed that the variances across the dosage groups were significantly unequal ($F = 4.39 \times 10^{30}$, $p < 0.001$). Since the assumption of equal variances was not satisfied, the use of a non-parametric approach was considered more appropriate. Therefore, the Kruskal–Wallis test was employed to determine whether there were significant differences among the dosage

groups. Table 5 presents a summary of the Kruskal–Wallis test results for cadmium concentration across different ACBA dosages, including the test statistic (H), degrees of freedom (df), and asymptotic significance (p-value).

TABLE 5. Kruskal-Wallis Test Results for Cadmium Across Dosages

Parameter	Total N	Test Statistic (H)	df	Asymp. Sig. (p-value)
Cadmium Removal	10	7.125	4	0.129

The Kruskal–Wallis test was performed to determine whether variations in activated cow bone ash (ACBA) dosage resulted in statistically significant differences in cadmium removal efficiency. The analysis produced an H value of 7.125 with 4 degrees of freedom and a p-value of 0.129. Since the p-value is greater than the significance level ($\alpha = 0.05$), the null hypothesis was not rejected, indicating that there is no statistically significant difference in cadmium removal efficiency among the tested dosage levels.

This suggests that, although variations in removal efficiency were observed across the dosage levels, these differences are not sufficiently large to be considered statistically meaningful. The data show a relatively similar pattern of cadmium removal efficiency across all treatments, with slightly higher values observed at dosages ranging from 9 g/L to 11 g/L; however, these variations remain minimal and do not indicate a clear difference in performance among the dosages. Statistical analysis has shown that small variations in removal efficiency across different adsorbent dosages are often not significant, indicating that increases in adsorbent amount do not meaningfully affect performance [10].

The statistical analysis indicates that activated cow bone ash (ACBA) is capable of removing cadmium across the tested dosage range; however, its performance remains relatively consistent regardless of dosage. This implies that increasing the dosage within the studied range does not yield a significant improvement in removal efficiency, and all tested dosages may be considered comparable under the experimental conditions.

IV. CONCLUSION

Activated cow bone ash (ACBA) effectively reduced cadmium (Cd) concentration in bilge wastewater under the tested conditions. The raw bilge wastewater contained 0.009 mg/L of Cd, which exceeded the allowable limit for Class SB marine waters, while lead (Pb) remained below the method detection limit (MDL). After treatment, Cd concentrations were reduced to very low levels, including values below the MDL, demonstrating the adsorption capability of ACBA. Among the tested dosages, 9–11 g/L consistently achieved the highest removal efficiency, indicating that this range provided the most effective treatment performance. Although no statistically significant differences were observed among the dosages, the results suggest that ACBA is a promising low-cost adsorbent for reducing Cd in bilge wastewater and has potential for wastewater treatment applications.

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