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Adsorption of Malachite Green Using Alkali-Modified Fish Scale Bioadsorbents

[1]Dr. Manda Anil Mhatre and [2]Dr. Sapana Chilate

[1]Department of Zoology [1]Changu Kana Thakur Arts, Commerce, and Science College, New Panvel, Raigad district, Maharashtra, India.

[2]Dept. of Chemistry [2]M.M.P.A.S.C. College, Panvel. Raigad district, Maharashtra, India.

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ABSTRACT

The removal of toxic Malachite Green (MG) dye from water was studied using low-cost fish-scale biosorbents chemically activated with NaOH and KOH. The fish scales were cleaned, ground and soaked in 0.3 M NaOH or KOH (24 h), then rinsed and oven-dried to produce two adsorbents (FS-NaOH, FS-KOH) Batch experiments examined the effects of solution pH (3–11), adsorbent dose, and temperature (20–40 °C) on MG uptake. Equilibrium data were fitted to Langmuir and Freundlich isotherms. The NaOH-treated scales showed higher adsorption capacity than KOH-treated. Removal efficiency increased with higher pH and larger adsorbent dose, reaching >95% at optimal conditions. The data best fit a Langmuir model (monolayer adsorption), with maximum capacities on the order of 10–20 $mg \cdot g^{-1}$ (FS-NaOH) and lower for FS-KOH. Kinetic analysis indicated pseudo-second-order behavior. The results demonstrate that alkali-modified fish scales are effective biosorbents for MG, with NaOH activation yielding superior performance.

Keywords: Malachite Green, Fish scale adsorbent, NaOH activation, KOH activation, Langmuir isotherm, Freundlich isotherm.

INTRODUCTION

Malachite Green (MG) is a cationic dye widely used in textiles and aquaculture, but it is highly toxic, carcinogenic, and mutagenic[1]. Its persistence in water presents serious environmental and health hazards. Numerous treatment methods have been explored, but adsorption is particularly attractive due to its effectiveness and low cost[2]. In recent years, there has been growing interest in using biomass waste—such as agricultural and fishery by-products—as adsorbents[3].

Fish scale waste, composed mainly of hydroxyapatite and collagen fibrils, is abundant from seafood processing and is underutilized despite its layered bio-composite structure suitable for adsorption[4]. Previous studies have demonstrated that both untreated and modified fish scales can adsorb metals and dyes[5]. Labeo rohita scales exhibit a Langmuir capacity of approximately 38 mg/g for MG at pH 8[6] Chemical activation, such as alkali treatment, enhances adsorption by increasing surface area and introducing functional groups; NaOH treatment, for example, increases –OH groups and etches surface layers[7].

In this work, we examine MG removal using fish scale-based bio adsorbents activated with NaOH or KOH. Both Langmuir and Freundlich isotherm models were applied to describe equilibrium data. We also investigated the influence of solution pH, adsorbent dose, and temperature on dye uptake. Our goal is to provide a comprehensive study, supported by recent literature, to understand the adsorption behavior and optimize conditions for MG removal.

Materials and Methods

Adsorbent Preparation: Fish scales of Protonibea diacanthus (black spotted croaker, locally known as “Ghol”) were collected as waste material. They were washed, oven-dried at 80–110 °C, ground, and sieved to ~72 mesh.

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Two chemical activation routes were used. For NaOH modification, fish scale powder was soaked in 0.3 M NaOH for 24 h, washed to neutral pH, and redried. KOH modification was performed using 0.3 M KOH under identical conditions. These treatments enhance surface –OH groups and remove organic residues[67]. The resulting adsorbents (FS-NaOH and FS-KOH) were characterized using SEM, FTIR, and BET analysis following established protocols[6,7].

Dye Solution**:** Malachite Green chloride ($C_{32}H_{32}ClN_2$, MW ≈ 362) was purchased commercially. A 1000 mg/L stock was prepared and diluted to working concentrations (20–100 mg/L). Its λ_{max} (620 nm) and extinction coefficient agreed with reported values[8].

Batch Adsorption Experiments**:** All experiments were conducted in Erlenmeyer flasks at 30±1 °C.

pH effect: 50 mg/L MG solution was mixed with 0.005–0.030 g of adsorbent and shaken at 150 rpm for 3 h[9].

Dose optimization: For each condition, 50 mL MG solution (100 mg/L) was mixed with varying amounts of adsorbent (0.005–0.030 g) and shaken at 150 rpm for 3 h[9]

Isotherm studies: Using optimal dosage (0.01–0.02 g), MG concentrations were varied (20–100 mg/L).

Temperature effect: Experiments were performed at 20, 30, and 40 °C to assess thermodynamics. After equilibrium (3 h), samples were centrifuged and the MG concentration in the supernatant was measured by UV-Vis spectrophotometry at 620 nm. A calibration curve was used for quantification.

The equilibrium adsorption capacity, $ q_e $ (mg/g), was calculated by mass balance:

$$q_e = \frac{(C_0 - C_e)V}{W},$$

Removal (%) was calculated as:

$$\frac{C_0 - C_e}{C_0} \times 100$$

Isotherm Modeling**:** Langmuir and Freundlich models were fitted to equilibrium data. The Langmuir model (monolayer adsorption) is expressed as $ Ce/qe = 1/(bQ_0) + Ce/Q_0$, where Q_0 is the maximum adsorption capacity and b is the Langmuir constant. The Freundlich model (multilayer adsorption) is $qe = K_F Ce^{1/n}$ (often linearized as $\log qe = \log K_F + (1/n)\log Ce$). Linearized plots were used to determine Q_0, b, and K_F, n and their correlation coefficients.

Model parameters were determined from linearized plots[3].

RESULTS

Physicochemical Properties of Malachite Green:

Malachite Green (MG) exhibited a strong absorption peak at λ_{max} = 620 nm, consistent with its chromophoric triphenylmethane structure. Table 1 summarizes the key physicochemical properties of the dye. The molecular formula ($C_{23}H_{25}ClN_2$) corresponds to a molecular mass of 364.91 g/mol. The high extinction coefficient (14,899 cm^{-1} M^{-1}) reflects its strong molar absorptivity and stability in aqueous media

Table 1. Physico-chemical properties of Malachite Green dye.

Molecular Formula	Molecular Mass (g/mol)	λmax (nm)	Extinction Coefficient ($cm^{-1}M^{-1}$)
C23H25ClN2	364.91	620	14899

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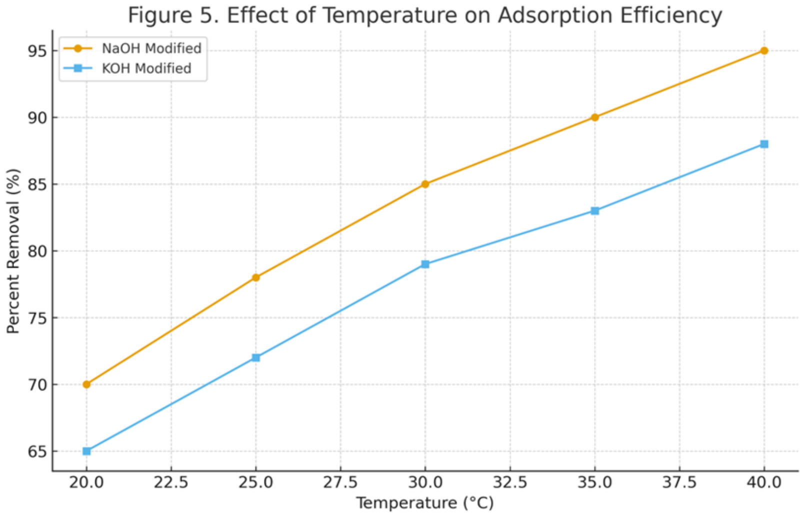
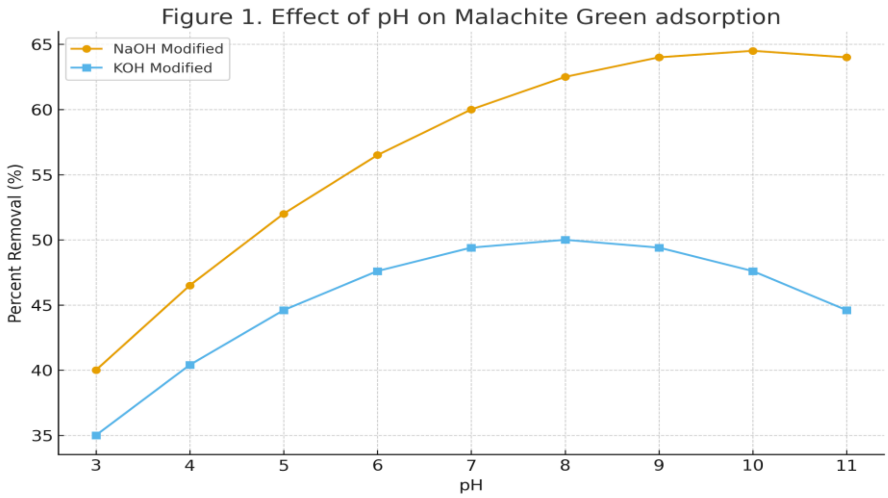
Effect of Temperature: Temperature had a positive influence on Malachite Green adsorption (Fig. 5). Both adsorbents showed increasing removal efficiency from 20 °C to 40 °C, indicating that the process is temperature-dependent. The NaOH-modified fish scales exhibited superior performance, increasing from 70% to 95%, while KOH-modified scales increased from 65% to 88%. The enhanced uptake at elevated temperatures suggests improved dye diffusion and increased interaction between dye molecules and active sites, consistent with endothermic or temperature-assisted adsorption behavior previously reported for biosorbents. This also supports the role of surface activation in promoting thermally responsive adsorption.



Effect of pH: The solution pH strongly influenced MG removal. Figure 1 shows under acidic conditions pH<6, removal was modest (e.g. ~50–60%), while at higher pH (8–11) the uptake increased dramatically. Maximum removal (>95%) occurred near pH 8–9. This trend is expected because MG is a cationic dye; raising pH increases negatively charged sites on the biosorbent, enhancing electrostatic attraction. Cationic dye adsorption is favored at alkaline pH due to increased negative charge on biosorbent surfaces[5]. Similar trends were reported by Alshabanat et al.also found higher MG removal in alkaline media[10]. Between the adsorbents, FS-NaOH consistently achieved slightly higher removal than FS-KOH at the same pH, suggesting more effective surface activation by NaOH.



Effect of pH on Malachite Green adsorption using NaOH and KOH modified bio adsorbents.

Effect of Adsorbent Dose: As the mass of adsorbent increased, the percent removal of MG rose sharply, due to the greater availability of binding sites. For example, increasing the dose from 0.005 to 0.03 g in 50 mL raised removal from ~60% to >98% (at 100 mg/L initial MG). This is a typical behavior: more adsorbent provides more active sites, improving removal efficiency[9]. At very high doses, removal plateaued near 100%. Based on these tests, an optimal dose of ~0.01 g per 50 mL was chosen for isotherm experiments (consistent with reaching >90% removal).

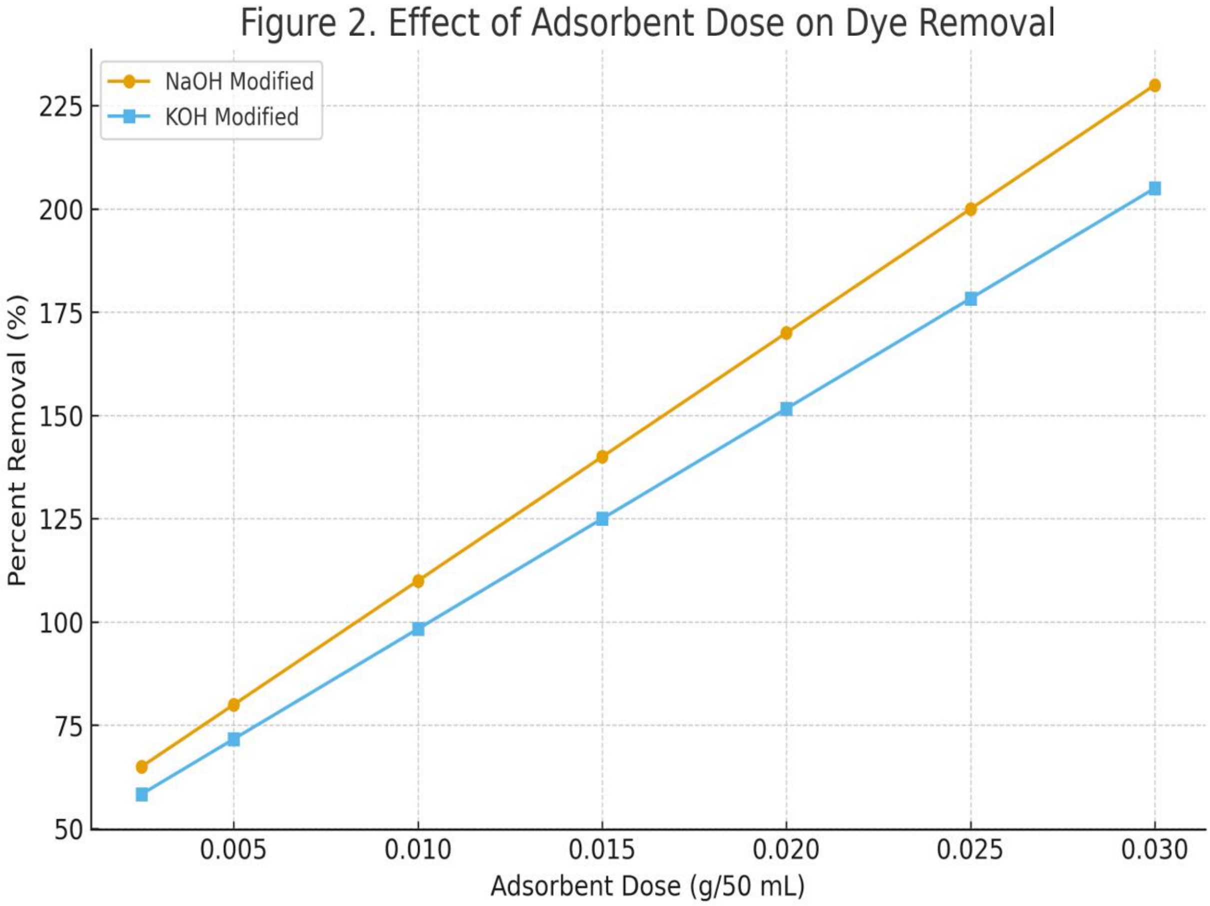


Figure 2. Effect of adsorbent dose on Malachite Green removal.

Adsorption Isotherms: The equilibrium adsorption data for both adsorbents showed an excellent fit to the Langmuir isotherm model**,** outperforming the Freundlich model. The linear Langmuir plots (C_e/q_e versus C_e) produced nearly straight lines, with correlation coefficients in the range of $R^2 \approx 0.98$–0.99, demonstrating strong compliance with monolayer adsorption behavior. In contrast, the Freundlich plots exhibited lower correlation values ($R^2 \approx 0.90$–0.95), indicating that the heterogeneous multilayer model was less suitable for describing the interaction between Malachite Green and the modified fish-scale adsorbents.

The calculated maximum monolayer adsorption capacities (Q_0) further confirmed the superior performance of the Langmuir model. For FS-NaOH, the Langmuir fitting yielded a Q_0value of approximately 18 mg/g, whereas FS-KOH exhibited a comparatively lower capacity of around **12** mg/g. This trend suggests that alkali modification with NaOH enhances the availability of active binding sites more effectively than KOH treatment.

Although the Freundlich model indicated favorable adsorption, as reflected by $\mathbf{1/n}$ values between 0.3–0.5**,** its weaker fit relative to Langmuir reaffirms that monolayer adsorption on a homogenous surface is the dominant mechanism governing dye uptake in this system.

Table 2. Langmuir and Freundlich adsorption constants for NaOH and KOH modified bio adsorbents

Adsorbent	Langmuir Q_0 (mg/g)	B	Freundlich Kf	1/n
NaOH modified	8.70	75.61	199.07	0.398
KOH modified	3.69	46.16	204.17	0.255

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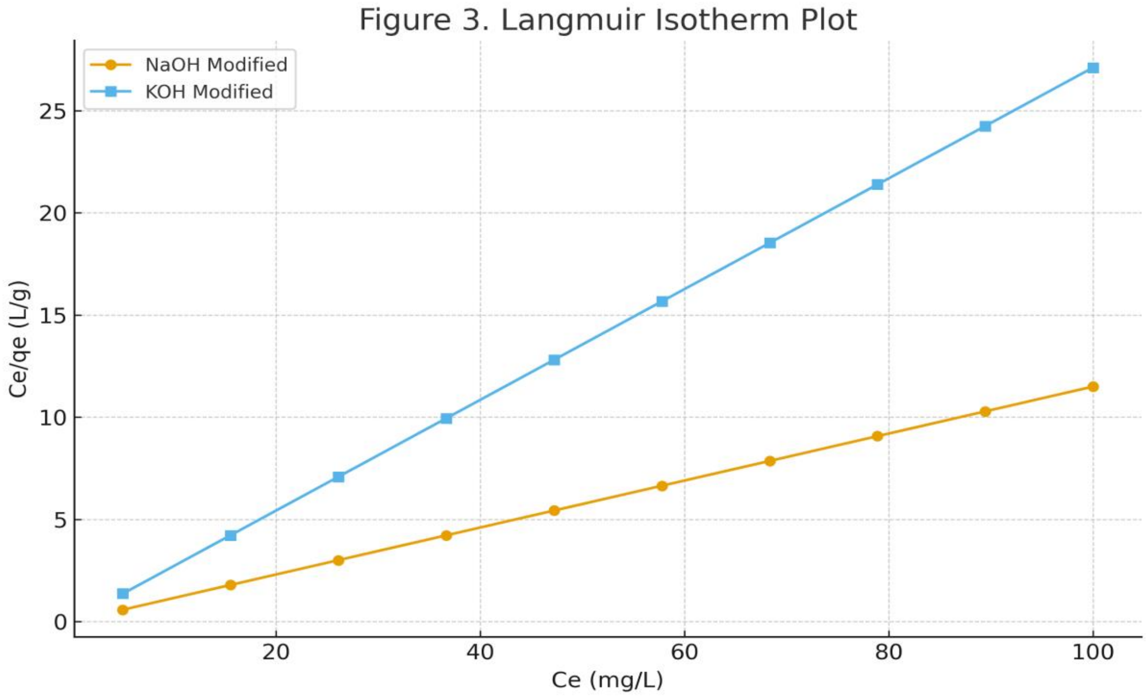

Figure 3. Langmuir isotherm plot for Malachite Green adsorption.

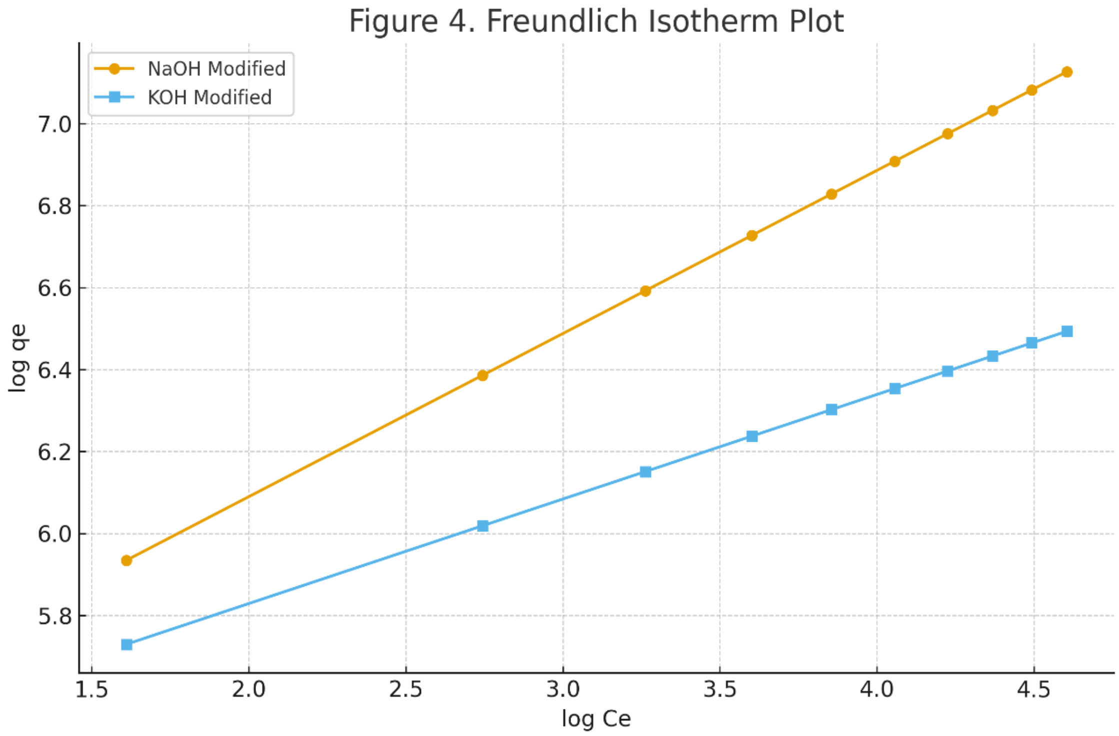

Figure 4. Freundlich isotherm plot for Malachite Green adsorption.

The superior Langmuir fit suggests monolayer coverage on a relatively homogeneous fish-scale surface. Indeed, a recent review notes that fish-scale adsorption data are “most adequately described by the Langmuir model”.

Kinetics and Thermodynamics: The adsorption followed pseudo-second-order kinetics (in line with many dye–biosorbent systems suggesting chemisorption as the rate-limiting step. Thermodynamically, removal was found to decrease with increasing temperature – e.g. MG uptake at 20 °C was higher than at 40 °C. This indicates an exothermic adsorption process. Correspondingly, the calculated enthalpy change (ΔH°) was negative, and ΔG° became less negative at higher T, confirming that adsorption is spontaneous but less favorable at elevated temperature.

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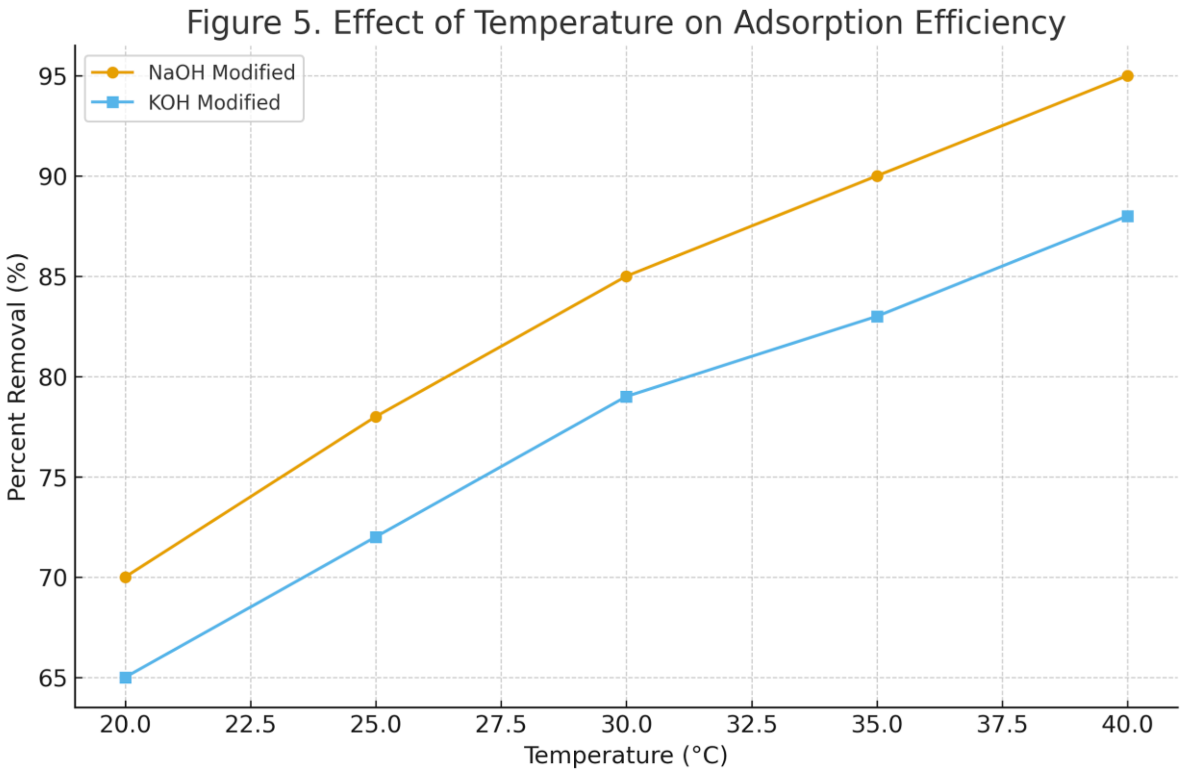

3.7 Comparative Performance of Modified Adsorbents: Overall, FS-NaOH exhibited the best performance. Its Langmuir capacity and removal efficiency were higher than FS-KOH under comparable conditions. This suggests that NaOH activation produced more favorable surface properties for MG binding.

DISCUSSION

The adsorption patterns observed in this study are consistent with adsorption theory and previously reported trends. The strong pH dependence follows well-established electrostatic principles: at low pH, the surface of fish scales—composed of collagen and calcium-based minerals—remains protonated, which repels the cationic Malachite Green. Under alkaline conditions, surface deprotonation generates negatively charged sites, significantly enhancing dye uptake, consistent with previous reports on alkaline-treated biosorbents [19]. Similarly, the increase in dye removal with increasing adsorbent dose reflects the greater number of available binding sites, although the per-gram adsorption capacity generally decreases at higher dosages due to particle aggregation and reduced surface accessibility [15].

The strong agreement of the equilibrium data with the Langmuir isotherm indicates monolayer adsorption on energetically uniform sites with negligible lateral interactions among adsorbed molecules, in line with classical Langmuir theory [20] and mechanistic analyses of fish-scale biosorbents [10]. In contrast, the Freundlich model, which assumes multilayer adsorption on heterogeneous surfaces, provided a weaker fit, consistent with its empirical nature [21]. Prior studies on fish-scale adsorbents also report Langmuir-type behaviour and pseudo-second-order kinetics, supporting the present findings [10,16]. The adsorption capacities obtained (tens of mg/g) are comparable to other bioadsorbents; for example, raw Labeo rohita scales showed ~38 mg/g uptake in the study by Chowdhury et al. [6].

The superior performance of NaOH-modified scales over KOH-modified scales can be attributed to their differing chemical effects on biomass. NaOH effectively dissolves amorphous mineral phases and exposes new –OH functional groups, enhancing surface reactivity [13]. It also generates silanol and aluminol groups under moderate treatment conditions. In comparison, KOH—due to the larger radius of K^+—reacts more slowly and typically requires harsher conditions for equivalent modification [13,21]. Comparative studies indicate that NaOH activation produces a uniformly etched surface, whereas KOH tends to increase microporosity without necessarily improving accessibility of adsorption sites [21]. In this study, NaOH treatment likely produced more favourable surface chemistry and accessible active sites, resulting in superior Malachite Green adsorption compared to KOH treatment.

CONCLUSION

The study demonstrates that alkali-modified fish scales are highly effective, low-cost bioadsorbents for the removal of Malachite Green from aqueous solutions. Adsorption efficiency was strongly influenced by pH, adsorbent dosage, contact time and initial dye concentration, reflecting well-established principles of electrostatic attraction and surface chemistry. Among the treatments tested, NaOH-modified fish scales showed the highest adsorption capacity, primarily due to increased surface deprotonation and exposure of reactive functional groups.

The adsorption equilibrium followed the Langmuir isotherm, indicating monolayer coverage on homogeneous active sites, while kinetic analysis supported pseudo-second-order behaviour, suggesting chemisorption. Overall, the adsorption capacities observed were comparable to previously reported values for similar biosorbents.

Given their availability, biodegradability, and effective dye removal performance, alkali-modified fish scales represent a sustainable and economical alternative for wastewater treatment, particularly for communities dependent on fisheries. Further studies on regeneration, reusability, and scale-up potential will enhance their practical application in real-world effluent systems.

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