Removal of Malachite Green in aqueous system using Groundnut based treated biochar

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Abstract

In the present study, we have prepared a biochar using the waste material of groundnut. Malachite Green is a synthetic refractory organic molecule that is created from triphenylmethane and has stable chemical features. MG and its metabolite, leucomalachite green, are carcinogenic and genotoxic, posing a risk to the immune and reproductive systems. According to researchers, MG has a negative influence on critical components of soil ecosystems, causing severe harm to the environment.

As a solution to the aforementioned problem, we have used this biochar to degrade MG from polluted water. We have also treated the biochar with HCl, zinc chloride, phosphoric and sodium hydroxide, tested the extent of removal at different pH, temperature, contact time and adsorption doses and results are discussed here.

Keywords: Ground nut, Biochar, Malachite Green, Bio-adsorbent.

Introduction

Water contamination begins with colour, which must be eliminated before discharge into bodies of water. Residual dyes are the primary source of colour in wastewaters produced by the textile and dye production sectors, among others[2]. Colour reduces light penetration, slows photosynthetic activity, decreases biota development and has a tendency to chelate metal ions, resulting in micro-toxicity to fish and other organisms[1]. It should be emphasised that dye pollution of drinking water at concentrations as low as 1.0 mg can add substantial colour, rendering it unsuitable for human consumption. Malachite green (MG) is a synthetic refractory organic molecule derived from triphenylmethane that has stable chemical characteristics[3,4].

MG, a water-soluble cationic dye, is commonly used in the textile sector for paper printing and dyeing, as well as in fisheries for antibacterial and antifungal properties[4,5]. MG and its metabolite, leucomalachite green, are carcinogenic and genotoxic, posing a risk to the immune and reproductive systems[4-9]. According to researchers[9,18], MG has a negative influence on critical components of soil ecosystems, causing severe harm to the environment. Since the mid-1990s, 28 EU member states have controlled the use of MG in the manufacturing and import of marine goods due to its hazardous nature[10]. In 2002, the Ministry of Agriculture of China issued Decree No. 235, which prohibits the use of MG in animal products and requires it to be undetectable in food. Several approaches have been explored to remove MG including adsorption, membrane separation, flocculation /solidification, chemical treatment and biological treatment[11-14].

Researchers prefer adsorption because to its inexpensive cost[3,9,14]. Made from biomass and frequently pyrolyzed in anaerobic conditions, biochar is a material high in carbon. Biochar has been examined for dye-containing wastewater treatment due to its porosity, hydrophobic surface, high specific surface area and great thermal stability[15]. A maximum of 2468 mg/g of MG could be adsorbed by the sample. Various technologies such as adsorption[19], membrane filtration[20], electro-coagulation[21], ion exchange[22], cloud point extraction[23] and advanced oxidation processes[24], are now used to remediate organic and inorganic contaminants in wastewater. Adsorption is a popular method for removing organic and inorganic contaminants due to its versatility, ease of application, cost-effectiveness and capacity to regenerate spent materials. When treating dirty water, it is best to use environmentally friendly adsorbents[25].

Biological, physicochemical and electrochemical treatment procedures are not suited for commercial usage due to long processing times, high costs, use of hazardous chemicals and secondary pollutant creation[26]. To effectively remove hazardous metals from contaminated water, eco-friendly processes are needed. Biochar has gained popularity due to its inexpensive cost, eco-friendliness, high adsorption capacity, large surface area and high porosity[27].

Biochar is an eco-friendly substance used in agriculture and mining to remove harmful metals, to manage water pollution and to reduce greenhouse gas emissions. Adsorption using green adsorbents is gaining attention due to its ease of operation, high efficiency, low energy requirements, economic feasibility and flexibility in primary and secondary contaminant removal[28].

Biochar from biomass has received significant attention for its ability to effectively remove harmful metals and pollutants from wastewater and water sources. Biochar's unique features and great thermal stability make it suitable for several industrial uses including the removal and adsorption of hazardous metals[29]. Biochar made from industrial and agricultural waste is becoming increasingly popular due to its biodegradability, economic feasibility and low cost.

Metal ion adsorption on biochar is primarily determined by the ion exchange surface and chemical crosslinking between hazardous metals and functional groups on the biochar surface. Another study utilised grape processing industry waste to create activated carbon for adsorbing cationic and anionic dyes[33]. Biochars generated from wood and wastewater-sludge were used to absorb sulfamethoxazole, a human and veterinary antibiotic. Researchers modified biochar with amino acids to improve its ability to adsorb Cu^{2+} ions from synthetic water. Two commercial biochars (Coconut shell and Bamboo) and homemade graphene were tested for adsorption of seven antibiotics[34].

In this work, ground nut powder was carbonized to prepare biochar which was further modified by chemical activation. The impregnating agents are hydrochloric acid, phosphoric acid, zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH). The next phase was conducting batch adsorption studies to investigate the adsorption of the pollutant malachite green dye (MG). The plausible mechanism of adsorption for MG dye was also hypothesized.

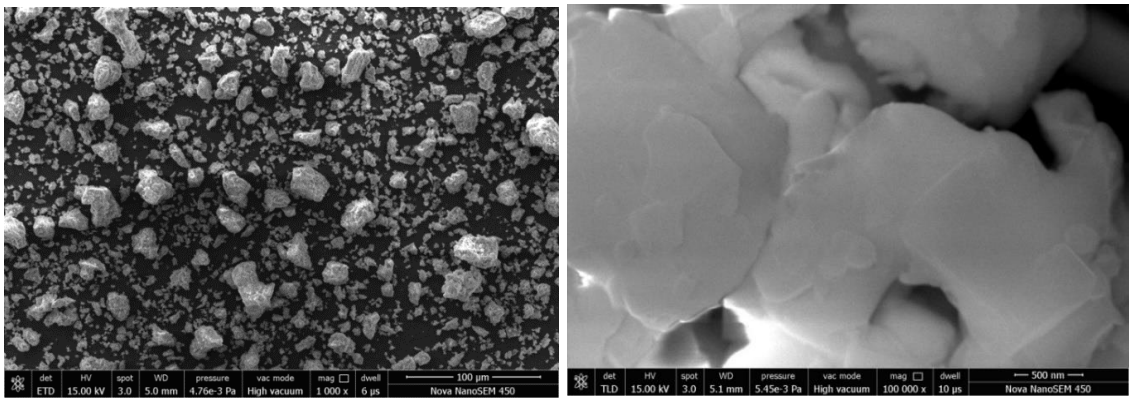
Material and Methods

Preparing biochars and stock solution: Groundnut shells collected from local market were converted into biochar using a Muffle furnace. We used two different methods to create biochar from groundnut or peanut shells: slow pyrolysis, which took place at 350 ± 5°C for 60 and 180 minutes and rapid pyrolysis, which took place at 700 ± 5°C for 45 and 90 minutes. The biochars were crushed and put through a 2 mm screen after cooling.

Results and Discussion

FESEM: SEM pictures of the as-prepared samples at different magnifications are displayed. The surfaces exhibited irregular fluffy structures with holes suggesting that NaOH degraded glycosidic connections in cellulose and hemicellulose. As opposed to this, lignin's cleaved surfaces have active areas in the aryl linkages that can aid in the adsorption of MG macromolecules.

The impact of bioadsorbent particle size: Because they varied the overall surface area available for dye sorption, the sizes of the bio-particle sorbent had a substantial impact on its sorption capabilities (table 1, figure 1). Smaller particles removed more dyes than larger ones, owing to the link between sorbent particle size and sorption capacity. q. The sieve analyzer produced different sizes of bio-adsorbent. Equilibrium was achieved faster with smaller bio-adsorbent particles than larger ones. The increased overall surface area provided more sorption sites for the metal ions.



SEM Pictures

Table 1
Seive size and percentage removal

Sieve size	% Removal
0.159	70
0.257	52
0.48	50
0.70	49
0.77	47
2.1	46

Table 2
Various treatments of biochar

Samples	% Adsorption
Biochar	**70%**
HCl	56%
Phosphoric acid	87%
Zinc chloride	80%
NaOH	92%

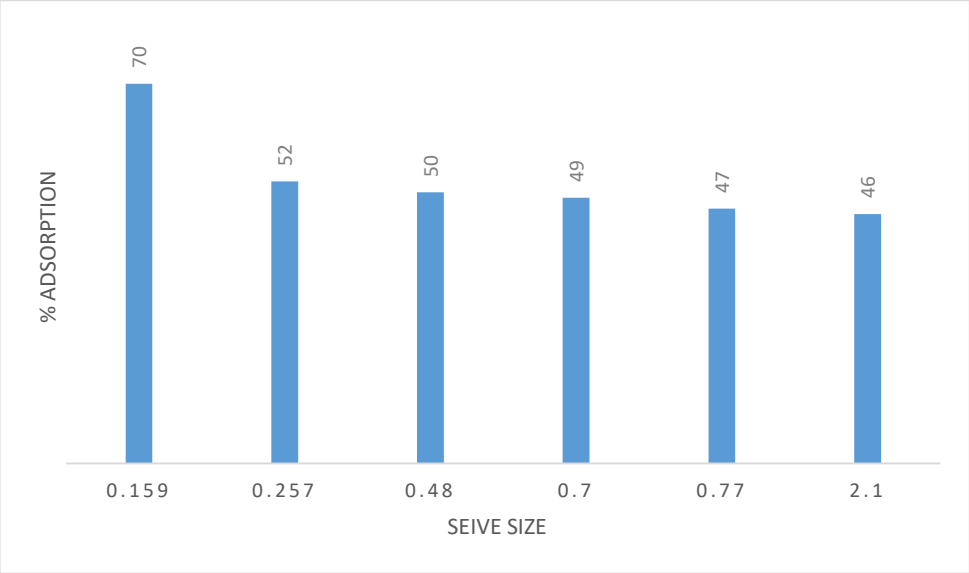


Figure 1: Graph of sieve size and percentage removal

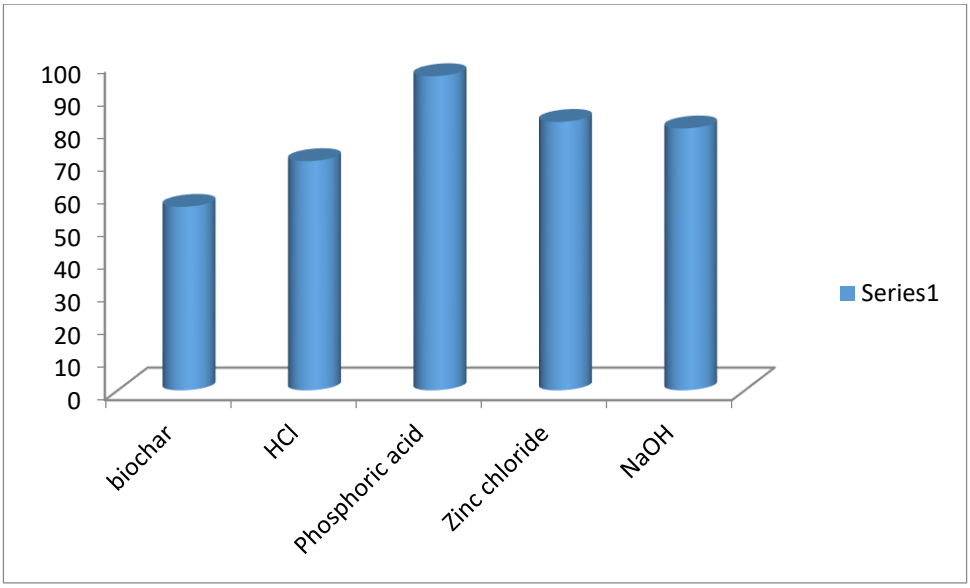


Figure 2: Graph of pre-treatment of biochar and percentage removal

The effects of primary therapies in different conditions: Two hours of 200 rpm shaking were used to test the impact of pretreatment on waste biomass. 25 mg/L of dye and 0.1 g/L of pretreated bio-adsorbent with a size of 0.155 mm were combined. Figure 2 displays the q values for dye sorption of untreated, chemically and physically altered biochar. The sorption capacity of the biomass has risen due to the removal of mineral materials and the formation of new sorption sites on the surface during the boiling process (table 2). Because heat treatment impeded intracellular absorption, it reduced the uptake of metals in biomass. Following an acidic pre-treatment, two parameters determine a given biomass's sorption capability.

The two parameters that affected the bioadsorbent's ability to absorb were similar to those in basic pretreatment. The biomass was cleaned up. Furthermore, above a specific alkali concentration, the proportion of amino groups in proteins that could participate in dye binding significantly decreased. In theory, deproteinization should produce a dye.

The effect of pH: The experiment using biochar was conducted to determine how pH affects dye adsorption. To accomplish so, mix 50 mL of a 15 mg/L dye solution with 0.1 g of chemically altered charcoal powder and 0.1 g biochar. For pH changes ranging from 4 to 8, samples were shaken at room temperature for 10 hours at 300 RPM with 1 N NaOH (figure 3, table 3). The pH impact is then absorbed when the biochar is combined with a 1 litre solution of 0.1M $FeSO_4$. The adsorption of dye on adsorbents is influenced by the pH of the solution.

It is demonstrated that adsorption rises with solution pH. Dye absorption was low because H^+ and dye competed for the same surface active sites on the protonated adsorbent. Dye absorption increased when the pH climbed from 4-6 and

the fixed biomass content (0.05 g/L). As can be seen, the dye's capacity to attach to surfaces is lowest at pH 4 and reaches as high as 60% at pH 8.

The effect of quantity of adsorbent: The elimination of dye from an aqueous solution is shown against the mass of biochar in figure 4. The adsorbent dosages for 50 ml of dye solution ranged between 0.02 and 0.3 g. Other parameters were constant including pH (4.0), contact time (2 hours) and temperature (50 °C). The results reveal that as adsorbent mass grows, dye removal percentage increases but adsorption capacity declines. This is because raising the dosage of biochar allows more active sites to interact with dye (table 4). Consequently, a higher proportion of dye is eliminated from the aqueous solution. However, the aggregation of biochar inside greater doses of adsorbent may produce unsaturation of active sites, resulting in a reduction in adsorption ability. Aggregation reduces the adsorbent's total surface area.

Table 3
Different pH values and percentage removal

pH	% removal
4	56
5	57
6	58
7	60
8	63

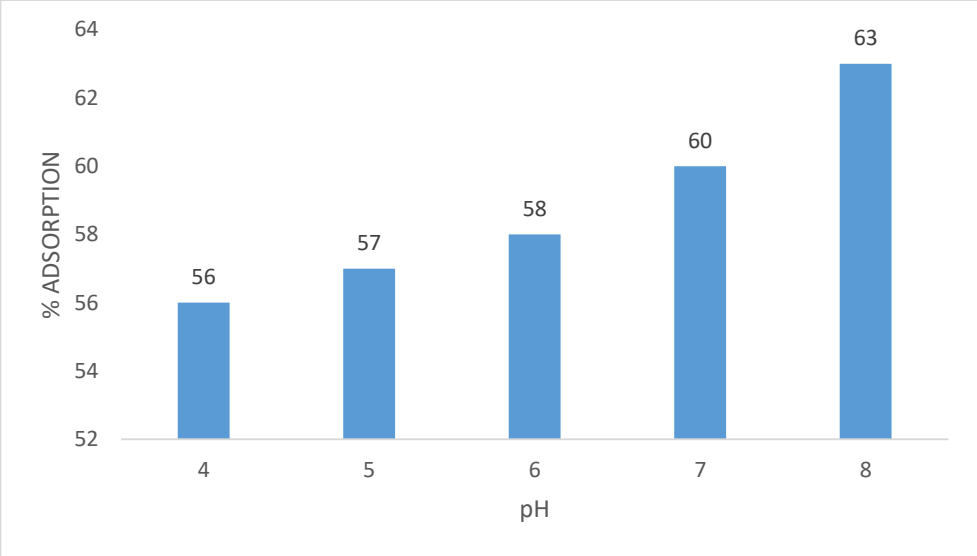


Figure 3: Graph shows percentage removal with different at different pH.

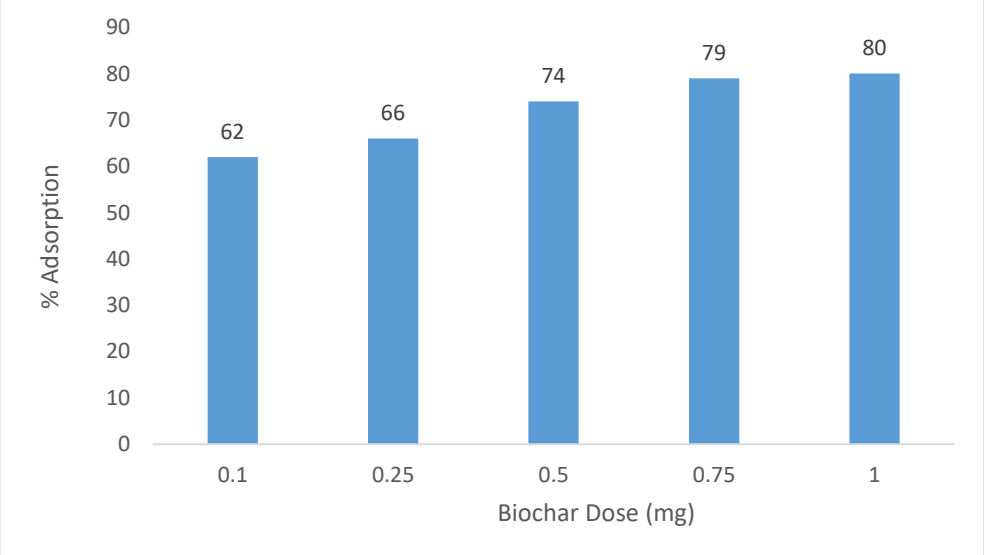


Figure 4: Graph of adsorption dose and percentage removal

Table 4
Different adsorption doses with percentage removal

Dose (mg)	Biochar
0.1	62
0.25	66
0.5	74
0.75	79
1	80

Table 5
Contact time with percentage removal

Time (min.)	Biochar
15	70
25	72
35	71
65	74
125	77
245	79

Table 6
Temperature change with percentage removal

Temperature (^{0}C)	Biochar
20	70
30	72
40	74
50	75

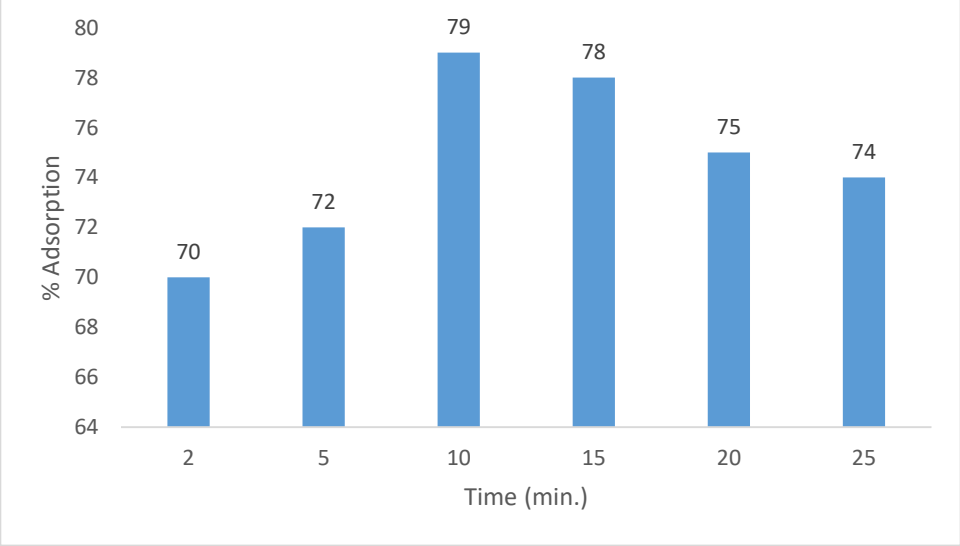


Figure 5: Graph of contact time with percentage removal

The effect of contact time on adsorption: The impact of contact time on dye removal by biochar is depicted in figure 5. Dye adsorption happened very fast at the three support ports, induced by caustic soda (NaOH) and other reagents, reaching saturation within 10 minutes (table 5). With natural support, adsorption proceeds much more slowly and saturation occurs after about ten minutes.

This is explained by the initial vacancy in the adsorption sites, which makes it easy for dye molecules to occupy them and to provide a high adsorption rate. One possible explanation for the delayed adsorption after this initial event is a slower diffusion of dissolved molecules via the adsorbent's pores.

Temperature impact on adsorption: Figure 6 shows how temperature influences dye adsorption by biochar. The maximum dye adsorption on the pretreated material occurred at 50°C (table 6). The process appeared to be endothermic since dye adsorption rose as the solution's temperature rose. Elevated temperature made the dye transfer from the solution to the exposed portions of the biochar while also reducing the thickness of the top layer of biochar.

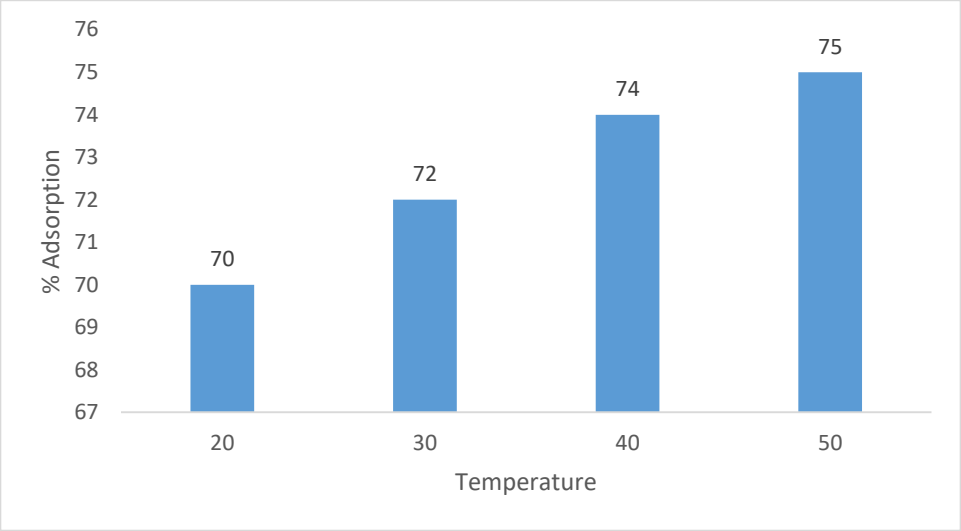


Figure 6: Graph of effect of temperature on percentage removal

Conclusion

To remove malachite green colour from aqueous solutions, we developed a bio-adsorbent based on efficient groundnut shell waste. The solid-liquid ratio, pH, temperature of the solution, amount of adsorbent and length of contact time can all be changed. Ground nut biochar has been discovered to be a high-capacity, economically viable and cost-effective adsorbent for dye removal.

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(Received 08th October 2024, accepted 29th November 2024)