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Comparative Studies of the Adsorption of Dyes on Raw Fish Bone

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Abstract:

The prepared raw fish bone was used as the effective sorbent for the removal of organic dyes. The waste fish bone was collected from the local market in Banmaw, Kachin State. Physicochemical properties of fish bone such as moisture, pH, bulk density and specific surface area were determined by recommended methods. Fish bone sample was characterized by modern techniques such as EDXRF and SEM analyses. Sorption studies of fish bone sample were carried out by spectrophotometric method. Two model dyes Congo red as acid dye and Malachite green as basic dye were used in sorption experiments. The effect of sorption parameters such as initial concentration, contact time and adsorbent dosage on the removal of specified colored dye was investigated. The maximum removal percent of Congo red was found to be 62.33% at the specified conditions such as initial dye concentration (50mgL^{-1}), dosage (0.1g/20mL), and contact time (90min). In the case of Malachite green as sorbate, the maximum removal percent was detected as 76.04% under the conditions which were the same as sorbate Congo red.

Keywords:

Adsorption, Adsorbent, Dyes, Malachite Green, Congo Reds

1. Introduction

Effluent discharged from industries such as textiles, paper, plastic and food is one of the main sources of environmental pollution. These industrial effluents usually contain synthetic dyes, which are toxic and carcinogenic for aquatic living organisms and humans [1]. However, it's difficult to remove dyestuffs from wastewater in a conventional way since they are non-biodegradable and resistant to light [2]. Several methods have been applied to the treatment of colored effluents, such as coagulation, photo-catalytic degradation, membrane separation, biological treatment, and adsorption [3]. Among these methods, adsorption is one of the most promising methods for its easy operation, high efficiency and low cost [3]. Hydroxyapatite (HA), (Ca_{10} $(PO_4)_6$ $(OH)_2$) has been marked as a potential adsorbent due to its specific structure and adsorption affinity to organics and metal ions. HA is one of the main components of natural bone meal [4]. Fish bone is the waste and cheaper source to obtain natural hydroxyapatite. In the last decades, researchers have paid to synthesize hydroxyapatite. Fish bones have been directly used as an adsorbent which results in the lower removal capacity for its impurity compared with pure HA [5]. The aim of the study is to examine the ability of raw fish bone for removing Congo red and Malachite green from synthetic solutions. After characterization of fish bone, the adsorption of Congo red and Malachite green were studied by taking into account the effects of adsorption parameters. A particular interest has been focused on the spectroscopic study, before and after adsorption. In present study, fish bones were powdered, and it's using as adsorbents under optimum conditions, for the removal of Congo red and Malachite green dyes from aqueous solution.

2. Experimental

2.1. Materials and Methods

All chemicals and reagents used in this research were analytical and reagent grade. In all the investigations, the recommended and standard procedures of both conventional and modern techniques were employed. Instruments employed in this work consist of lab wares, glass wares and other supporting facilities. The sorption experiments were carried out in the Laboratory of the Department of Chemistry, Banmaw University.

2.2. Preparation of Adsorbents

Fish bones used as adsorbent were purchased from the local market in Banmaw Township, Kachin State. The bones were first washed with warm water to remove flesh on the bones then rinsed several times with distilled water. The bones were then dried in the sun for a period of two weeks. They were then ground using mechanical grinder and sieved with 80-mesh size [6].The resultant raw fish bone sample was stored in a sealed bottle and denoted as FB. The raw fish bone was analyzed for its chemical and physical characteristic such as pH, moisture, bulk density and surface area. Moreover, its surface morphology and mineralogical analysis were carried out by SEM and ED XRF. The prepared raw fish bone sample is illustrated (Figure 1).

Figure 1. *The prepared raw fish bone.*

2.3. Preparation of Adsorbate

The dye Congo red (Chemical formula = $C_{32}H_{22}N_6O_6S_2Na_2$, Formula weight = 696.65 g/mol) and Malachite green (Chemical formula = $C_{23}H_{25}ClN_2$, Formula weight = 364.911 g/mol) [7] were supplied by British Drug House Chemical Co.Ltd. The stock solution (1000 mgL^{-1}) of dye was prepared by dissolving 1000 mg (accurate weighed) of dry powered dye in distilled water (1L) [8]. The experimental solutions at desired concentrations were obtained by diluting the stock solution.

2.4. Color Removal of Dye

a. Effect of initial concentration on dye removal: Different concentrations of dye solution were prepared from 10 mgL^{-1} to100 mgL^{-1}. Accurate weights (0.1 g) of the sorbents (raw fish bone) were equilibrated with an appropriate concentration of the test solution. Then they were shaken by electric shaker for 1 h with 150 rpm of rotation speed [9]. After shaking the solution were filtered. The remaining concentrations of Congo red and Malachite green were determined by using UV 259 spectrophotometer at 497nm and 624nm. The results are described in Table 2 and Figure 3. Generally, the amount of dye removal was calculated from following equation:

$$\text{Removal \%} = \frac{(A° - A)}{A°} \times 100$$

A°= concentration of dye before adsorption
A = concentration of dye after adsorption

b. Effect of dosage on dye removal: Accurately weighed raw fish bone sample varying from 0.02 g to 0.16 g were thoroughly mixed with 20 mL of 50 mgL^{-1} dye solutions. Then they were shaken by electric shaker for 1 h with 150 rpm of rotation speed. After shaking the solutions were filtered. The remaining concentrations were determined by UV 259 spectrophotometer at 497 nm for Congo red and 624 nm for Malachite green. The results are shown in Table 2 and Figure 3.

c. Effect of contact time on dye removal: In the contact time experiment 0.1 g sorbents (raw fish bone) of known particle size were brought into contact with a fixed volume of each dye solution (20 mL) at a prefixed initial dye concentration. Then they were shaken by electric shaker for 1 h with 150 rpm of rotation speed. After shaking the solutions were filtered. The contact time measurements were made at ambient temperature. The remaining dye concentrations were determined by using UV 259 spectrophotometer. Using the equilibrium contact time the nature of the sorption properties of various dyes was evaluated. The decolorization of Congo red and Malachite green dyes with raw fish bone samples is shown in Table 2 and Figure 3.

3. Results and Discussion

3.1. Physicochemical Properties of Fish Bone Sample

Table 1 indicates that the bulk density, moisture, surface area and pH of raw fish bone in the form of the proximate analyses. The bulk densitiy and pH value of raw fish bone are 0.81gcm^{-3}.and 6.79. The higher the bulk density of sorbents, the more porosity on the surface of sorbent can exist. The surface area and moisture content of raw fish bone are 42 m^{2}g^{-1} and 8.40 %. According to these results, it can be found that the raw fish bone has adsorptive nature to be used as adsorbent for the organic dyes removal.

Table 1. *Physicochemical Properties of Fish Bone.*

No.	Parameters	Values
1	Moisture (%)	8.40
2	Bulk density (gcm^{-3})	0.81
3	pH	6.79
4	Surface area (m^{2}g^{-1})	42

3.2. Characterization of Fish Bone Samples

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a. ED XRF Analysis: It is clear from Figure 2 that the chemical analysis of raw fish bone sample shows calcium, and phosphorus in major constituents and others in minor constituents. According to literature, fish bone is composed of phosphate compound that hydroxyapatite (HA, Ca_{10} $(PO_4)_6(OH)_2$) has been marked as a potential adsorbent due to its specific structure and adsorption affinity to organics and metal ions[10]. HA is one of the main components of natural fish bone. Therefore, fish bone can be directly used as an adsorbent to treat wastewater and removal for organic dyes.

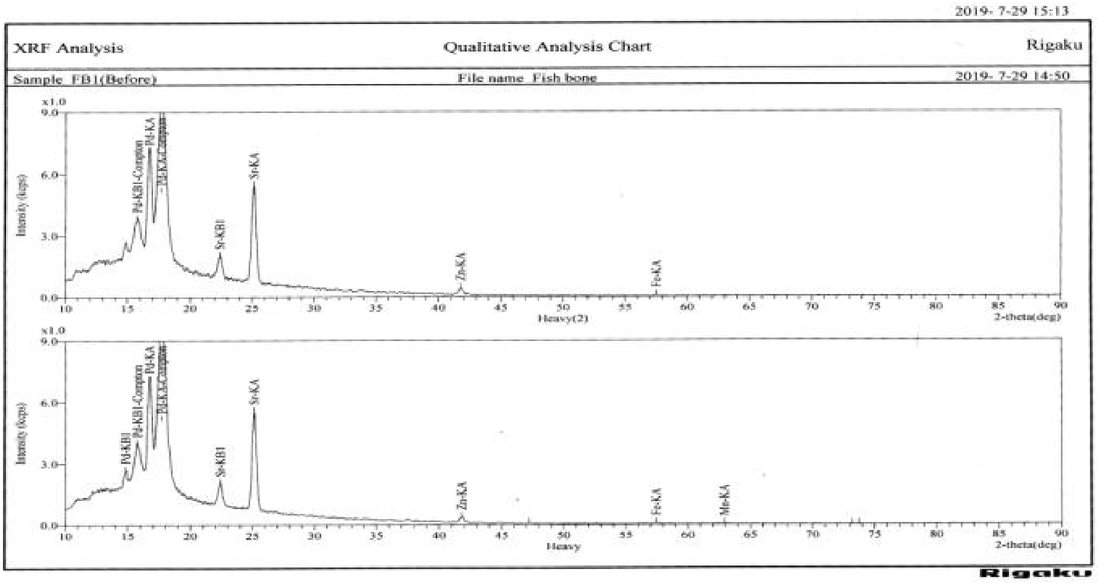

Figure 2. *EDXRF spectrum of raw fish bone.*

Table 2. *Elements present in raw fish bone.*

Elements	Relative Abundance (%)	Elements	Relative Abundance (%)
Mg	0.67	Ca	75.20
Si	0.58	Mn	0.10
P	22.20	Fe	0.08
S	0.34	Zn	0.11
K	0.13	Sr	0.50

b. SEM analysis: The SEM images for surface characterization of the fish bone before and after adsorption are presented in Figure 3(a) (b) and (c). The SEM model is Jeol-JSM-5610. It is found that the fish bone has a rough surface with heterogeneous holes and pores that make a large free surface area, which indicates that dyes can be adsorbed onto its surface. After adsorption, the surface of fish bone is relatively smoother and less porous because of the formation of a layer over the adsorbent surface.

c. The effect of initial concentration: Table 2 and Figure 3 show the removal of both dyes by a constant amount of adsorbent with initial concentration in range from10 mgL^{-1} to 100 $mgL^{-1}$of dye solution. Figure 3 shows the corresponding data in terms of percent removal with respect to initial concentration. It can be seen that as the percent removal of both dyes decrease with increase in initial concentration. For the initial concentration 50mgL^{-1} in 20 mL of dye solution and 0.1 g of fish bone, it was found that after 90 min agitation time, the amount of Congo red and Malachite green being adsorbed is 62.33 % and 76.07 %.

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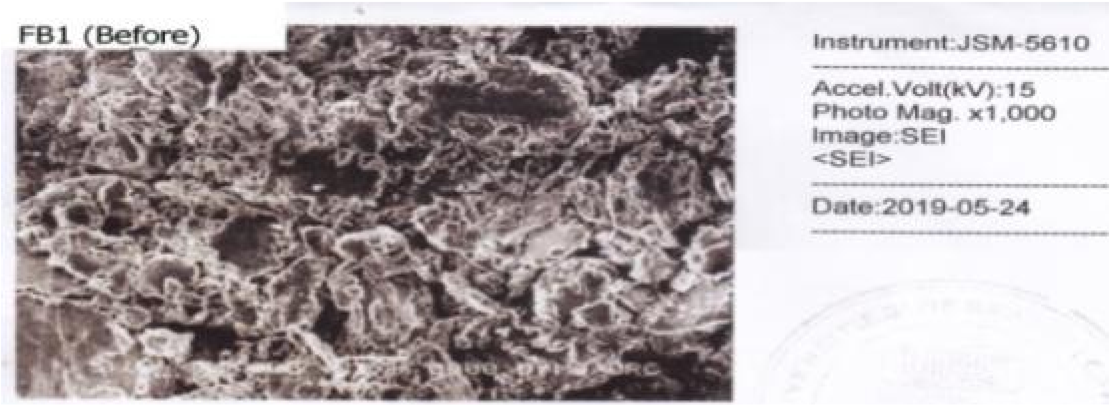

Figure 3a. *FB1 (Before).*

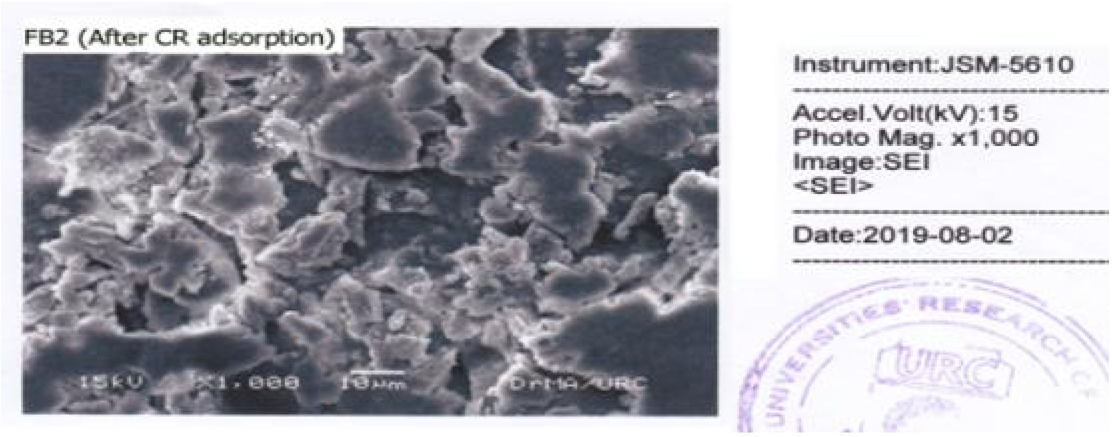

Figure 3b. *FB2 (After CR adsorption).*

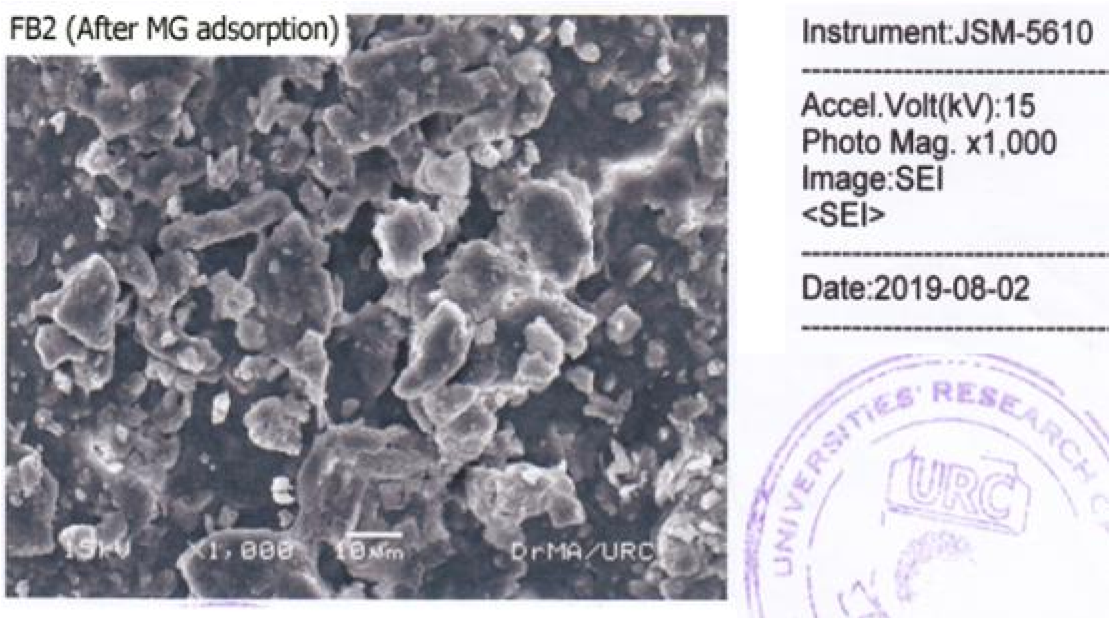

Figure 3c. *FB2 (After MG adsorption).*

Figure 3. *SEM image of fish bone (a) before dye removal (b) after the removal of congo red and (c) after the removal of malachite green.*

4. Conclusion

In this study, the adsorption of two dyes from aqueous solution by the fish bone as a low-cost adsorbent was examined. The physicochemical properties of raw fish bone are determined by conventional methods and EDXRF shows that raw fish bone sample contain phosphorus and calcium in major constituents and others in minor constituents. The SEM figures indicate that fish bone sample has a rough surface with heterogeneous holes and pores that make a large free surface area, which indicates that dye can be adsorbed onto their surface. The effect of contact time, initial concentration and dosage are also investigated for the removal of dyes on fish bone sample. According to the results, it is deduced that the percent removal of dye increases with the increasing time and decreases with the increasing initial concentration. Moreover, it is found that the percent removal of dye increases with the increasing dosage. The overall results showed that fish bone can be effectively used as a low-cost adsorbent for the removal of organic dyes from wastewater.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Acknowledgement

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