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Removal of Methyl Orange from Aqueous Solutions Using Thermally Treated Egg Shell (Locally Available and Low Cost Biosorbent)

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Abstract
The effluent water of any industries such as textile, leather, paper, printing, cosmetic, etc. contains large amount of hazardous dyes. There is a huge number of treatment process as well as adsorbent which are available in low cost adsorbents for the removal of hazardous dyes from aqueous waste by adsorption treatment. In this study, thermally treated egg shell was used as an adsorbent for the removal of methyl orange from an aqueous solution. All operating parameters like; adsorbent dose, contact time, particle size and initial concentration of methyl orange were effective on their removal efficiency of the dye.
Key words: Adsorption, egg shell, methyl orange and Uv-vis spectroscopy

1. INTRODUCTION

Progress in industrialization in particular textile industries have led to the discharge of unprecedented amount of wastewater containing synthetic dyes, which pollutes the rivers and consequently causes harm to human and other living organisms [1]. A majority of the used dyes are azo reactive dyes which are bright in color due to the presence of one or several azo (─N═N─) groups associated with substituted aromatic structures [2]. Methyl orange (MO) is a commonly used **an anionic** monoazo dye in laboratory assays, textiles and other commercial products and has to be removed from water due to its toxicity [7-8].These dyes or their breakdown products are toxic to living organisms [3]. Furthermore, dyes in wastewater are difficult to remove because they are stable to light, heat and oxidizing agents. In short, they are not easily degradable [4].

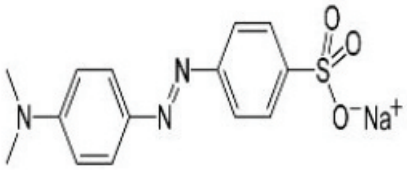

Figure 1. Molecular structure of Methyl Orange

Dyes are chemicals, which on binding with a material will give color to them. Dyes are ionic, aromatic organic compounds with structures including aryl rings, which have delocalized electron systems. The color of dye provided by the presence of a chromophore group. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalized electrons. The Chromogen, which is the aromatic structure normally containing benzene, naphthalene or anthracene rings, is part of a chromogenchromophore structure along with an auxochrome. The presence of ionizing groups known as auxochromes results in a much stronger alteration of the maximum absorption of the compound and provides a bonding affinity. Colored dye wastewater arises as a direct result of the production of the dye and because of its use in the textile and other industries. There are more than 100,000 commercially available dyes with over 7 x 10^5 of dyes produced annually worldwide [11].

In recent years, numerous low cost natural materials such as rice husk [4], activated carbon prepared from coir pith [9] and fruit shell [13] have been used and investigated for removal and adsorption of MO from aqueous solution.

Meanwhile, eggshells are used in enormous quantities by food manufacturers, restaurants and household and the shells are disposed of as solid waste. Investigations have been conducted to explore the possibility of useful applications of eggshells, especially for wastewater. Research has shown that eggshells and eggshell membrane may be used as an adsorbent for cationic dye[15], azo dye[16] and malathion[17], however, there has so far been no study reported in academic literature related to the use of powdered eggshells as an adsorbent for removing MO from aqueous solution. Therefore the main aim of this study was the use of powdered eggshells as adsorbent material for removal of MO from aqueous solution. The effects of adsorbante concentration, adsorbent dose, particle size and effect of contact time of MO were investigates. Objective of the current work are

- To remove organic dyes from aqueous solution by using natural product as bioadsorbane

- ✓ To study the effect of operating parameters (initial adsorbante concentration, adsorbent dosage, contact time and particle size)

1.1. Treatment for Dyes Removal

The removal of colored and colorless organic pollutants from all industrial waste water is difficult to treat. This is due to their complex aromatic molecular structure and synthetic origin, which make them inert and non-biodegradable [9]. There are different methodologies that are used to remove dyes. This includes physical – chemical fluctuation combined with fluctuation, electro flotation, membrane filtration, electro kinetic coagulation, precipitation, biological treatment under aerobic or an aerobic conditions, photocatalytic degradation and adsorption, conditions [2].

1.2. Effect of various parameters on dye removal

Adsorption isotherm is a functional expression for the variation of adsorption relative to the concentration of adsorbate in the bulk solution at constant temperature. It describes the relation between the adsorbate
adhered by adsorbent and the adsorbate equilibrium concentration [6]. The parameters that determine the shape of an isotherm are adsorbent dosage, initial dye concentration, and contact time and particle size of the adsorbent.

2.7.1. Effect of Adsorbent dosage

The adsorption of methyl Orange dye and carbon were studied by varying the carbon concentration mostly from (10-250mg/50ml) for 60 mg/l of dye concentration. The percentage sorption increased with the increased in absorbent dosage [20]. This is attributed to increased carbon surface area and availability of more adsorption sites [10]. The percentage uptake of methyl Orange dye increased very fast at low dosage up to a point, after which the increase in dosage did not increase the uptake of methyl Orange significantly. There are many factors which can contribute to this adsorbent dose effect. These are:-

- As the dosage of adsorbent increased, the adsorption sites remain unsaturated during the adsorption reaction leading to drop in adsorption capacity.
- The aggregation /agglomeration of adsorbent particles at higher doses, which lead to decrease in the surface area and an increase in the diffusion path length [13]. Increase the adsorbent dosage at constant methyl Orange concentration provided more available adsorption sites for dye and thus increased the extent of dye removal. Therefore the removal of dye increases as the dosage of composite increases but up to optimum amount.

2.7.2. Effect of initial dye concentration

Adsorption of methyl Orange at various concentrations was tested using different adsorbents and it was found that percent adsorption decreased with increase in initial dye concentration. But the actual amount of methyl Orange dye adsorbed per unit mass of carbon increased with increased in dye concentration of dye. Because at lower concentration, the ratio of the initial number of methyl Orange dye molecules to the available surface area is low subsequently the fractional adsorption becomes in dependent of initial concentration. However, at high concentration, the available sites of adsorption become fouler and hence the percentage removal of methyl Orange dye is dependent up on initial concentration [10]. As concentration increases the percentage removal decreased but the adsorbed amount of dyes increased. At low adsorbate concentration, the ratio of surface active sites to total dye is high. Hence the dye ions could interact with the sorbent to occupy the active sites on the carbon surface sufficient and can be removed from the solution [5]. But with the increase in adsorbate concentration, the number of active adsorption sites is not enough to accommodate dye ions. Generally, as the initial dye concentration plays an important role in the adsorption capacity of dye [5].

2.7.3 Effect of contract time

The extent of dye removal by activated carbon increased with the increased of contact time. The removal of dye by adsorption using activated carbon was found to be rapid at the initial period of contact time and then become slower with the increase of contact time [19]. This is due to the strong attractive forces between the dye molecules and the adsorbent. As contact time increased, initially percentage removal also increased, but after some time it gradually approached almost constant value at after equilibrium reached [20]. The changes in the rate of removal with time might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high.
The dye up take rate by adsorbent was decreased significantly due to the decrease in adsorption sites. Decreased removal rate indicates the possible monolayer of adsorbate on the outer surface and pores of the adsorbent leading to pores diffusing on to inner surface of adsorbent [16].
The removal of methyl Orange dye organic kaolin composite was found to increase, reach a maxim value with increase in contact time [18]. The removal of methyl Orange dye from aqueous solutions by adsorption on organic kaolin composite increases with time until equilibrium is attained [1].

2.7.4. Effect of particle size

The percentage removal of dye decreased with increase in particle size of the carbons was due to non-availability of more surface active sites for adsorption maximum percent removal is possible with particle size below 45 mm due to the presence of large number of smaller particles which provide the sorption system with larger surface area available for the dye adsorption [8].

2. MATERIALS AND METHODS

2.1. Apparatus

The materials employed in this work include among others, spectrophotometer (Model 722, Shanghai), Electronics weighing balance (Ohaus,USA), Dryer/ Oven, Sieve, Conical flasks, Stop watch, Centrifuge, egg shell , methyl orange(Beijing Chemical Co.). All chemicals used were of analytical grade.

2.2. Chemicals and reagents

Sodium bi carbonate, Sulfuric acid, Methyl Orange dye

2.3. Experimental Site

Egg shell sample was collected from different cafeterias of Adigrat town which is located in the northern part of Ethiopia, Tigray region 898km far from Addis Ababa and 120km away from north of Mekelle city, which is capital city of Tigray regional state.

2.4. Biosorption Study

2.4.1. Adsorbent collection and preparation

The eggshell used in the experiment were collected free of charge from different hotels located in Adigrat, Ethiopia using plastic bags and washed with tape water to remove surface adsorption then dried at 105 °C for 1 h in a convection oven, grounded using mortar and pestle then socked with H_2SO_4 solution 1:1 ratio weight per volume for overnight to increase adsorption efficiency.

Then washed with distilled water till it attained neutral P^H and treated 2% $NaHCO_3$ over night in order to remove excess of acid present then it was washed with distilled water to remove dirt and boiled to remove color and dried at oven at 105C^o for 1 hours and activated in muffle furnace at 450C^o for an 1 hours.
Finally allowed to pass through 0.5, - 2 mm sieves. Then the powdered eggshell was washed with distilled water to remove dirt and boiled to remove color. The eggshell powder comprises of 94% $CaCO_3$, with small amount of $MgCO_3$, Calcium phosphate and other organic matter including protein [20].

2.4.2. Preparation of Adsorbate solution

Methyl Orange, 4-dimethylaminoazobenzene-4'- sulfonic acid (MO), a bright orange crystalline powder with a molecular formula of $C_{14}H_{14}N_3NaO_3S$, molecular weight of 327.34 , melting point around 300 ^oC and maximum absorption (λ_{max}) 465nm used without further purification. The molecular structure of MO a water soluble dye is shown in Figure 1.MO is dark red in aqueous solution below pH 3 and the color brightens to orange as pH increases. A stock solution of MO was prepared by dissolving 12.5 g of the dye in 1 L of distilled water and filtered via Whatman filter paper (No. 1). The prepared stock solution was then wrapped with aluminum foil and stored in a dark to prevent exposure to direct light.

2.5. Batch Adsorption Studies

Batch mode adsorption studies for individual eggshell were carried out using 250 ml Erlenmeyer flask. The effects of different parameters such as adsorbate concentration, adsorbent dose were studied. The Erlenmeyer flasks were pretreated with the respective adsorbate for 24 hours to avoid adsorption of the adsorbate on the container walls. Standard solutions of the dye were mixed with the egg shell and agitated at different agitation rate on a mechanical shaker. This was carried out by varying the dye concentrations, and the mass of egg shell used for adsorption. Finally, the resulting suspension of each of the dye was filtered using a Whatman No.1 filter paper and the filtrate was analyzed for the corresponding dye concentration. Removal efficiency was finally calculated by using the relationship.

$$\textbf{Adsorption (\%)} = ((Co - C_f)/Co) \times 100 \quad \textbf{eq……(1)}$$

Where Co = the initial concentration (mg/L) and C_f = final concentration (mg/L) of the dye being studied. The adsorption capacity of the egg shell is the concentration of the dye on the adsorbent mass and was calculated based on the mass balance principle.

2.6. Sorption studies

Dye concentration was estimated spectrophotometrically by monitoring the absorbance at 465 nm nm using a UV-vis spectrophotometer. The samples were withdrawn from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifugation at 20.000 rpm for 10 min. The absorbance of supernatant solution was measured. The effect of particle size was investigated by using four different particle sizes: 0.50, 1.00 and 2.0 mm, of powdered chicken eggshells. The experiments were carried out using 20 g of powdered eggshell for 60 minutes.

2.6.1. Effect of adsorbent dosage

The effect of adsorbent dosage was studied by adding Samples of egg shell 0.5, 1.0, 1.5, 2.0 and 2.5 g to 50 mL dyes solution in 250 ml Erlenmeyer flask and the adsorption efficiency for different dose was determined by keeping other parameters constant.

2.6.2. Effect of adsorbent particle size

The effect of adsorbent particle size was studied by using 5, 10, 15 and 20 g of adsorbent after passing with 0.5mm, 1.0mm, 0.20mm sieve and evaluate it's absorbance by using spectrophotometer by keeping the other parameters constant.

2.6.3. Effect of contact time

Contact time is one of the most important parameters for the assessment of practical application of sorption process [2]. For the determination of the rate of dye biosorption by the egg shell from 100 ml of standard solutions, the quantity of dye adsorbed was determined by varying the contact time: 5, 10, 15 and 20 min. Other parameters were kept constant.

2.6.4. Effect of initial dye concentration

This step determines the effect of MO concentration on dye removal efficiency of adsorbent. The effect of dye concentration were determined using different concentrations of the eggshell (5, 10, 15 and 20 mg/L) and keeping other parameters uniform.

3. RESULT AND DISCUSION

3.1. Effect of adsorbent dosage

The effect of powdered egg shell dosage on the adsorption of methyl orange is shown in fig.1. So as the amount of adsorbent egg shell increases the removal efficiency also increases with some continuous variation.
As the dosage of adsorbent increases the adsorption increases proportionately. The increase of dosage increases adsorbent sites thus surface area of contact with the dyes increases. Therefore the amount of dye uptakes increases and consequently leads to a better adsorption [23]. This observed trend is mainly due to the increase in sorptive surface area and availability of more adsorption site.

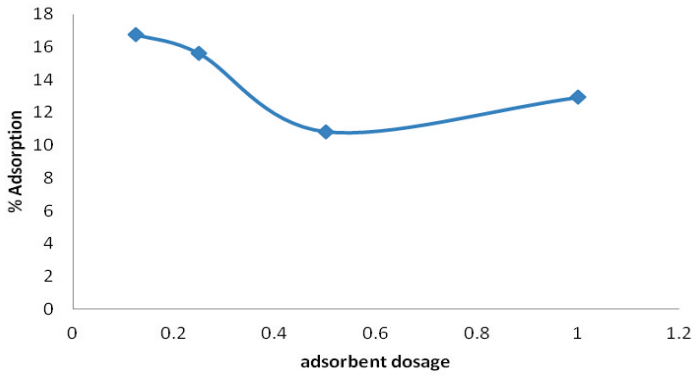

fig.1. % adsorption Vs adsorbent dosage

3.2. Effect of adsorbent particle size

Determination of the effect of particle sizes on sorption was conducted using samples of four different average particle sizes (5 mm, 10mm, 15mm, and 20mm) at constant temperature for 80 minutes. So as it is supported in fig2 . as the particle size of adsorbent material increases then there is a constant decrement of on the removal efficiency of methyl orange because surface area of adsorbent material decreases so adsorption was high in 5mm particles size due to high surface area.

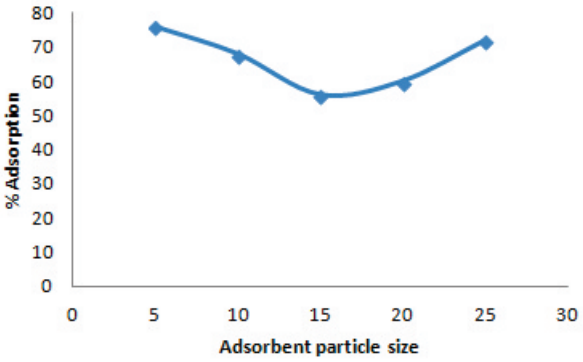

Fig2. % adsorption Vs particle size

3.3. Effect of contact time

The adsorption rate was rapid during the first 5 min and then continued at a slower rate from 5 to 35 min, and almost reached a plateau after approximately 40 min of the experiment (see Figure 2). This was due to the fact that, at the initial stage the number of free adsorption sites was higher, and the slow adsorption rate in the later stage was due to slower diffusion of solute into the interior of the adsorbent. The maximum adsorption occurred after 40 min and there was almost no adsorption beyond this time because the equilibrium is attained.

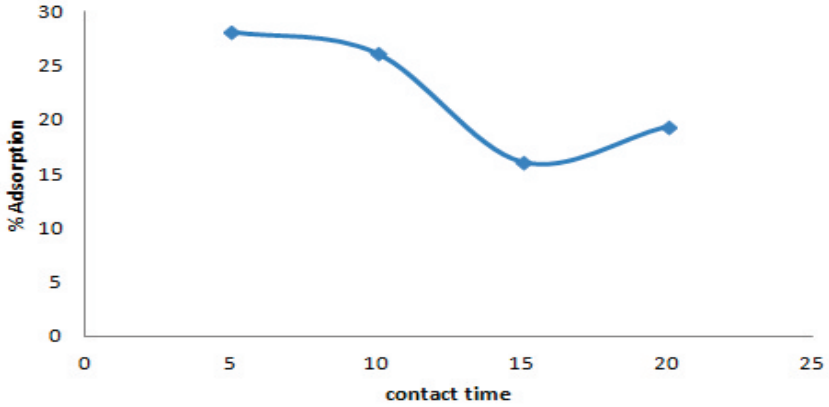

Fig. 3 . % adsorption Vs contact time

3.4. Effect of initial dye concentration

The results displayed in Figure 4 show that an increase in initial concentration enhances the interaction between the dye molecules and the surface of the fibers. The dye molecules have to encounter the boundary layer effect before diffusing from boundary layer film onto the adsorbent surface followed by the diffusion of the dye into the porous structure of the adsorbent which eventually will take relatively longer contact time. The time profile of the dye uptake by the adsorbent is a single, smooth and continuous curve leading to a saturation point [22]. In addition,
Increasing the initial dye concentration increases the number of collisions between dye molecules and the adsorbent, which enhances the adsorption process.

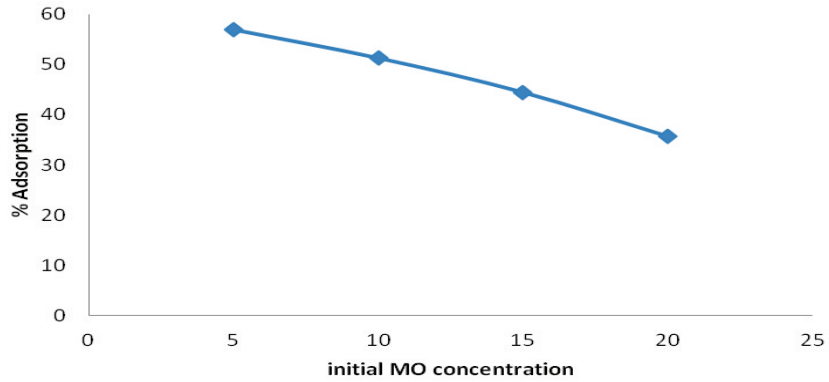

Fig. 4. % adsorption Vs initail MO concentration

4. CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusion

This study is focused on the removal of methyl orange using egg shell from aqueous solution. The operating parameters: adsorbent doses, contact time, adsorbent particle size and initial MO concentration were effective on the removal efficiency of dye. The maximum removal efficiency of egg shell was found as 98.8% for 12.5 mg/L at conditions of 2 g adsorbent dosage,20 min contact time. Activated egg shell increased the removal efficiency of Methyl orange from aqueous solution as a result of the increased internal surface area. Based on the results of this study, it can be concluded that the egg shell adsorbent is an effective and alternative adsorbent for removal of methyl orange from aqueous solution because of its considerable adsorption capacity, being of its abundance and low-cost.

MO exhibited a fast biosorption rate during the first 5 minutes of contact time due to a great availability of surface area/binding sites or large number of vacant surface sites is available for dye molecules to be biosorbed. Generally, MO anions will bind to all the active sites until they are fully occupied or until it attains equilibrium. Hence with time, fewer active sites are available and thus reduce the amount of dye being adsorbed or after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

When the initial concentration increases the removal efficiency decreases. This is probably due to high driving force for mass transfer. The reduction of dye removal as a function of its concentration can be explained by the limitation of available free sites for adsorption of dye with the increase in dye concentration in bulk solution for a fixed mass of adsorbent, as well as by the increase in intraparticular diffusion.

As the dosage of adsorbent increases the adsorption increases proportionately. The increase of dosage increases adsorbent sites thus surface area of contact with the dyes increases. Therefore the amount of dye uptakes increases and consequently leads to a better adsorption. This observed trend is mainly due to the increase in sorptive surface area and availability of more adsorption site.

The removal efficiency was high at smaller particle size of adsorbent material because as the particle size decreases the surface area increases and this leads to high removal efficiency.

4.2. Recommendations

The following recommendations are made in order to benefit those who need to intervene with the result of the study under consideration.

- Further study should be conducted in order to make use of egg shell adsorbent to remove dyes from wastewater from different factories.

- The adsorbent should characterized by using FT-IR.
- The use of adsorbent for removal of other toxic heavy metals should be studied.
- Other factors such as P^H, temperature and kinetic isotherm should be studied.

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