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# The eggshell powder as a potential a low-cost adsorbent for the removal of methylene blue dye from the industrial effluents

**Madhura Mukadam**
R.P. Gogate College of Arts and Commerce and R. V. Jogalekar College of Commerce, Ratnagiri-415612, Maharashtra, India.
E-mail - madhuramukadam111@gmail.com

## ABSTRACT

The textile industry is the main source of dye wastewater which results in environmental pollution. It is difficult to treat dye wastewater because of the synthetic and complex structure of the dye. Many physical and chemical methods including adsorption, coagulation, precipitation, filtration and oxidation have been used for the treatment of wastewater. However, many of these treatments are expensive. This leads to searches for new, cheap, easily available resources for dye wastewater treatment. Adsorption has become one of the most effective and low-cost methods for the decolourization of textile wastewater. Chicken eggshell is a waste material discarded from various domestic sources such as poultries, homes, food manufacturers and restaurants. The eggshells have unique characteristics of porosity which makes it an attractive substance to be used as an adsorbent. Therefore, the main objective of this study is to determine the potential of eggshell powder as an adsorbent for the removal of methylene blue and find out the best-operating conditions for the colour adsorption at a laboratory scale. In the present study, the effect of various factors such as contact time, temperature, pH, adsorbent concentration was studied. The best-operating conditions for it to operate efficiently were at 30 minutes of contact time, pH 10 and 50 °C temperature. At pH 10 it could remove up to 80 % of the dye solution. These results indicated that the eggshell waste could be employed as an effective adsorbent for the removal of methylene blue from aqueous solution.

**Key words:** Methylene blue, eggshell waste, adsorption, dye, waste water etc.

## INTRODUCTION:

Dyes and pigments have been used in many industries for colouration purpose. Dyes are mostly used in the paper, pulp, paint, and textile industries and therefore a large amount of water is required for the washing and cleaning purpose. At present, more than 10000 various types of synthetic dyes are available worldwide. According to some estimates, about 1.5 million tons of dyes are produced annually. Fifty percent of these dyes are used by the textile industry for the colouring process and about 1–10% of these dyes are then discharged into water bodies (Forgacs *et al*., 2004 and Elkady *et al*., 2011). It can adversely affect the aquatic environment by reducing light penetration and photosynthesis. Hence, it is important to remove these pollutants from wastewater before their final disposal. But because of the synthetic and complex structure of dye, it is very difficult to treat the dye wastewater. Furthermore, dyes and degraded by-products of dyes are toxic and carcinogenic (Gonzales *et al*., 1988 Singh and Chadha, 2016).

The majority of dyes are recalcitrant and usually take a very long time for biodegradation. Various methods have been applied for the removal of harmful contaminants from water and wastewater, involving adsorption on activated carbons, reverse osmosis, chemical oxidation, membrane filtration, bacterial action, coagulation, and flocculation, activated sludge, ozonation, precipitation, electro-dialysis, ion exchange, and electrochemical techniques (Ngah *et al.,* 2010 and Carvalho, *et al.,* 2011) Activated carbon is the most widely used adsorbent for this purpose because of its high adsorption capacity, but its use is limited because of its high cost (Kannan and Sundaram, 2001 and Robinso *et al.,* 2001). Most of the physicochemical techniques available for color removal are either costly or inefficient. Among them, adsorption is proven to be one of the most efficient techniques (Khaled, *et al.,* 2009 and Yang,*et al*., 2010).

However, as the cost of conventional adsorbents is just too high, it's necessary to look for low-cost adsorbents. Numerous approaches have been made by various researchers to develop cheaper and effective adsorbent to remove dyes from wastewater. Recently, more effective and cheaper adsorbents based on by-products from poultry waste, agricultural waste, and other natural waste have been developed as an alternative to conventional wastewater treatment processes (Burakov *et al.,* 2017).

Methylene Blue is the most commonly used material for dying cotton, wood, and silk with molecular weight 373.9. Its molecular formula is $C_{16}H_{18}N_3SCl$. MB, a cationic dye, is not regarded as acutely toxic, but it has various harmful effects like nausea, vomiting and mental confusion (Dotto *et al*., 2015 and Datta *et al.,* 2011). For this reason, removal of it from effluent containing the dye is important. There are various chemical and biological methods (like coagulation/flocculation, advanced oxidation processes, membrane filtration and ozonation) for treatment of dye effluents but these effluents are hardly treated by conventional biological wastewater treatments (El Qada *et al*., 2008). At the present time, adsorption is reliable to be a simple technique and successful in water and wastewater treatment process and the success of the method largely depends on the evolution of a capable adsorbent ( Etim, 2019). Sort of absorbents has been studied to the removal of MB from water and wastewater like clay, clinoptilolite, almond gum, rice husk and ash, etc.(Ghaedi *et al*., 2015, Fernandes, 2007 and Gupta and Suhas, 2009). However, the application of discarded eggshells in the removal of reactive dyes by the adsorption method still have received very little attention.

Chicken eggshell is a waste material discarded from domestic sources such as poultries, homes, food manufacturers and restaurants (Fajobi *et al.,* 2005) It was estimated that each eggshell contains between 7000 and 17000 pores (Pramanpol and Nityapat, 2006; Elkady *et.*

*al, 2011*). Due to its porous nature, eggshell is a very good material to be used as an adsorbent. It is a potential material for the removal of reactive dyes from industrial wastewater. Therefore the main objective of the present study is to explore the potential of the eggshell powder as an adsorbent for the removal of dyes.

## MATERIALS AND METHODS :

Discarded eggshells were collected from various restaurants and poultry farms present in the Ratnagiri city and washed thoroughly with distilled water to remove all the unnecessary materials adhered to the eggshells. Then eggshells were dried at 105 °C in an oven for 2 hours to remove the moisture (Elkady *et al*., 2011). Then the dried eggshells were ground and sieved to 150-200 µm particle size. Finally, the eggshell powder was formed and stored in a sealed bottle for later use in adsorption studies. Methylene Blue was purchased from Merck limited, India and was used without further purification. A stock solution of the dye was prepared by dissolving 1 gram of dye in 1000 ml distilled water to make a stock solution of 1000 mg/L. Six standards of dye solution with different dye concentrations like 10, 20, 30, 40, 50 and 60mg/L were prepared. A standard calibration graph with absorbance versus concentration was plotted which was in linear form. With this calibration curve, the concentration of the dye samples after reacted with eggshell powder was determined.

## EFFECT OF CONTACT TIME :

1.0 g of eggshell was added to 50ml of dye solution with a concentration of 50 mg/L at room temperature. This mixture was stirred continuously with a magnetic stirrer. The samples were taken after every 10 minutes interval i.e 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 and 130 minutes. The temperature and pH of the solution were kept constant at 27°C and pH 6, respectively. At the above mentioned time intervals, the dye samples were sucked by a dropper. All the samples were centrifuged for 5 min at the speed of 9000rpm and the concentration of dye was determined with UV-VIS Spectrophotometer at a wavelength of 565 nm. The effect of contact time on colour removal efficiency was investigated by observing the colour changes of the dye solution.

## EFFECT OF ADSORBENT DOSAGE :

The adsorption studies were carried out at room temperature by mixing various amounts of eggshell powder (0.2g, 0.6g, 1.0g, 1.5g, 2.0 g) into 50 ml of five 50 mg/L dye solution respectively and stirred at room temperature for 30 minutes. After that the dye samples were centrifuged for 5 min at the speed of 9000rpm and the concentration of dye was determined with UV-VIS Spectrophotometer wavelength of 565 nm. The pH of the solution was kept constant 10.

## EFFECT OF TEMPERATURE :

The experiment was carried out by setting the temperature of 50 ml of dye solution with concentration 50 mg/mL in the range of room temperature to 80 0C in order to study the performance of adsorbent at different temperatures. Five sets of 50ml volumes of samples were prepared by mixing 1.0g of eggshell powder and stirred for 30 minutes with different temperature (27°C, 35°C, 50°C, 60°C, 80°C). After that, the dye samples were centrifuged for 5 min at the speed of 9000rpm and the concentration of dye were determined with UV-VIS Spectrophotometer the wavelength of 565 nm. The pH of the solution was kept constant at 10.

**EFFECT OF PH :**

The pH of 50 ml dye solution with concentration 50mg/L was manipulated to study the performance of adsorbent in different pH (2, 4, 6, 8, 10). The samples were titrated with Sodium hydroxide (NaOH) to the desired pH value. The samples were then mixed with 1.0g of eggshell powder and stirred at a constant temperature of 27°C for 30 minutes. All the samples were centrifuged for 5 min at the speed of 9000rpm and the concentration of dye was determined with UV-VIS Spectrophotometer wavelength of 565 nm.

**ANALYTICAL ANALYSIS :**

After the adsorption process had attained equilibrium, all the samples were centrifuged and the residual concentration in the supernatant dye solution was determined with the help of absorbance. By determining the residual concentration of the dye samples, the percentage of dye removal and the amount of dye adsorbed by the eggshell powder was calculated. Amount of dye adsorbed per unit mass of the adsorbent was calculated by $q = (C_0 - C_f)\, V/W$ and % removal of dye was calculated by $(C_0 - C_f) / C_0 \times 100$

Where $C_0$ = the initial concentration (mg/L)

$C_f$ = the final concentration(mg/L)

**RESULTS AND DISCUSSION:**

The results obtained from the present investigation revealed the ability of egg shell powder in treating methylene blue effluents. It was found that adsorption is highly dependent on the contact time, absorbance dose and dye concentration.

**EFFECT OF CONTACT TIME :**

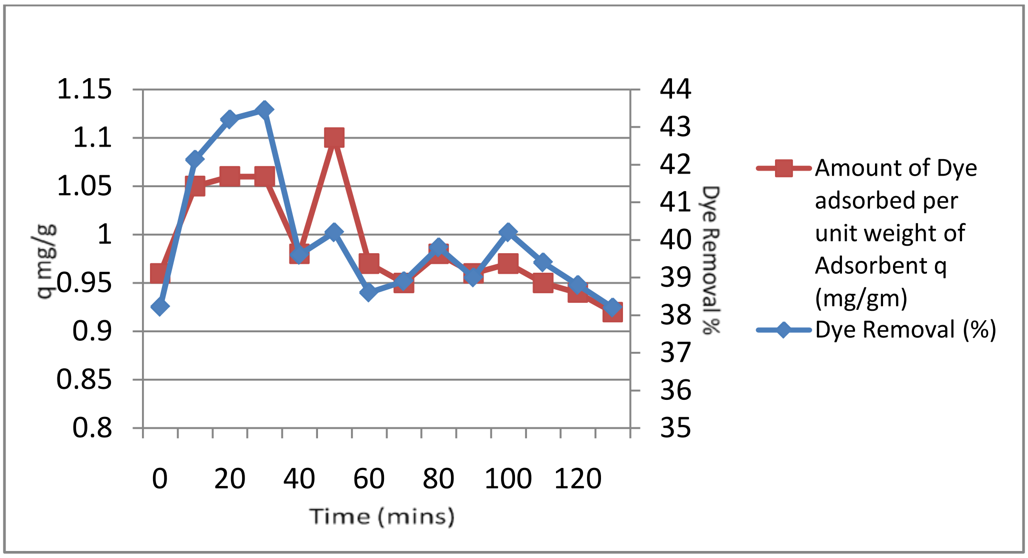


**Fig. 1 Effect of contact time on percentage of dye removal**

Figure 1 illustrates the effect of contact time towards dye removal percentage (%) and q, the amount of dye adsorbed per unit adsorbent weight (mg/g). Initially, the methylene blue dye was removed rapidly in 5 minutes. The quantity of adsorbed dye molecules rose with time and started to attain an almost constant value of around 40 minutes. When the contact time was increased to 10, 20, 30 and 40 minutes, the percentage of dye removal showed a slightly increased trend and became almost constant with 39.6%, 40.2%, 38.6%, 38.9%, 39.8%, 39% 40.2%, 39.4%, 38.8%, and 38.2% respectively. The amount of dye on adsorbent also showed the same trend with 0.97, 0.95, 0.98, 0.96 0.97, 0.95 0.94 and 0.92mg/g respectively. However, the percentage of dye removal exhibited a slightly fluctuated and downward trend with time after 40 minutes ranging from 39.6 % to 38.2%. These results were similar to the results shown by (Ngdi *et al.*, 2013**).** From the graph, it reveals that the rate of percent dye removal was higher at the beginning. This was probably due to the larger surface area of the eggshell powder being available at the beginning for the adsorption of dye ions. As the contact time was increased, the active sites were decreased and remaining vacant sites of the eggshell surface were difficult to be occupied due to repulsive forces between the molecules of the eggshell surface and the aqueous solution. The dye molecules which carried positive charged ions adsorbed on the adsorbent repelled with the unabsorbed dye molecules. As a consequence, it prevented the remaining molecules to move towards the eggshell structure. Apart from that, the small fluctuation in the amount of dye adsorbed might due to the weak physical adsorption of eggshell powder. This result was supported by Tsai *et al.*, (2006) which is the basic dye methylene blue is very poorly adsorbed by both eggshells and their membranes.

**EFFCET OF ADSOBENT DOSAGE :**

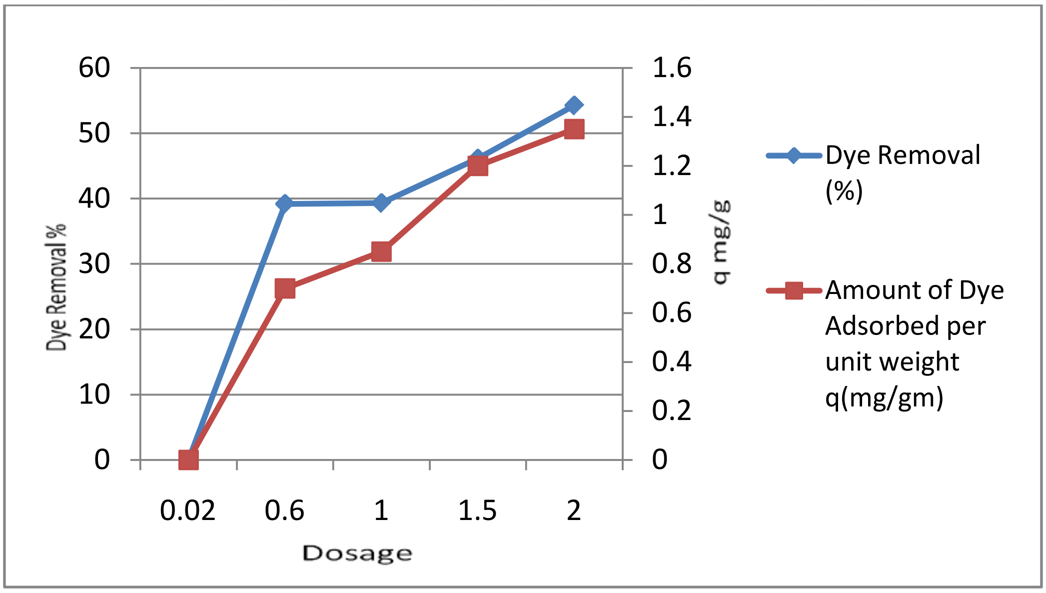


**Fig. 2 Effect of adsorbent dosage on percentage of dye removal**

Figure 2 shows the effect of adsorbent dosage on the dye removal percentage (%) and q, the amount of dye adsorbed per unit adsorbent weight (mg/g). When the adsorbent dosage increases, the percentage of dye removal also increases. From the result obtained, the dye removal was 0.03 %, 39.18%, 39.31%, 46.12% and 54.25% at adsorbent dosage 0.02g, 0.6g, 1.0g, 1.5 g and 2.0 g respectively. Then the adsorbed dye was increased from around 0.00mg/g to 1.35 mg/gm by increasing the dosage from 0.02 g to 2.0 g. The adsorption efficiency increased with the adsorbent dosage because there was plenty of surface area and more adsorption sites available to interact with the dye molecule. In contrast, the low adsorption capability is due to the saturation of adsorption sites and hence cannot further adsorb the dye molecule.

**EFFECT OF TEMPERATURE :**

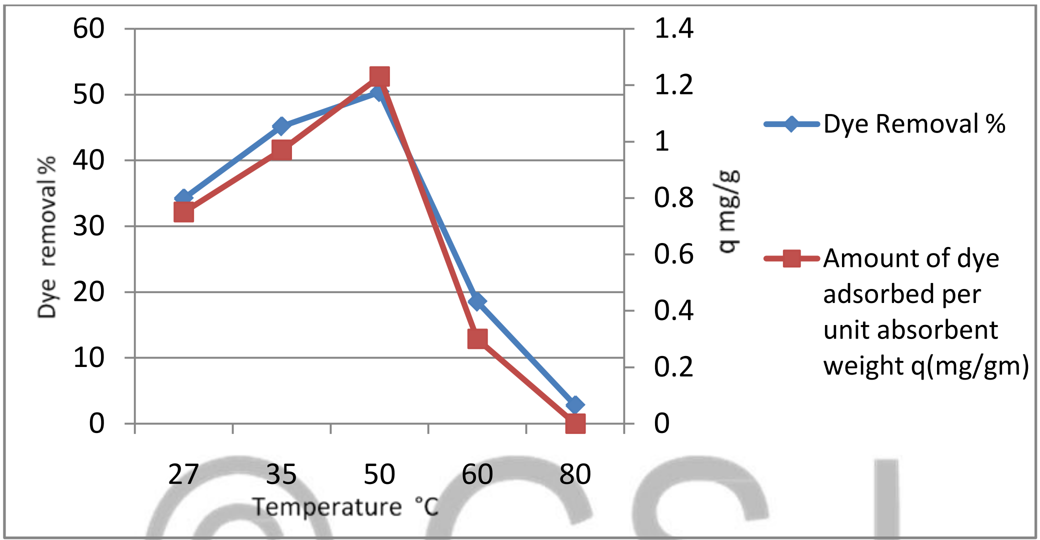


**Fig. 3 Effect of temperature on percentage of dye removal**

Figure 3 illustrates the effect of temperature towards the dye removal percentage (%) and q, the amount of dye adsorbed per unit adsorbent weight (mg/g). The percentage of dye removal increases from 34.22 % to 50.37 % up to 50 °C after that there was a steep drop. The percentage of dye removal for temperature 27°C, 35°C, 50°C, 60°C and 80°C were 34.22%, 45.18%, 50.37%, 18.53% and 2.79% respectively. The increase of adsorption temperature from 27 °C to 50 °C significantly enhanced the adsorption capacity of the Methylene Blue. The q was elevated from 0.75 mg/g to 1.23 mg/g respectively when the temperature was increased from 27 °C to 50 °C. After that, there was a steep drop of q from 1.23 mg/g until approximately 0.00mg/g when the temperature was beyond 60 °C. At 50 °C, the eggshell powder exhibited the best adsorption affinity with the dye molecule. This phenomenon indicated that the elevation of solution temperature to around 50°C can provide a suitable driving force to raise the mobility of dye molecules. These results showed that temperature is another factor that can influence the efficacy of dye removal from the solution. The phenomenon revealed that elevation of solution temperature increases the mobility of dye molecules and the number of molecules that acquire sufficient energy to undergo an interaction with the eggshell membrane surface (Hameed *et al.*, 2007). Furthermore, the increasing temperature may lead to swelling effect within the internal surface of the eggshell membrane which enabling large quantities of methylene blue molecules to penetrate into the eggshell membrane structure (Ehrampoush *et al.*, 2011). Nevertheless, the adsorption efficiency of eggshell powder was declined sharply from temperature 50°C to 80°C and even lost its adsorption ability with high temperature. Further elevated solution temperature might damage the structure of the eggshell and lead to the failure of the eggshell capability to act as an adsorbent.

## EFFECT OF PH

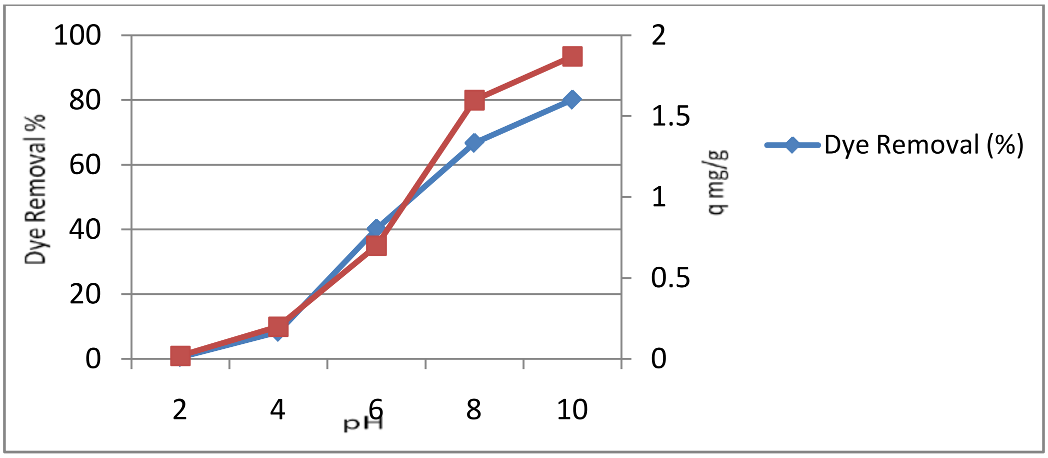


**Fig. 4 Effect of pH time on percentage of dye removal**

Figure 4 shows the effect of pH towards dye removal percentage (%) and q, the amount of dye adsorbed per unit adsorbent weight (mg/g). By increasing the pH of the aqueous solution, it led to the improvement of the dye adsorption efficiency. Dye solution with pH value 2, 4, 6, 8 and 10 was observed to have an elevated trend of dye removal percentages which were 0.58%, 8.37%, 40.25%, 66.75% and 80.11% respectively. On the other hand, q was increased tremendously from 0.02 mg/g to 1.87 mg/gm as the pH value was increased from 2 to 10. pH of an aqueous solution is the main parameter that affects the adsorption capability which is a function of hydrogen ion and hydroxyl ion concentration. It was observed that methylene blue was best adsorbed by eggshell powder in alkaline conditions and quite difficult to remove in acidic conditions. These results can be attributed to the effect of the solution pH on the charge of the reactive group within the eggshell membrane which, in turn, makes it more effective to adsorb dye in alkaline pH and increase the ionized able sites. The eggshell membrane composed of protein and polysaccharides which contained functional groups such as, hydroxyl, amine, and sulfonic groups (depending on the pH of the aqueous solution) can react with the dye (Koumanova *et al*., 2002; Allen and Koumanova, 2005). Furthermore, the dye charges have been changed with pH values.

Eggshell powder possesses a good adsorption capability for methylene blue. The best operating conditions for it to operate efficiently was at 30 mins contact time, pH 10 and 50 °C by using 2.0 g of eggshell powder in a 50 ml of methylene blue solution with a concentration of 50mg/L. At pH 10 it could remove up to 80 % of dye solution.

## CONCLUSION:

In recent years much attention has been focused on the use of biomass residues as low – cost adsorbents for the removal of dyes and heavy metals from contaminated waters. Eggshell and abundantly available material that is currently disposed of as solid waste, are potentially suitable for such applications. These results clearly support the possibility of using eggshells for the removal of methylene Blue from the contaminated waters. In addition to having a high adsorption capacity, they do not require any pretreatment or activation. Their use as an adsorbent can, therefore, be expected to be economically and technically feasible and low-cost technique.

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