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Removal of methylene blue dye by burned coal from brick field and eggshell as an adsorbent

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Abstract

Methylene blue (MB) is released with the effluent from textile, leather, paper and other industries. Study was conducted to observe the removal efficiency of MB dye from aqueous solution by burned coal and eggshell as adsorbents. The concentration of MB decreased from 25 ppm to 2.102 ppm for burned coal as an adsorbent and from 25 ppm to 0.656 ppm for eggshell powder as an adsorbent. Adsorption capacity of eggshell was higher than burned coal at pH value of 7. Approximately 3 million tons of burned coal is produced every year in Bangladesh and the price of burned coal is only about BDT 3.00 per Kg. Large amount of eggshell is also produced every day and it is available in our country. So the burned coal and eggshell particularly eggshell could be an excellent low cost bio-adsorbent for cationic dye removal.

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Introduction

Textile is one of the largest and vital industrial sectors of Bangladesh with regard to earn foreign exchange and labor employment. This sector provides 4.5 million jobs of which 80% are women and contributes 13% to GDP (BTMA annual report, 2007). Textile processing employs a variety of chemicals, depending on the nature of the raw material and product. These chemicals are mostly enzymes, detergents, dyes, acids, alkalis and salts. The quantities and characteristics of discharged effluent vary from mill to mill depending on the water consumption and the average daily product (Saha, 2007). Environmental problems of the textile industries are mainly caused by discharges of wastewater/effluents (Roy *et al.,* 2010). Dyes are basically chemical compounds that can attach themselves to fabrics or surfaces to impart color. Most dyes are complex organic molecules and are need to be resistant to many things such as the weather and the action of detergents. Dyes are widely used in industries, such as textiles, paper, plastics and leather, etc., for the coloration of products. The effluents emanating from these industries often contain high concentrations of dye wastes Synthetic dyes are extensively used in many fields of up-to-date technology, e.g., in various branches of the textile industry (Gupta *et al*., 1992; Shukla and Gupta, 1992 and Sokolowska-Gajda *et al.,* 1996), of the leather tanning industry (Tünay *et al.,* 1999 and Kabadasil *et al.,* 1999) in paper production (Ivanov *et al.,* 1996), in food technology (Bhat and Mathur, 1998 and Slampova *et al.,* 2001), in light-harvesting arrays (Wagner and Lindsey,1996), in photo electrochemical cells (Wrobel *et al.,* 2001), and in hair colourings (Scarpi *et al.*,1998) in agricultural research (Cook and Linden, 1997 and Kross *et al.*,1996), in light-harvesting arrays (Wagner and Lindsey, 1996), in photo electrochemical cells (Wrobel *et al.,* 2001), and in hair colorings (Scarpi *et al.,* 1998).Two percent of the dyes produced are discharged directly in aqueous effluent, with a further 10% subsequently lost during the textile coloration process (Easton, 1995). It has been reported that over 100,000 dyes are commercially available, with a production of over 7×105 tons per year (Zollinger, 1987; Aksu, 2005). Dyes are generally believed to be toxic and carcinogenic or prepared from other known carcinogens (Banat *et al.,* 1996)

Methylene blue (CI 52015) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of methylene blue. Methylene blue should not be confused with methyl blue another histology stain, new methylene blue, nor with the methyl violets often used as indicators. The International Nonproprietary Name (INN) of methylene blue is methylthioninium chloride. Various techniques have been employed for the treatment of dye/metal bearing industrial effluents, which usually come under two broad divisions: abiotic and biotic methods. Abiotic methods include precipitation, adsorption, ion exchange, membrane and electrochemical technologies. Much has been discussed about their downside aspect in recent years (Atkinson *et al*., 1998; Crini, 2006), which can be summarized as expensive, not environment friendly and usually dependent on the concentration of the waste. Active carbon is the most used adsorbent (Namasivayam and Kavitha, 2002; Lin *et al.,* 2008; Ong *et al.,* 2008); however, due to its high cost and considering the huge quantities of wastewater to be treated, efforts have been made to use the bio adsorbents of considerable lower cost, such as cellulose, chitosan, sawdust, sugar cane. The adsorption process has demonstrated to be relevant when compared to other techniques for water reuse, since it has very low initial cost, easy operation, flexibility and simplicity. For this process to be efficient, in addition to its low cost, it is necessary to choose an adsorbent with high adsorptive capacity, high selectivity, stability and availability (Crini, 2006).

Burned Coal has higher adsorbent capacity and it is available in Bangladesh at low cost. On the other hand the chemical composition of egg shell (94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and 4% organic material), as well as the porous nature of egg shell structure (7000-17000 pores)(William and Owen, 1995) makes it an attractive material to serve as an adsorbent agent. Furthermore, the inner eggs hell membrane has a good adsorption characteristics due to its composition (polysaccharides fibers and collagen like protein) (Allen and Koumanova,2005), which containing substituting group sites such as hydroxyl, amine and sulfonic groups can react with dye(Allen and Koumanova, 2005 & Salman *et al.*,2012).

Numerous brick field industries are crisscrossed over the country. Coal is the mail fuel to burn bricks. The residual coal are useless after its fuel demand. On the other hand poultry industries are widely expanded in Bangladesh. Eggs are the main protein source of our daily life.Infact it is the cheapest protein source in our country. The outside part call eggshell is just a waste or so called burned in terms of environmental perspective. Huge amount of eggshell can used to another purpose because of its enrichment of carbonate materials. This study is developed using this discarded materials to remove potential dye as an absorbent.Main objectives of this work are to remove the methylene blue dye from aqueous solution by using burned coal and eggshell powder.

Materials and methods

Preparation of Dye Stock Solution

The dye stock solution was prepared by dissolving accurately weighed in distilled water to the concentration of 25 ppm. For this, 0.025 gm. (Weight machine, Model No-PT-A1200800) methylene blue dye powder is needed for the preparation of stock solution. The value of was measured by pH meter. Calibration was done for that purpose.

Preparation of Standard Solution

From another solution - this can also be referred to as a dilution. A small volume of a solution of known concentration is used to make a diluted solution. The new concentration can be calculated using the equation: $C_1V_1=C_2V_2$

Where,

C_1=Concentrations of mother solution

V_1=Volume of mother solution

C_2=Concentration of new solution (Standard Solution)

V_2=Volume of new solution (Standard Solution)

First, an exact volume of a solution of known concentration is pipetted into a clean volumetric flask. Second, the solution is diluted to the volumetric mark using distilled water

Procedure

For 100ml, 0.025 ppm solution, it was taken 1ml stock solution and added 99ml distilled water to achieve desired concentration. For 100ml, 1 ppm solution, it was taken 2ml stock solution and added 98ml distilled water to achieve desired concentration. For 100ml, 2 ppm solution, it was taken 4ml stock solution and added 96ml distilled water to achieve desired concentration. For 100ml, 3 ppm solution, it was taken 6ml stock solution and added 94ml distilled water to achieve desired concentration. For 100ml, 4 ppm solution, it was taken 8ml stock solution and added 92ml distilled water to achieve desired concentration. For 100ml, 5 ppm solution, it was taken 10ml stock solution and added 90ml distilled water to achieve desired concentration.

Analysis of Methylene Blue Solution

The concentration of methylene blue in the standard solution before adsorption was determined using a double beam UV spectrophotometer (Shimadzu, Japan, model 1240) at 670 nm. It was found that the standard solutions give some absorbance value and which is important for preparing standard curve.

From the Fig.2 we see that, absorbance of standard solution is determined and plotted in the Y axis and concentration of standard solution is plotted in X axis. Value of absorbance and concentration gives a straight line equation which has a slope m, and the value of slope is determined and is 0.137. Value of m is important for determining unknown concentration and absorbance.

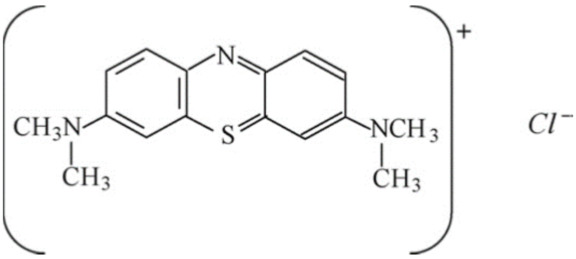

Fig. 1. Structure of methylene blue (MB).

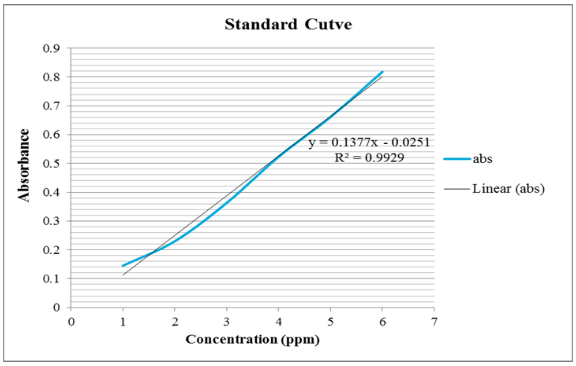

Fig. 2. Curve shows absorbance of the standard solution.

Preparation of Adsorption Column

An acrylic column of 12 cm length and ~3 cm internal diameter with 0.2 cm wall thickness was used to contain coal eggshell powder fixed bed. The bed height is ~3 cm. The natural gravitational force is applied for controlling flow of dye solution. The particle size both for coal and eggshell was less than <1mm selected. Coal was grinding by quack and deserve particle size was separated by soil sieve. Eggshell was cleaned by distill water and after that it was dried under sunlight. Then eggshell was grinding by mortar pestle. Coal and eggshell powder was packed by zip type polythene bag. Around 10 gm. of coal and 16 gm. of eggshell powder was needed to prepare the column.

Treatment of Dye Solution

At first, 50 ml and 25 ppm methylene blue dye solution was taken in ten individual beakers. The solutions were heated at 40-500C temperature. After heating the solution, it was passed through the column. The solution was treated and collected it in individual beaker. Then the absorbance of the solution was measured individually by UV spectrophotometer. From the above absorbance value we can measure the concentration of treated solution.

Calculation

By using the following formula the value of concentration of treated solution was determined.

Concentration (ppm), X=Y/m

Here,

X= Concentration (ppm)

Y= Absorbance, %

m= Slope of standard curve

Results and discussion

Burned coal and eggshell powder used as an adsorbent in the present study to remove methylene blue dye. The results of this study are discussed in Table 1

Table 1. Determination of absorbance and concentration of treated pH 7 solution (coal as an adsorbent).

Sample ID.	Volume (ml)	Absorbance %	Concentration (ppm)	Flow rate (min.)
SC -01	50	0.288	2.102	45
SC -02	50	0.588	4.291	41
SC -03	50	1.305	9.525	39
SC -04	50	1.705	12.445	35
SC -05	50	2.160	15.766	34
SC -06	50	2.387	17.423	33
SC -07	50	2.478	18.087	29
SC -08	50	2.617	19.102	26
SC - 09	50	2.759	20.138	20
SC -10	50	2.997	21.875	17

Here, SC=Coal treated sample

From the Fig.3 we see that, concentration of treated solution is determined and plotted in the Y axis and treated solution volume is plotted in X axis. The absorbance of treated solution is low and it is 0.288 ABS. The concentration of treated solution is also low at the first stage and it is 2.102 ppm. But, have passed some stock solution the absorbance and concentration of the solution increased. Because the adsorbent (Coal) loses the capacity of absorbance and the column compaction is also decreasing with time. At the beginning of passing the sample, the flow rate is low but after passing some sample the flow rate is increasing Because of decreasing the compaction of column.

Table 2. Determination of absorbance and concentration of treated pH 7 solution (eggshell as an adsorbent).

Sample ID.	Volume (ml)	Absor-bance %	Concen-tration (ppm)	Flow rate (min.)
SE-01	50	0.090	0.656	56
SE-02	50	0.139	1.012	55
SE-03	50	0.203	1.481	50
SE-04	50	0.272	1.985	49
SE-05	50	0.321	2.343	45
SE-06	50	0.479	3.496	43
SE-07	50	0.522	3.810	40
SE-08	50	0.567	4.138	38
SE-09	50	0.661	4.824	35
SE-10	50	0.739	5.394	32

Here, SE=Eggshell treated sample

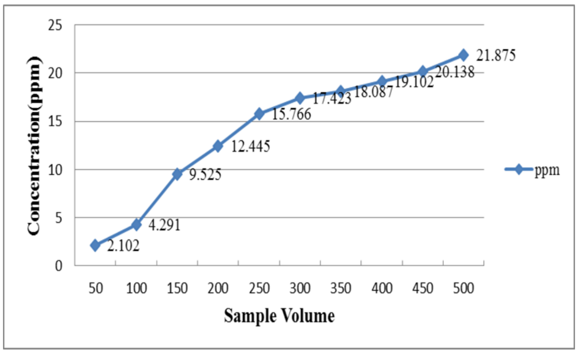

Fig.3. Concentration graph of treated pH 7 solutions (coal as an adsorbent).

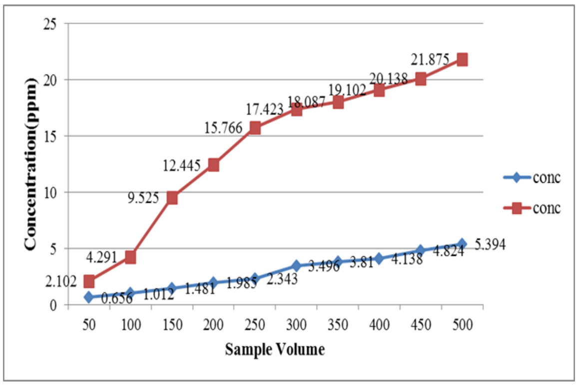

Fig. 3.3. Combined concentration graph of coal and eggshell as an adsorbent.

Here, Red line indicates coal as an adsorbent and blue line indicates eggshell as adsorbent.

From the Fig.4 we see that, concentration of treated solution is determined and plotted in the Y axis and treated solution volume is plotted in X axis. The absorbance of treated solution is low and it is 0.090 ABS. The concentration of treated solution is also low at the first stage and it is 0.656 ppm. But, have passed some stock solution the absorbance and concentration of the solution increased. Because the adsorbent (eggshell) loses the capacity of absorbance and the column compaction is also decreasing with time. At the beginning of passing the sample, the flow rate is low but after passing some sample the flow rate is increasing because of decreasing the compaction of column.

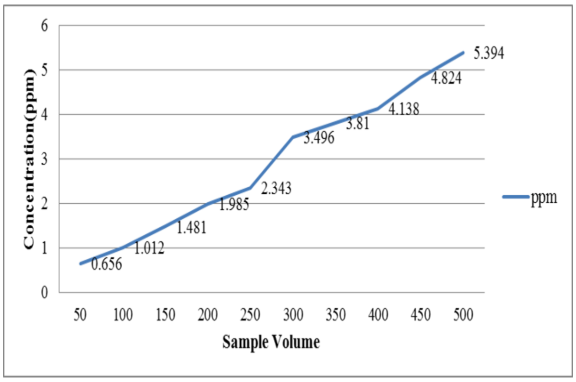

Fig.4. Concentration graph of treated pH 7 solutions (eggshell as an adsorbent).

It shows that, the coal and eggshell powder is a low-cost bio adsorbent for the removal of methylene blue dye. The concentration of methylene blue solution is decreasing from 25 ppm to 2.102 (in case of coal as an adsorbent) and the concentration of methylene blue solution is also decreasing from 25 ppm to 0.656 ppm at pH value 7 (in case of eggshell as an adsorbent).The concentration is increasing with decreasing the absorption capacity of adsorbent both for coal and eggshell.

There are about six thousand brick field in Bangladesh. Wood is used as a burning material in most of the brick field. The department of environment said that the 4,000 brick kilns burn nearly 20 lakh tons of coal and another 20 lakh tons of wood every year to meet the demand for 400 to

1200 tons of fuel (Roy, 2004).The number of pores is higher in burned coal than other coal. The porous nature of burned coal makes it an attractive material to serve as an adsorbent agent. Huge amount of burned coal is produced every year and the price of burned coal is very low and is about BDT 3 per Kg, which is very cost effective material than any other dye removal agent or commercially activated carbon.

On the other hand, large amount of eggshell is produced by every day. We are using egg as a food in our house, restaurant, hotel and many other occasions. After using it, we dispose it as a waste material. But if we use it as adsorbent material we can minimize our cost for treating textile dye and we can also manage our waste. Large amount of eggshell is also produced every day and it is available in our country.

The egg shell membrane is constructed of a network of fibrous proteins (95%) with small amount of polysaccharide (Parsons, 1982; Tsai *et al.,* 2006). The membrane surface bears positively charged sites produced by the basic side chain of the amino acids(amines and amides) like arginine and lysine depending on the pH of the aqueous solution and this attribute to electrostatic attraction to oppositely charged species (Pramanpol and Nitayapat, 2006). Allen and Koumanova (2005) reported that, the membrane has good adsorption characteristics due to the availability of sites containing substituting groups such as hydroxyl, amine and sulfonic groups which can react with reactive dye. On the other hand, the porous nature of egg shell which contain about 7000-17000 pores makes it a good material to be used as adsorbent (William and Owen, 1995). There are many factors effecting the rate of adsorption including, dye structure, size or molecular weight, concentration and the charged groups (Allen and Koumanova, 2005).

From the above result we can say that the adsorption capacity of eggshell is comparatively higher than coal. Solution treated by eggshell powder is clearer than solution treated by coal as an adsorbent. Less time is required to pass the solution in case of coal as an adsorbent than eggshell. It means that compaction quality is very good condition in eggshell powder than burned coal particles. Difference of concentration is high in case of coal as an adsorbent. But, difference of concentration is low in case of eggshell powder as adsorbent. Above discussion proved that the efficiency of eggshell is higher than efficiency of burned coal particles. So it is concluded that the coal and eggshell especially eggshell could be a good bioadsobent for cationic dye removal (methylene blue).

Conclusion

The concentration of methylene blue solution decreases from 25 ppm to 2.102 at pH value 7 in case of coal as an adsorbent. Approximately 3 million tons of burned coal is produced every year in our country and the price of burned coal is very low and is about BDT 3.00 per Kg which is very cost effective material than any other dye removing agent or commercially available activated carbon. The other adsorbents eggshell powder also behaved as better adsorbent in removing dyes from aqueous solution in our study. The concentration of methylene blue solution decreases from 25 ppm to 0.656 ppm at pH value 7. Large amount of eggshell is produced every day. Large amount of eggshell is also produced every day and it is available in our country.

From the above result it can be said that the adsorption capacity of eggshell is comparatively higher than burned coal. So it can be concluded that the burned coal and eggshell especially eggshell could be an excellent low cost bio-adsorbent for cationic dye removal. Because, most physico-chemical techniques used earlier have several shortcomings which include excess amount of chemical usage or sludge generation with obvious disposal problem, costly plant requirements or operating expenses.

There is a bigger scope of research of utilization of used adsorbents for further treatment processes. For example MB adsorbed adsorbents can further be explored for their application in second stage adsorption which is completely an unexplored area of research. Another possibility of exploration is the recovery and reuse of adsorbed substances. All future researches might be accompanied by adsorption process so that there is no net sludge generation and, if any, it should be kept minimum. Such a strategy will fulfill the goal of zero waste.

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