The Removal of Dye from Aqueous Solution by Adsorption on Low Cost Adsorbents

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Abstract: Removal of color from aqueous solution by using low cost easily available adsorbent was conducted by batch experiment. The potential of the low cost adsorbent (Marble powder - treated and untreated) to remove methylene red from aqueous solution were assessed at room temperature. Laboratory investigation of the potential of marble powder and sulphuric acid treated marble powder to remove dye color from aqueous solution has been studied. Parameters studied included pH, adsorbent dose, initial dye concentration and contact time. The influence of these system variables were investigated to observe the effect on the rate of dye uptake. Sulphuric acid treated marble powder has shown better adsorptive capacity than untreated marble powder and thus it has become an interesting option for dye removal from industrial effluents.

Keywords: Azo dye, Methylene red, Sulphuric acid treated marble powder (SATMP), Untreated marble powder (UTMP).

Introduction

Major pollutants in wastewaters from food processing, cosmetics paper, dye manufacturing, printing and textile are color left by dyes. Colored dye wastes frequently contains a spectrum of dye color may indicate the existence of toxicants. The discharge of dye bearing wastewater into natural stream or on land has created significant concern as the dye impact toxicity and impedes light penetration and thus upsets the biological activity¹⁻³. In the last decade, water resources have been decreased because of global warming and limited water treatment methods are available such as filtration, oxidation, sedimentation and adsorption⁴⁻⁶. Among these treatment methods adsorption of pollutants on low cost materials are the cheapest method. Recently, adsorption process has offered most economical and effective treatment method for removal of dyes⁷. Most conventional adsorption systems use activated carbon which is expensive and necessitates regeneration, so there was a search for low cost materials to remove organic contaminates such as dyes from industrial effluents⁸⁻⁹. Literature survey reveals that there has been numerous works reported using low cost adsorbents for dye removal, which are economical viable, easily available, highly effective in adsorption process.

The aim of the present study was to determine the optimum conditions for the removal of an azo dye *i.e.* methylene red from aqueous solution by adsorption technique using sulphuric acid treated marble powder (SATMP) and untreated marble powder (UTMP) also to show the comparative adsorptive capacities of SATMP and UTMP for azo dyes.

Experimental

Now a day there is numerous numbers of low cost commercially available adsorbents which has been used for the dye removal (Table 1). So many adsorbents are more economical easily available.

Table 1. Comparison for adsorption of some dyes on various adsorbents.

S. No.	Adsorbents	Dye(s)
1	Duckweed	Methylene blue ⁹
2	Sewage Sludge	Basic red ¹⁰
3	Waste Newspaper	Basic Blue ¹¹
4	Rice Husk	Malachite Green ¹² Acid yellow ¹³ Acid blue ¹⁴
5	Sugarcane bagasse	Acid orange ¹⁵
6	Coir Pith	Congo red ¹⁶
7	Straw	Basic lue ¹⁷
8	Treated sawdust	Methylene blue ¹⁸
9	Neem leaf powder	Congo red ¹⁹
10	Banana peel	Congo red ²⁰
11	Bagasse fly ash	Congo red ²¹
12	Mahua oil cake	Congo red ²²

Preparation of adsorbents

The adsorbent material (marble powder) were collected and washed with distill water to remove dirt, impurities and then for acid treatment it was mixed with concentrated sulphuric acid (1:2 v/w) and left to dry at room temperature for 24 h. The dried material (sample) was then kept in oven for 24 h at 180 °C for activation and was allowed to cool at room temperature. The product so obtained from activation step were blended to produce granular activated adsorbent and washed with distill water to remove excess acid. The pH of it becomes constant and the filtrations during washing were carried by vacuum filtered through whatman filter paper. The product obtained was wet-screed and dried in oven at 80 °C overnight.

Preparation of dye solution

For the present study adsorbate methylene red was procured from the local supplier. The characteristics of methylene red are enlisted in Table 2. An accurately weighed quantity of methylene red (0.5635 g) was dissolved in distilled water to prepare the stock solution (500 mg/L). The stock solution was then properly wrapped with aluminum foil and stored in a dark place to prevent direct sunlight, which may cause decolourisation. Experimental solutions of the desired concentrations were obtained by successive dilutions. Dye concentrations were determined by using absorbance values measured before and after the treatment at 617 nm with shimadzu UV visible spectrophotometer (model UV mini 1240). Experiments were carried out at initial pH values ranging from 2 to 9. Initial pH was controlled by addition of sodium hydroxide (NaOH) or hydrochloric acid (HCl)

Table 2. Characteristic of the methylene red.

Chemical Formula	$C_{15}H_{15}N_3O_2$
Molecular Weight	269.31
Melting Point	179 – 182 °C
Dye Content	95%
Adsorption Max pH 4.5	523 – 526 nm
Adsorption Max pH 6.2	430 - 434 nm
Absorptivity (1%, 1 cm pH 4.5)	> 1330
Absorptive (1% 1 cm pH 6.2)	> 700
Transition Range	pH 4.2 - 6.2 (Red Yellow)

Adsorption experiments

In each adsorption experiment, 100 mL of dye solution of known concentration and pH was added to 1 g of adsorbents in 250 mL round bottom flask at room temperature (27 ± 1 °C) and the mixture were stirred on a rotary orbital shaker at 160 rpm the initial pH of the mixture were varied between 2-8 this was controlled by the addition of dilute hydrochloric acid or sodium hydroxide solution. The experiments were carried by varying the amount of adsorbents (1 to 5.0 g/100 mL), concentration of dye solution (50-250 mgL⁻¹) and pH (2 to 8) at different time intervals.

Results and Discussion*Effect of initial dye concentration*

The influence of the initial concentration of methylene red on the rate of adsorption onto the surface of SATMP and UTMP adsorbent was studied. The experiments were carried at fixed adsorbent dose (1 g / 100 mL) in the test solution at (27 ± 1 °C) room temperature, pH=7.0 and at different initial concentrations of methylene red (50,100,150,200 and 250 mg / L) and for different time intervals (10, 20, 30, 40, 50 and 60 minutes). The results obtained are presented in Table 3. It is evident that the percent adsorption efficiency of SATMP and UTMP decreased with the increase in the initial concentration in the solution. However for SATMP and UTMP equilibrium attainment was achieved only after 40 and 50 minutes. It may be attributed to the fact that SATMP have macro and microspores resulting in longer contact time between the dye molecule and the adsorbent.

Table 3. Effect of methylene red concentration on the dye adsorption.

Initial dye concentration, mg/L	Percent dye removal with time, min					
	10	20	30	40	50	60
Sulphuric acid treated marble powder						
50	82.3	82.5	82.7	83.2	84.0	85.8
100	81.2	80.5	80.6	82.1	83.4	83.9
150	79.4	79.2	79.0	80.0	80.6	80.9
200	72.4	74.0	74.0	77.7	78.5	78.6
250	65.1	68.4	69.2	72.0	75.0	77.2
Untreated marble powder						
50	40.0	42.4	46.6	47.8	48.0	49.1
100	35.5	39.6	42.4	40.3	41.3	41.7
150	32.2	36.2	40.4	38.2	40.2	40.6
200	26.8	29.4	33.2	31.0	31.8	32.9
250	21.3	22.7	25.1	29.4	30.8	30.8

In the process of dye adsorption initially dye molecules have to encounter the layer effect before diffusing from boundary layer film onto adsorbent surface. This is followed by the diffusion of dye into the porous structure of the adsorbent and takes relatively longer contact time. The time profile of dye uptake is a single smooth and continuous curve leading to saturation, suggesting the possible monolayer converge of dye on the surface of the adsorbent²³. The efficiency of dye removal was increased as the agitation time increased and lowers initial dye concentration²⁴.

The effect of adsorbent dose

The adsorption of methylene red on SATMP was studied by changing the quantity of adsorbent (1, 2, 3, 4 and 5 g/100 mL) in the solution while keeping the initial dye concentration (250 mg/L) temperature (27 ± 1 °C) and pH (7.0) constant. Experiments were carried out at different contact times for 60 minutes as shown in Table 4. The percent adsorption increased and equilibrium time decreased with increasing adsorbent doses. The adsorption increased from 59.0 to 95.1% as the sulphuric acid treated dose increased from 1 g to 5 g/100 mL at equilibrium time (60 min.) for UTMP adsorption increased from 21.9 to 56.4% as the adsorbent dose increased from 1 to 5 g/100 mL maximum dye removal was achieved within 50 to 60 min. after which methylene red concentration in the test solution was almost constant increase in the adsorption with adsorbent dose can be attributed to the increase in adsorbent surface area and availability of more adsorption sites. The number of available adsorption sites increases by increasing the adsorbent dose.

Table 4. Effect of adsorbent dose on the dye adsorption.

Adsorbent amount in g	Percent dye removal with time, min					
	10	20	30	40	50	60
Sulphuric acid treated marble powder						
1	35.2	39.5	45.4	49.5	54.7	59.0
2	53.3	62.4	68.0	69.4	74.8	75.4
3	73.5	77.3	70.7	80.6	80.6	86.0
4	87.9	90.9	81.5	91.5	90.8	93.2
5	90.4	92.2	82.4	91.7	91.2	95.1
Untreated marble powder						
1	17.1	18.8	19.3	20.5	21.4	21.9
2	24.3	25.4	27.2	28.3	29.6	30.2
3	29.0	30.4	32.3	33.4	34.7	35.0
4	38.4	40.2	42.0	43.4	44.5	45.3
5	48.6	49.8	51.6	54.3	55.2	56.4

Effect of pH

In order to study the effect of pH on methylene red adsorption on sulphuric acid treated marble powder experiments were carried out at 250 mg/L initial dye concentration with 1 g / 100 mL adsorbent mass at room temp (27 ± 1 °C) for 2 h equilibrium time results are shown in Figure 1. In case of untreated marble powder maximum dye removal of 50% was recorded at pH 8. Between pH range of 2-6 the percentage of dye was nearly equal 48% significant increase in dye removal efficiency for sulphuric acid treated marble powder (SATMP) when compared with untreated marble powder (UTMP) it was not significantly affected by pH. Thus not favoring the adsorption of the positively charge dyes cation²⁵. There might be another mode of adsorption such as ion exchange. As the pH value increased from 6 to 8, the efficiency of the dyes removal is slightly become lesser. The dye adsorption by SATMP was (67-82%) in the studied pH range and untreated marble powder (UTMP) (50 %). The minimum percentage removal was recorded at pH 2 is 42.31% the highest percentage recorded at pH 8 is 83%.

Figure 1. Effect of pH on adsorption of methylene red.

Conclusions

The removal of methylene red from simulated waste water by using chemically treated marble powder with sulphuric acid under different experimental conditions shows that as the amount of the adsorbent was increased the percentage of dye removal. Higher adsorption percentages were observed at lower concentrations of methylene red SATMP showed a better perform compared to UTMP. This study had shown that UTMP had a lower adsorption efficiency compared to SATMP at any given pH value. Initial dyes concentration over a range of 2 to 6 decreased the efficiency of the dyes removal for both adsorbents. This study proved that treated marble powder is an attractive option for dye removal from dilute industrial effluents.

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