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Removal of methylene blue dye from aqueous solutions by adsorption in combination with ozonation on iron loaded sodium zeolite: role of adsorption

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ABSTRACT

Despite growing research efforts in water and wastewater science and technology, results for the combined effect of catalytic oxidation in combination with adsorption in a semi-continuous process are still largely unknown. The current study will help to solve an important research question in this area regarding the role of the adsorption of pollutants on materials in ozone-based processes. To the best of the authors knowledge, this kind of study using a separate ozonation and adsorption process and their combined effect using zeolites for the removal of dyes (focusing on the role of adsorption) was studied previously. Iron-coated sodium zeolite has been selected as a catalyst and methylene blue was selected as the target pollutant. Colour removal efficiency by ozonation was investigated compared with adsorption and combined effect. The study revealed that the highest colour removal efficiency around 95% in 20 min was achieved by the combined process, which was also the quickest route to dye removal. Additionally, the combined process show higher MB removal efficiency as compared with adsorption and ozonation alone. In the first 10 min, the removal efficiency was 84%, 60% and 57% for combined process, O3 alone and adsorption alone respectively. Moreover, the results further indicate that the presence of hydroxyl radical scavengers significantly affects the processes. The synergic process shows significantly high reuse performance with a difference of 3% only; hence the catalytic oxidation saves our time and energy. Moreover, the roles of adsorption and zeolites have been established.

Keywords: Adsorption; Catalytic ozonation; Fe-coated zeolites; Methylene blue; Semi-continuous process

1. Introduction

Environmental pollution has become a major challenge in many countries around the globe. Most of the industries especially the textile industry utilize huge amounts of fresh water and as a result, produces a huge amount of wastewater [1]. The wastewater produced from the textile industry contains pigments, dyes, heavy metals, and persistent organic compounds (POCs) etc. The wastewater is highly coloured which is mainly due to the prevalence of dyes [2,3]. Methylene Blue (MB), a recurrent cationic dye, is toxic and creates many health problems such as nausea, eye burn, breathing problems, vomiting etc. as well as environmental concerns. As the dyes are a toxic and visible pollutants, so their removal is necessary to protect the environment [4].

Conventional techniques such as biodegradation, adsorption, desorption, coagulation and filtration etc. have

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been frequently employed in past for the treatment of dyes with not much success [5]. Researchers reported excellent results with adsorption techniques, however, the efficiency of adsorption may deviate in real wastewater matrix and large dye concentrations [6]. Recently, advanced oxidation processes (AOPs) have become substantially popular for the treatment of wastewaters [7–10]. Among the AOPs, the catalytic ozonation processes (COPs) showed an excellent performance to treat various wastewaters. Various types of catalysts such as zeolites, activated carbon, metal oxides, clay minerals, etc. were employed in COPs in the recent past. By now, much focus has been towards the developing novel and new catalysts, however, the mechanisms of COPs and catalytic activity studied have been largely ignored [13–15].

Zeolites were found to be efficient catalyst regardless of which mechanism they follow (non-radical or radical based) [15–19]. In some recent findings, metal loaded zeolites were studied as a catalyst and it was found that they are liable to cause the decomposition of aqueous ozone, therefore producing a sufficient amount of hydroxyl radicals [15–18,20]. However, it was not clear whether the reactions on the surface of zeolite or inside the solution are important. In previous findings, both the catalyst and the pollutants were placed together in a reactor while ozonating the solution [15–17]. However, in the current investigation, the solution will be first ozonated and later it was passed through a column containing iron-loaded natural zeolites. Hence, the pollutant and the remaining aqueous ozone may both pass through the zeolite column, which further helps to understand the role of involvement of zeolites surface in such processes.

It was recently investigated that adsorption can play a significant part in catalytic ozonation [12,14,18]. The current study investigates the effect of the single ozonation process, adsorption alone process and combined ozonation/adsorption process for removing MB dye in aqueous solutions operating in a semi-continuous mode. This study may further contribute to understanding the effectiveness of natural zeolites as catalysts in the more practicably applicable process. In addition, the effects of catalyst dose and hydroxyl radical scavenger and reuse performance of the process were also investigated.

2. Methods

2.1. Materials and reagents

Experimental work was conducted using ultra-pure deionized water. A monovalent cationic dye Methylene blue ($C_6H_{18}ClN_3S$) was used as an adsorbate. For the preparation of a stock solution of dye having concentration of 1,000 ppm, 1 g of methylene blue dye was dissolved in 1 L (1,000 mL) of distilled water. For preparation of working solution, 45 ml of an aqueous solution of dye from the stock solution was taken in a 3 L volumetric flask and filled with distilled water up to the mark. The whole of the experimental work involves iron coated zeolite 4A and it was obtained from Sigma-Aldrich UK Pvt., Ltd., in uncoated form. Both the zeolite [19] and process loading [11] have been previously described in literature. The properties of zeolite 4A have been listed in Table 1.

Table 1
Properties of zeolite 4A

Pore size (Å)	4
Composition (dry)	$2Na_2O$-Al_2O_3-1.75SiO_2-6H_2O
Thermal decomposition (°C)	700
BET surface area (m^2/g)	91.3
Point of zero charge (pH_{pzc})	6.2 ± 0.3

2.2. Ozonation and adsorption experiments (standalone and combined)

Ozone generator used for ozone generation was procured from Sky Zone Private Ltd. Ozonation experimentation was performed in a continuous flow reactor. In the reactor, 3 L of Methylene blue aqueous solution having 15 ppm concentration were taken, and ozonation was done using the ozone generator for 60 min. After every 10 min, a 20 mL sample was collected.

Adsorption experiments were done in continuous flow reactor, by taking 10 g adsorbent (iron coated natural zeolite) in an adsorption column (height = 15 inch; width = 2 inch). In the reactor, 3 L of Methylene blue solution (15 ppm) was circulated in a semi-continuous mode; adsorption was done for fixed time intervals, and after every 10 min, a 20 mL sample was collected.

To investigate the combined effect of ozonation and adsorption, ozonation and adsorption were simultaneously carried out in experimental setup shown in Fig. 1. In the reactor, a 3 L volume of methylene blue aqueous solution having a concentration of 15 ppm was taken, ozonation was done using an ozone generator, and 10 g adsorbent iron coated sodium zeolite was taken in the adsorption column. The semi-continuous flow process was carried out for 60 min. After every 10 min, a 20 ml sample was collected.

UV-spectrophotometer (double beam UV-Vis spectrophotometer, Perkin Elmer Lambda 35) was used to measure methylene blue dye concentration in samples taken from all the above experiments, at λ_{max} = 664 nm [21]. A quartz cell of 5 ml served the purpose.

By using the following relationships, the values of percentage removal were calculated [22]:

$$\text{Percentage removal} = \left[\frac{C_i - C_f}{C_i}\right] \times 100 \quad (1)$$

Then the graph between percentage removal efficiency and time was drawn.

where C_i = initial concentration measured by absorbance at time 0; C_f = final concentration measured by absorbance at time t.

2.3. Dose optimization

For optimization of dose, adsorbent was taken in different quantities in the column. First time 10 g, second time 5 and 1 g for the third time adsorbent were taken in the column. For every adsorbent dose, adsorption in combination with ozonation was done for 60 min as a continuous flow process. Samples were collected after every 10 min.

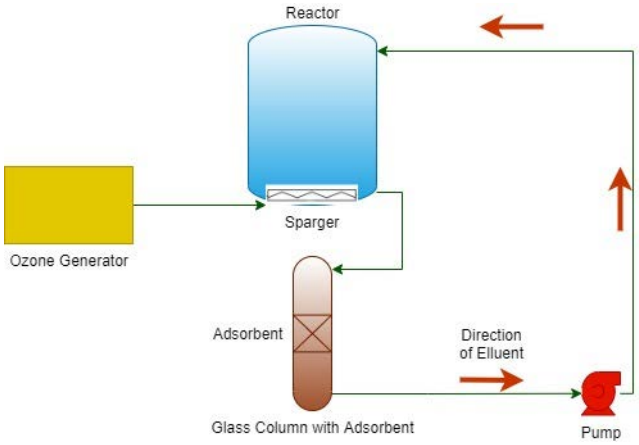

Fig. 1. Instrumental set up for ozonation, adsorption and combined process.

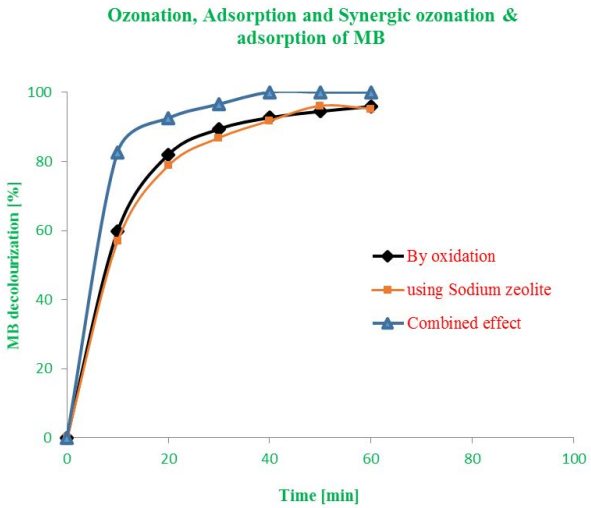

Fig. 2. Decolourization of methylene blue by adsorption, ozonation alone and combined ozonation and adsorption processes (Co (MB) = 25 mg/L; time = 60 min; ozone dose = 0.9 mg/min; zeolite dose = 10 g; T = 25°C; pH = 6.5; V = 3 L).

2.4. Reuse and quenching

To investigate the reuse performance of adsorbent for removal of colour from the aqueous solutions of methylene blue: the adsorbent amounting to 10 g was taken in the column, and thereafter, the aqueous solution of dye was taken in the continuous flow reactor and catalytic ozonation was done. This experiment was done for 30 min and samples were taken firstly at time t = 0 and then after 30 min. Using the same adsorbent without washing the whole cycle was repeated 3 times. To remove dissolved ozone from the aqueous solution of Methylene blue dye, the aqueous solution was quenched with 1.5 g sodium bicarbonate ($NaHCO_3$). And then two experiments, that is, ozonation and catalytic ozonation were done for 60 min. The quantity of adsorbent (catalyst) taken was 5 g. Samples were collected after every 10 min.

3. Results and discussion

3.1. Methylene blue decolorization

The effect of ozonation for decolourization of methylene blue in aqueous solutions was analyzed for 60 min. Results, as shown in Fig. 2, reveal that percentage colour removal efficiency increases with time. For example, at the start, for the first 20 min of interval, the highest rate of MB removal took place; after 40 min it decelerated [23] and the reduction kept on happening up to 60 min with the lower slope of the curve. This may be due to the reduction in concentration gradient with time in the aqueous solution.

Results further reveal that percentage of colour removal efficiency increases with time (Fig. 2) in the case of adsorption alone. For example, at 10 min it was 56.98%, at 20 min it was 78.77% and after 60 min it reached 95.25%. The linear portion is the fastest sorption stage, because at the initial stage; an increased number of vacant sites was available [24]. The high adsorption at the studied pH may be due to the charge on the zeolite surface. At the studied pH, the zeolites may be negatively charged, and MB was positively charged. Therefore, high adsorption was achieved due to the electrostatic forces of interactions.

The results of combined adsorption and ozonation were found to be significantly better as compared with ozonation alone and the adsorption process. Required results can be obtained just within 20 min when utilizing ozonation in combination with adsorption. This demonstrates that synergy between adsorption and ozonation exists in the combined process.

3.2. Effect of adsorbent dosage on percentage removal efficiency

For investigating the effect of the amount of adsorbent on decolourization of methylene blue in the catalytic ozonation process, experiments were performed using 1, 5 and 10 g iron coated sodium zeolite in a continuous flow reactor. Results, shown in Fig. 3, reveal that with the increase in the amount of dosage, percentage colour removal efficiency also increases. These results support that the higher the catalyst dose, the higher will be the decolourization [25]. The percentage removal efficiencies using 1, 5, and 10 g of adsorbent are 92.2%, 94.3% and 100% respectively.

3.3. Reuse performance of adsorbent

To check the reuse performance efficiency of iron coated sodium zeolite, a continuous series of experiments of catalytic ozonation was performed. The results shown in Fig. 4 make it clear that the catalytic activity of Iron coated natural Zeolite does not change significantly even after 120 min of ozonation time.

It is important to mention here that iron coated sodium zeolite may not act as a simple adsorbent, rather it acts as a catalyst. Because, if it acts as an adsorbent alone, the removal efficiency should be significantly reduced after reusing the adsorbent. Therefore, it is suggested that the surface reactions may be important on iron-coated zeolite and the removal mechanism may follow the reactions of ozone, hydroxyl radicals and methylene blue on the catalyst surface [12].

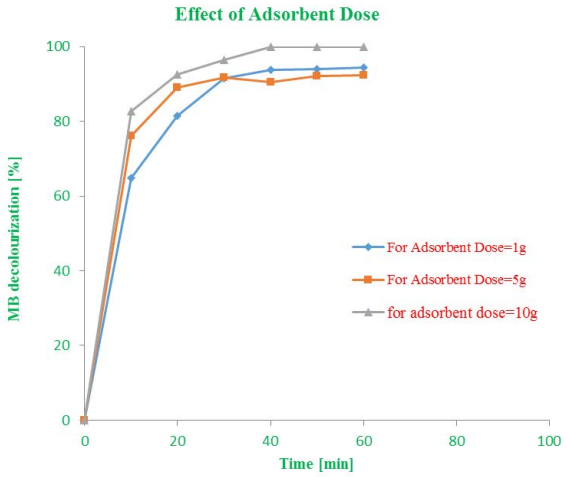

Fig. 3. Effect of adsorbent dose on colour removal efficiency of MB (zeolite dose = 1 g, 5 g, and 10 g; time = 60 min; Co (MB) = 25 mg/L; ozone dose = 0.9 mg/min; T = 25°C; pH = 6.5; V = 3 L).

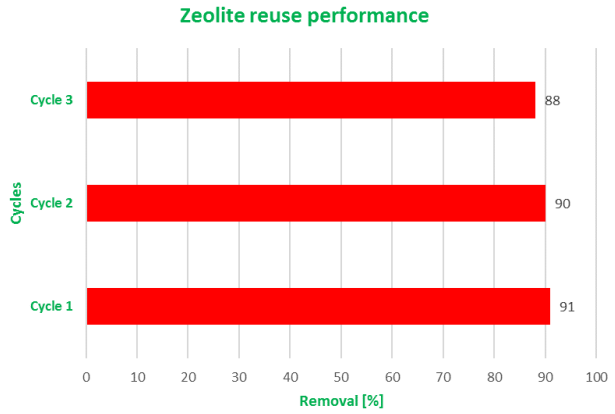

Fig. 4. Percentage removal efficiency of colour from aqueous solution by catalytic ozonation (amount of adsorbent = 5 g; t = 60 min; Co (MB) = 25 mg/L; ozone dose = 0.9 mg/min; T = 25°C; pH = 6.5; V = 3 L).

3.4. Effect on decolorization when quenched with hydroxyl radical scavenger

To check the effect of sodium bicarbonate on methylene blue removal, 1.5 g of $NaHCO_3$ was added to the reactor containing the aqueous solution of methylene blue (concentration = 15 ppm). Both experiments namely single oxidation and combined adsorption-oxidation were performed for 60 min. Results have been shown in Fig. 5, and these depict that over time, the efficiency of removal increases. However, it can be observed that percentage removal efficiency, when quenched, is less as compared to when not quenched with sodium bicarbonate. For example, the single oxidation removal efficiency at 10 min when quenched with sodium bicarbonate is 38.4%, but without quenching, it was 59.7%. On the other hand, by the combined process, removal efficiency at 10 min by quenching

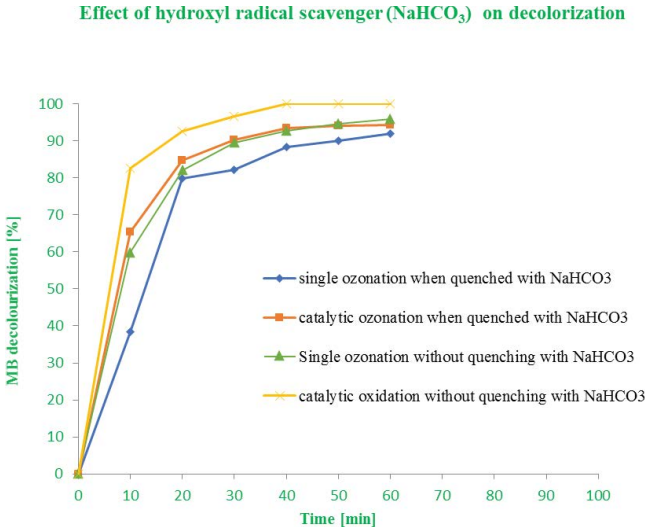

Fig. 5. Colour removal efficiency of MB when aqueous solution was quenched with $NaHCO_3$ (C $NaHCO_3$ = 1.5 g/3 L; zeolite dose = 10 g time = 60 min; Co (MB) = 25 mg/L; ozone dose = 0.9 mg/min; T = 25°C; pH = 6.5; V = 3 L).

with sodium bicarbonate was 65.29%, but without quenching, it was 84.7%. The reason for less colour removal efficiency when the aqueous solution has been quenched with sodium bicarbonate is that $NaHCO_3$ is a radical scavenger. Due to the non-availability of free radicals, removal efficiency decreased. This, in turn, suggests that both the single ozonation and combined processes follow the radical mechanism at the studied pH value. Previous findings also suggested that iron coated materials help produce the hydroxyl radicals in such processes [26,27].

4. Conclusions

Following conclusions were drawn from this study.

- Iron coated zeolite is an obvious candidate to be utilized as an effective adsorbent in oxidation processes for removing methylene blue dye from an aqueous solution.
- The activity of the combined process is dependent on the extent of the adsorption of the pollutant on its surface.
- Catalytic ozonation (the combined effect) shows excellent percentage removal efficiency as compared to single ozonation or adsorption and removes the colour in less time.
- Reuse performance was excellent indicating actual catalytic activity on the surface of the catalyst.

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