



Fabrication of MnO₂-Amberlite for Photocatalytic Degradation of Alizarin Red S under Visible Light

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Alizarin red S is a common toxic dyestuff causes water pollution that disturbs biota life in river and seawater. This study attempts to apply MnO₂ immobilized in amberlite matrix to degrade Alizarin red S under UV illumination. With regard to various stirring time of MnO₂-amberlite (6, 12, 18, 24 and 30 h) at room temperature, the BET verification shows the 18 h-stirring time of MnO₂-amberlite possessed the largest surface area (65.11 m²/g for 0.032 g sample). A strong peak of Mn-O linkage at 588 cm⁻¹ is shown in FTIR spectra of MnO₂-amberlite at 18 h stirring. The XRD of MnO₂-amberlite at 18 h-stirring time shows a characteristic peak cluster at 25° (2θ) related to additional crystal structure due to collision mechanical effect. SEM imaging of pure amberlite and different stirring time of MnO₂-amberlite are also investigated. The fabricated MnO₂-amberlite successfully degrades Alizarin red S under 1 h UV illumination (265 nm) applying 18 h-stirring time.

Keywords: MnO₂-Amberlite, Alizarin red S, Photocatalytic degradation, Aqueous solution.

INTRODUCTION

Titanium dioxide, ZnO and MnO₂ are well known as catalyst for many reactions due to its pretty stability [1-5]. Manganese dioxide is largely used for removing heavy metals, phosphates and nitrates in water purification. Moreover, MnO₂ heterogeneous catalysts were applied for enhancing water treatment [1-3]. Besides, MnO₂ nanocomposite materials were used as photocatalyst for dyes removal such as methyl orange and methylene blue under visible region [4,5].

Granular amberlite known as a trade name of polymer resin has been recognized as strong acid cationic exchanger due to its low cost and stable reason. Besides, amberlite is largely used as solid phase adsorbent for removing contaminants in wastewater treatment [6-8]. Hoque *et al.* [6] applied amberlite solid phase for extracting selected heavy metals (copper, cadmium and lead) from dairy cow's milk and Darwish *et al.* [8] used fractionized amberlite XAD resin for removing boron from water, as well as Navarro *et al.* [7] applied amberlite XAD-7 extracting bismuth(III) from hydrochloric acid solution.

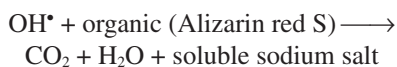
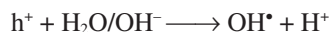
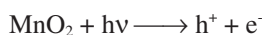
Most of the amberlites are commonly used as solid phase extraction, however, this investigation has attempted to use amberlite XAD resin as solid phase catalyst after impregnated with MnO₂ to degrade Alizarin red S pigment in aqueous solution and therefore, this study can be viewed as a semi novel investigation. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analyses have been carried out for characterizations of MnO₂-amberlite. Scanning electron microscopy (SEM) imaging is used for surface morphology examination with respect to various stirring times (6, 12, 18, 24 and 30 h) and BET (Brunauer Emmett and Teller) examination is applied for the study of surface area. A UV-visible spectrophotometer is used to know the degradation percentage of Alizarin red S by fabricated MnO₂-amberlite photocatalyst in this study.

Alizarin red S has been widely used in coating industry. Alizarin red S is a dyestuff usually found in the form of orange crystals. Besides, Alizarin red S has been used in textile industry known as Rose madder due to its turning to red colour. Due to its changing to red colour, Alizarin red S is also used in paint

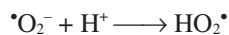
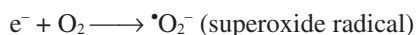
industry. Since Alizarin red S widely used in several industries, it is the reason to investigate Alizarin red S for photocatalytic degradation in this study. Additional benefit obtained from Alizarin red S that it will form various coloured complex compounds after mixing with certain polyvalent salts. Alizarin red S is classified as mordant anthraquinone dyes. A German chemist successively produced Alizarin red S synthetically from anthracene and used Alizarin red S as a model compound for anthraquinone classes [9]. The colour of Alizarin red S is sensitive to solution pH, below pH 10.1 it has Red S colour, while above pH 12 it turns to red colour. Due to its pH sensitive, Alizarin red S is broadly used as pH indicator in many acid-base reactions. The Alizarin red S is commonly formed as its sodium salt.

The MnO_2 immobilized in amberlite catalyzes the decomposition reaction of Alizarin red S organic compound into disposable product of CO_2 , H_2O and soluble sodium nitrate salt in the presence of UV light. The mechanism of photocatalytic reaction is as follows: (i) the electron in valence band of MnO_2 becomes excited when illuminated by UV light; (ii) the excess energy of this excited electron will form negative electron in conduction band and positive hole pair in valence band; (iii) this process produces a redox reaction of adsorbed species, *e.g.* Alizarin red S, in the presence of MnO_2 catalyst; (iv) adsorbed water molecule reacts with positive hole pair in valence band to yield hydroxyl radicals (OH^\bullet) and decompose Alizarin red S into CO_2 , H_2O and soluble inorganic salt.

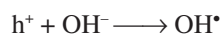
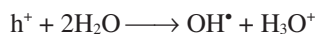
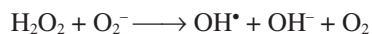
The scheme of Alizarin red S decomposition in the presence of MnO_2 and UV light (wavelength range of 200-700 nm) is as follows:



Electrons trapped in MnO_2 surface react with surface adsorbed oxygen molecules as follows:



Regeneration of hydroxyl radicals:



The hydroxyl radical, OH^\bullet , poses important role on photo-degradation of Alizarin red S to produce non-toxic disposable species. From the mechanism study and reaction scheme, it is clear that harmful Alizarin red S can be converted into removable non-toxic species in aqueous solution. Therefore, it is interesting to investigate the degradation of Alizarin red S by MnO_2 immobilized in amberlite in the presence of UV light as the main target of this study. The amberlite as the solid phase media may trap MnO_2 onto its surface through its cross-linking structure of amberlite matrix and therefore, MnO_2 will

be more concentrated on amberlite matrix. The photocatalytic reaction of Alizarin red S decomposition will be more effective through MnO_2 immobilization in amberlite matrix.

EXPERIMENTAL

All chemicals used in this study are of analytical grade. The MnO_2 used for synthesis of MnO_2 -amberlite was purchased from Merck Schuchardt OHG, amberlite IRA 400 (Cl) used for ion exchange resin purchased from Sigma Aldrich Chemi GmbH, Riedstr and Alizarin red S obtained from Fluka Chemie AG CH-9470 Buchs.

Synthesis of MnO_2 -amberlite: About 15 g amberlite IRA 400 (Cl) was grinded to obtain fine powder and dried in an oven about 98-99 °C. Then about 0.500 g amberlite was dissolved in 15 mL distilled water and stirred for 5 h. Next, about 0.200 g MnO_2 was added to amberlite solution and vigorously stirred with magnetic stirrer at different time (6, 12, 18, 24 and 30 h). The suspended solid were obtained by centrifuging all MnO_2 -amberlite solutions at 3700 rpm for 15 min with respect to different stirring time. The MnO_2 -amberlite product with respect to different time of stirring was dried in an oven at temperature about 98-99 °C followed by calcination in a furnace at 250 °C for 5 h. The product was characterized by FTIR, XRD and SEM, as well as BET analysis.

BET examination: A micrometrics PulseChemiSorb 2705 is used for BET analysis and the conditions are as follows: (i) room temperature: 24 °C; (ii) outgas temperature: 130 °C; (iii) outgas time: 1 h and (iv) gas composition: 30 % nitrogen and 70 % helium. The BET analysis is useful to compute specific areas of MnO_2 -amberlite product with respect to different stirring time (6, 12, 18, 24 and 30 h). BET analysis is useful for elucidation of physical adsorption of gas molecules onto solid surface through examination of specific surface area. The nitrogen adsorption is useful to describe the behaviour of surface adsorption attributed as monolayer adsorption and the quantity of nitrogen needed to cover surface area is known as monolayer capacity, which will be used to determine the surface area. It has to be known that BET examination is the basic research procedure for any surface area measurement.

FTIR, XRD and SEM characterizations: FTIR analysis has been used for characterizations of amberlite IRA 400 (Cl) and MnO_2 -amberlite. The FTIR characterization was carried out by a Perkin Elmer instrument using a KBr pelletizer with a scanning region from 4000 to 400 cm^{-1} . In addition, the FTIR characterization is important to know whether the MnO_2 -amberlite was successfully produced. XRD analysis has been applied for phase identification of MnO_2 -amberlite photocatalyst and it was conducted applying a Siemens D5000 X-ray diffractometer using CuK_α radiation with specifications as follows: operated at 50 nA 40 kV, angular range of 20.80°, speed of 0.01°/s and step at 0.01° to examine the pore structure of pure MnO_2 and MnO_2 -amberlite at different stirring times. SEM imaging of pure MnO_2 and fabricated MnO_2 -amberlite at different stirring times (6, 12, 18, 24 and 30 h) has been investigated using Philips XL 40 Holland instrument operating at 25.0 kV to study the surface morphology. A gold sputter coater (Polaron Divisio System SEM coating Bio-Rad) was applied to coat material powder before running SEM.

Photocatalytic degradation of Alizarin red S: The Alizarin red S degradation was examined using UV-visible spectrophotometer (Perkin Elmer Lambda 25). An Alizarin red S stock solution of 1000 ppm was prepared for series of standard solutions of Alizarin red S with concentration ranging from 10 ppm to 50 ppm. The Alizarin red S standard solutions were examined with UV-visible spectrophotometer to obtain the maximum concentration (absorbance < 1) in order to get the proper examination. An aqueous solution of MnO₂-amberlite mixed with a given Alizarin red S standard solution (50 ppm) placed in a bottle covered with aluminium foil was exposed to UV light at 420 nm for 120 min stirring. The aluminum foil cover is useful to protect sample from other contaminations due to UV light exposure. The percentage degradation of the Alizarin red S can be determined using the following equation:

$$\text{Degradation (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100$$

RESULTS AND DISCUSSION

BET examination: The results of BET analysis are shown in Table-1. According to the results, the largest surface area is referred to MnO₂-amberlite with 18 h stirring time, however, it should be noted that it referred to highest sample weight (0.032 g) among those of other samples. The photocatalytic degradation of dyestuff is encountered with the MnO₂ adsorption onto the surface of amberlite matrix. It is reasonable that larger matrix surface will absorb more MnO₂ that it is leading to better MnO₂ immobilization in amberlite matrix. More quantity of MnO₂ impregnated in amberlite is assumed to better photocatalytic dyestuff degradation. Further examination on Table-1 regarding the 18 h-stirring time with the largest surface area of MnO₂-amberlite. However, it is corresponding with the largest sample quantity (0.0321 g), therefore, this result cannot be taken as a deduction at the moment. Nevertheless, this study selected the 18 h-stirring time as the optimum parameter with regard to the BET examination. In addition, MnO₂ adsorption on amberlite is assumed to be related to physical interaction and monolayer adsorption.

TABLE-1
BET ANALYSIS OF MnO₂-AMBERLITE
AT DIFFERENT STIRRING PERIODS

Sample	Stirring period (h)	Sample weight (g)	Surface area (m ² /g)
MnO ₂ -amberlite 1	6	0.0294	52.38
MnO ₂ -amberlite 2	12	0.0148	38.51
MnO ₂ -amberlite 3	18	0.0321	65.11
MnO ₂ -amberlite 4	24	0.0084	61.90
MnO ₂ -amberlite 5	30	0.0101	48.51

FTIR investigation: The FTIR spectrum of 18 h stirred MnO₂-amberlite shows a remarkable peak of Mn-O linkage at about 588 cm⁻¹ indicated a strong MnO₂ immobilization in amberlite (Fig. 1). It indicates that the 18 h stirred yielded better MnO₂ immobilization in amberlite rather than that of the 16 h stirred related to more collisions in longer stirring time. A remarkable peak cluster is also shown at 25° (2θ) in XRD spectra indicated more crystal formation during 18 h stirring

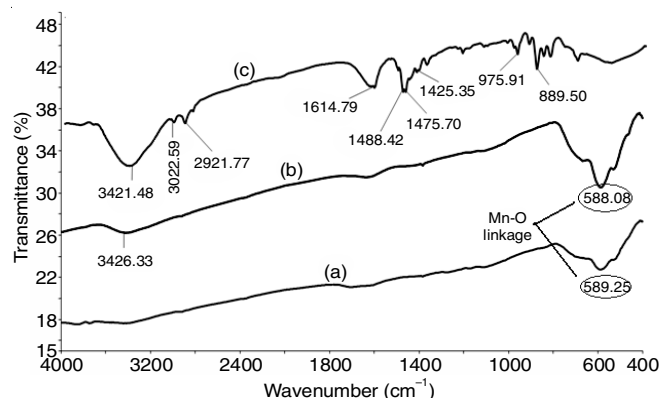


Fig. 1. FTIR spectra of (a) MnO₂-amberlite 6 h stirring, (b) MnO₂-amberlite 18 h stirring and (c) pure amberlite (KBr pellet method)

MnO₂-amberlite (Fig. 2). It is probably related to longer stirring time (18 h) of MnO₂-amberlite yielding higher number of particles collisions.

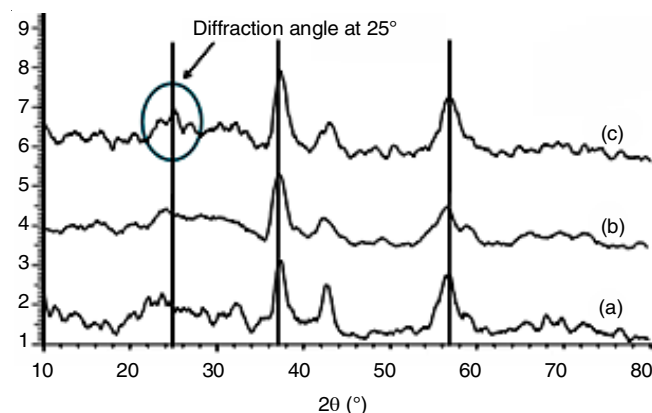


Fig. 2. XRD spectra of (a) pure MnO₂, (b) MnO₂-amberlite 6 h stirring and (c) MnO₂-amberlite 18 h stirring (50 nA and 40 kV)

Regarding the FTIR spectra, the MnO₂ impregnated in amberlite yielded a strong remarkable peak in the area of 588 cm⁻¹ related to the characteristic crystal structure due to MnO₂ inclusion in amberlite matrix. The inclusion of transition metals in immobilized matrix such as amberlite, alumina, silica, ferrite, etc., is related to tetrahedral and octahedral structures in FTIR region of 700-400 cm⁻¹ [10,11].

Further examination on FTIR spectra of pure amberlite (Fig. 1c), the remarkable peaks of 3421, 1614, 1488 and 1475 cm⁻¹ corresponding with benzene sulphonic groups in cross-linked polymeric amberlite (Fig. 1c) were disappeared after impregnated with MnO₂ and stirred for a given hour (Fig. 1a-b). The metal oxide inclusion and mechanical effect destroyed the weaker organic bonds indicated by the disappearance of organic functional groups of amberlite. However, the main skeleton of amberlite was not destroyed by the metal inclusion and mechanical effect as shown by the main frame of FTIR spectra of MnO₂-amberlite but replaced by another remarkable peak at 588 cm⁻¹. In addition, MnO₂ inclusion in amberlite matrix and longer stirring time (18 h) show that the FTIR spectrum presents remarkable peak of Mn-O linkage at 588 cm⁻¹ (Fig. 1b) on that this wavelength number indicated typical bond of transition metal with oxygen as agreed with previous

FTIR studies reported by Pradeep and Chandrasekaran [10] for inclusion of Ni, Cu and Zn in Mg-ferrite.

XRD investigation: A remarkable peak cluster is also shown at 25° (2 θ) in XRD spectra indicated more crystal formation during 18 h stirring MnO_2 -amberlite (Fig. 2). It is probably related to longer stirring time yielding higher number of particles collisions turning to increase crystal structure formation.

According to the XRD spectra of Mn-ferrite [11], the diffraction angle of 25° is related to 211 plane, while the diffraction angles of about 37° and 57° are referred to 400 and 440 planes, respectively. Basically, the mechanical stirring did not affect those related crystal structures, however, an interesting feature can be drawn from this study by the remarkable appearance of peak clusters at 25° assumed corresponding with the 211 plane. It is assumed that the stirring effect triggered the formation of certain structure closely associated to 211 plane. Moreover, it is found that longer stirring time producing remarkable peak cluster at 25° (2 θ) as verified by XRD spectra related to formation of remarkable crystal structure corresponding to more collisions giving chance to form more crystalline phase (Fig. 2c).

SEM imaging: With regard to SEM imaging (50 μm working distance, 500 \times magnification, 25.0 kV), longer stirring time of MnO_2 -amberlite produced finer particles of MnO_2 -amberlite (Fig. 3). It is reasonable since more mechanical effects yield more collisions among particles.

Moreover, the SEM imaging reveals the detail of surface distribution of elements. As reported by Tang & Rita [11] from the SEM-EDAX analysis, the Mn distributions on ferrite surface varied with different thermal treatment as an indication that mobile Mn atoms are moved through the entire material due to thermal effect. On the other side, this study shows the SEM imaging corresponding with different kinetic effects with respect to different stirring periods. According to collision theory,

increasing the kinetic rate yields higher number of particle collisions leading to producing much finer particles. This is in agreement with the phenomenon obtained by this investigation (Fig. 3). Unfortunately, the Mn distribution on the matrix surface is unknown since the EDAX data were not available and therefore, the quantitative analysis cannot be reported at the moment.

Theoretically, longer stirring time promoting finer granules on material surface as shown by SEM imaging related to more mechanical effects on number of particle collisions. In addition, previous SEM studies reported about 23 % Mn distributed on ferrite surface at 100 $^\circ\text{C}$ treatment for synthesis of ferrite sol-gel as reported earlier [11].

Photodegradation of Alizarin red S: For photodegradation of Alizarin red S, MnO_2 -Amberlite was used which has the largest surface area, which is stirred for 18 h with surface area of 65.11 m^2/g . From the BET test results as shown in Table-1 it can be seen that MnO_2 -Amberlite stirred for 18 h has a larger surface area than stirring for 24 or 30 h.

Effect of pH: The pH of the aqueous solution is an important parameter in controlling the photocatalytic Alizarin red S. The effect of solution pH on the catalytic Alizarin red S is presented in Fig. 4. As shown in Fig. 4, the percentage catalytic Alizarin red S increased from pH 5 to pH 6 and reached 92 % maximum percentage uptake at pH 7. At low pH, competition of MnO_2 and hydrogen ions occurs and the high concentration of proton in solution inhibiting catalytic process. Hence, pH 7 is the ideal pH condition for percentage catalytic Alizarin red S using MnO_2 -amberlite. The solution of pH 7 was then selected for other optimization experiment. Because at pH 7, the surface of MnO_2 -amberlite has maximum positively charged site at this pH range, which give rise to a strong electrostatic attraction between the positively charged MnO_2 -amberlite.

Effect of contact time: The catalytic experiments to evaluate the contact time effect on percentage catalytic using

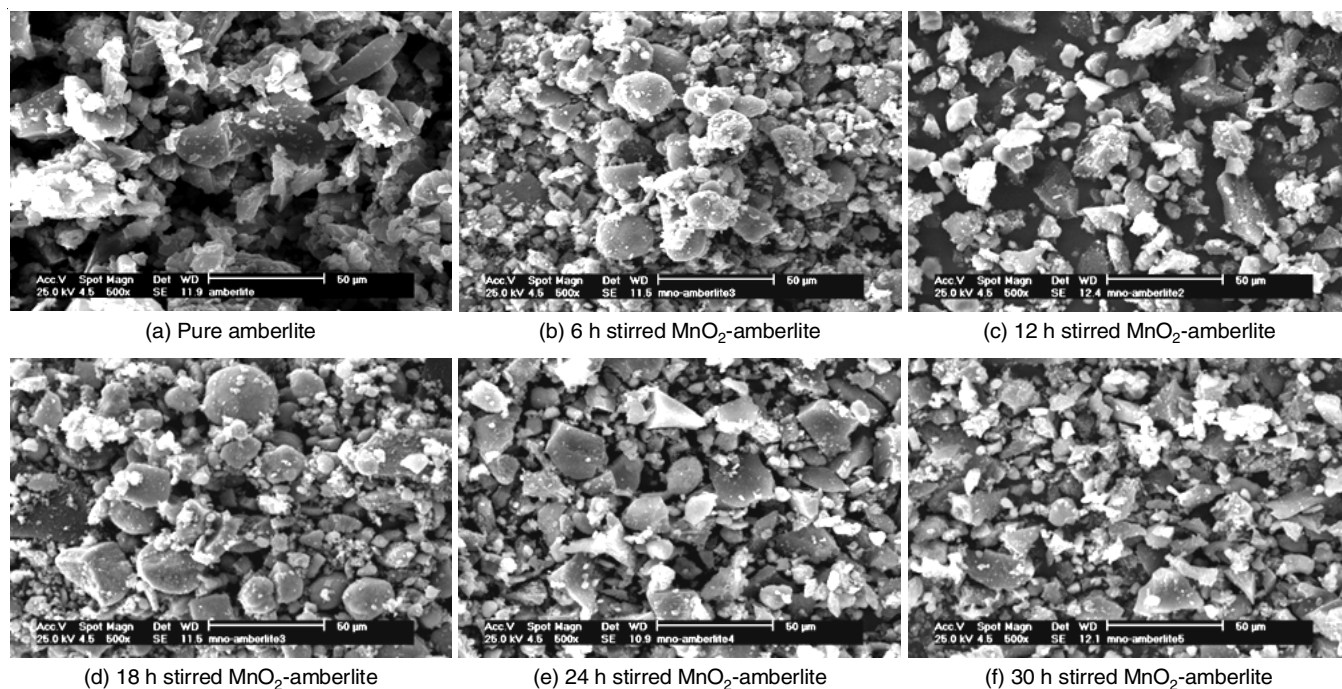


Fig. 3. Surface morphology using SEM imaging of pure amberlite and immobilized MnO_2 -amberlite. 50 μm working distance. 500 \times magnification. 25.0 kV

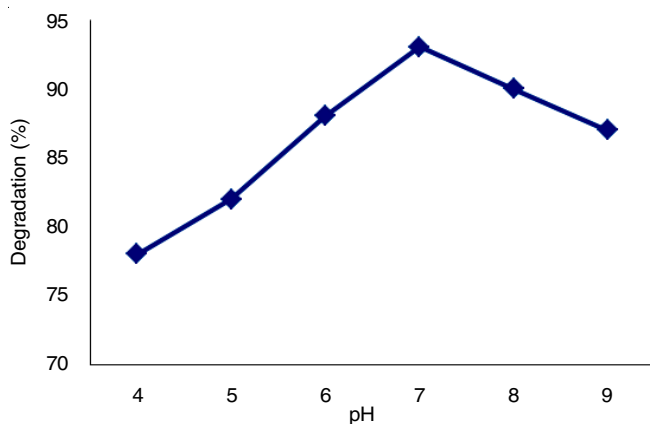
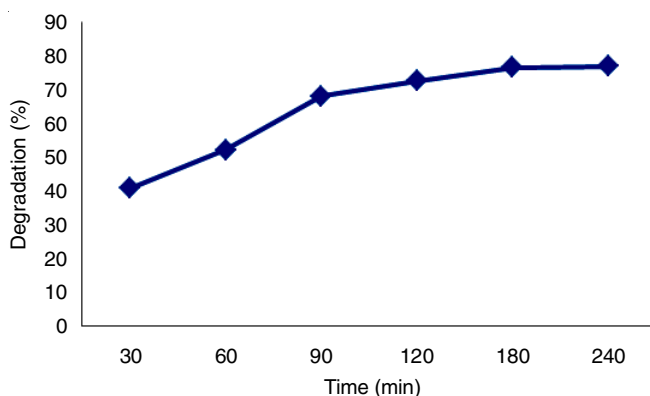
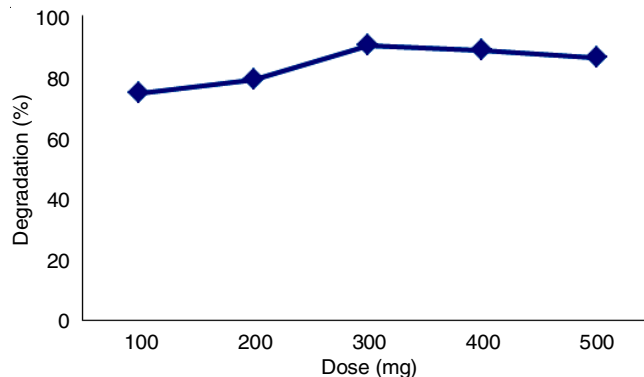


Fig. 4. Effect of pH on degradation percentage Alizarin red S

MnO₂-amberlite was brought within 120 until 240 min. As shown in Fig. 5, amounts percentage catalytic increased rapidly within 1 h and remained constant after 3 h indicated an equilibrium state. At the contact time of 3 h, the percentage catalytic for 100 ppm are 76.36 %, respectively. A contact time at 3 h was then selected for other optimization experiment. After 3 h no noticeable difference in the percentage removal was examined due to the reason that the surface of MnO₂-amberlite gets saturated with Alizarin red S molecule which inhibits further degradation

Fig. 5. Effect of contact time on degradation percentage of Alizarin red S solution using MnO₂-Amerliete

Effect of catalyst dosage: The adsorption study with different MnO₂-Amberlite dosage at a fixed pH 7, temperature of 298 K, 3 h contact time and concentration of Alizarin red S 100 ppm were carried out. The dosages were selected from 100 to 500 mg. The effect of adsorbent dosage on percentage degradation Alizarin red S is presented in Fig. 6. The maximum percentage degradation Alizarin red S of around 96.68 % was observed (Fig. 6) at catalyst dose 300 mg and then a decrease is observed at higher dose. Though the number of availability of active site increases with higher catalyst loading but due to the shielding effect the penetration of radiation through the suspension decreases, thereby the photocatalytic activity of the catalyst get reduced.

Fig. 6. Effect of MnO₂-amberlite dosage on degradation percentage of Alizarin red S

Conclusion

This study shows a successful MnO₂ immobilization in amberlite using simple procedure verified by its characterization study. Although the percentage of Alizarin red S degradation is still low, nevertheless, this fabricated MnO₂-amberlite shows good prospect for toxic dyestuff degradation in the future using some modifications

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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