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Potential of Iron Pillared Clay as Active Nanocatalyst for Rapid Decolorization of Methylene Blue

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Abstract—In this study, the iron-pillared clay nanocatalyst (ICN) was employed as a nanocatalyst for decolorization of methylene blue (MB) in aqueous solutions without hydrogen peroxide. The changes in clay structure after the incorporation of iron-oxide particles was studied with the help of XRD analytical data. The SEM micrographs showed higher heterogeneous structure of ICN compared to pristine clay and the specific surface area of ICN (82.54 m^2/g) is considerably higher than the unmodified clay (63.41 m^2/g). Further, the EDX analytical data indicate the successful incorporation of iron-oxide into bentonite clay. Batch experiments showed that ICN could degrade MB within pH 3.0 to 11.0 and it is efficient even at higher concentrations. The degradation is very fast and more than 90% is removed within 30 mins. A small amount of ICN is effective for degradation of MB and the reusability test showed that ICN can be reuse for several times for the degradation of MB in aqueous solutions. The effect of scavengers studies indicate that the ·OH radicals generated from the ICN are responsible in the degradation of MB. This study indicates that ICN must be low cost and environmentally friendly active nanocatalyst for degradation of MB present in aquatic environment.

Keywords: *Nanocatalyst, dye, clay, degradation, kinetic, ·OH radical*

INTRODUCTION

Wastewaters produce from dye manufacturer and application industries pose a serious concern in the environmental points of view due to their negative impact towards aquatic organisms [1,2]. Existence of dye effluent in environmental water bodies is becoming a growing concern to environmentalists and civilians. A long term sustainable and efficient dye effluent treatment method should be established to eliminate this issue. Dye wastewater should be treated first before release to minimize its negative impacts towards the environment and living things. However, due to lack of information on efficient dye removal methods, it is difficult to decide on a single technique that resolves the prevailing dye effluent issue. Although there are numerous existing tried and tested methods to accomplish dye removal, most of them have a common disadvantage which is the generation of secondary pollution to the environment. Methylene blue is one of the most common dyes contributing to colored effluents. It has been reported that an acute exposure to methylene blue caused various disorder in human body [3]. Therefore, various techniques have been developed to remove dyes from effluents before release in the aquatic environment. Among the common methods employed for dye removal, advanced oxidation process (AOP) has attracted significant attention of environmentalists due to their potential ability to degrade a wide range of organic pollutants [4,5]. Reactive oxygen species (ROS) such as singlet oxygen, superoxide, hydrogen peroxide, and hydroxyl radicals are the important

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species in AOP and they have been proved to be very effective in oxidation of wide range of organic pollutants in water. Fenton process has been widely used for removal of various types of organic contaminants. In Fenton process, the reaction between hydrogen peroxide as an oxidant and iron ions as a catalyst produce highly active species, mainly non-selective ·OH radicals with oxidation potential of 2.8 V [6]. Usually, a quantity of hydrogen peroxide is required in Fenton reaction to generate active hydroxyl radicals for the degradation of pollutants [7]. Nonetheless, for real application in wastewater treatment plant, use of excess hydrogen peroxide is not suitable. Therefore, it is an interest of a researcher to find out a catalyst which could degrade certain organic pollutants in absence of hydrogen peroxide.

Recent study has shown the production of reactive oxygen species by natural materials such as clay minerals and sediments in absence of hydrogen peroxide and it was observed that the hydroxyl radicals (•OH) produced from oxygenation of structural Fe(II) in clay minerals significantly degraded high concentrations of 1,4-dioxane under circumneutral pH and dark condition. This study has shown that the •OH production was linearly correlated with the Fe(II) amount and the 1,4-dioxane degradation efficiency was different by different clay minerals [8]. In another study, the ferrocenated iron oxide nanocatalysts was successfully used for the decolorization of methylene blue in the absence of light and hydrogen peroxide within two hours and the material could be reuse for several times using aqueous sodium chloride as a reactivator [9]. Similarly, the ferrocenated compounds were successfully synthesized without co-precipitation with other iron species and the catalyst showed a good performance in the decolorization of methylene blue and oxidation of phenylboronic acid without light and excess addition of hydrogen peroxide [10]. In the light of these reports, the development of a simple, low cost and environmentally friendly method for generation of ROS without radical initiator has attracted the attention of our research group.

To implement a solid catalyst in real water treatment process, a catalyst must have high efficiency, marginal leaching of active cations, stability over a wide range of pH, temperature, and also must be available at a reasonable cost [11]. In this study, the iron oxide nanoparticles were prepared and immobilized into natural bentonite clay to obtain the iron-pillared clay nanocatalyst. Use of iron oxide in water treatment technology has advantages since iron-oxide is abundant in nature and is relatively inexpensive [12]. Moreover, clays and clay minerals are widely-used for environmental applications, mostly due to their non-toxicity, worldwide abundance, low cost and physicochemical properties (high surface area, ion exchange capacity, high sorption and catalytic properties)[13]. The synthesized catalyst was characterized and further assesses for its capability to degrade methylene blue dye in aqueous solutions in absence of hydrogen peroxide under batch experimental systems.

MATERIAL AND METHODS

Chemicals and Materials

Methylene blue powder was procured from Acros organics, USA. $FeCl_3$ was purchased from Junsei chemicals Co. Ltd., Korea and Duksan pure chemicals Co. Ltd., Korea, respectively. $NaHCO_3$, NaOH and HCl were purchased from Duksan pharmaceuticals Co. Ltd., Korea. Bentonite clay was obtained from Daejung Chemicals and metals Co. Ltd., Korea and use without further purification.

Preparation of Iron Pillared Clay

The appropriate amount (5.84 g) of $FeCl_3.6H_2O$ was dissolved in 500 ml of water and then 2.0 g of sodium carbonate was slowly added into the ferric chloride solution with continous stirring. The solution was kept at room temperature for 24 h to form the polycations of iron. The solution was taken in a beaker and then 20 g of bentonite was added slowly and magnetically stirred for 15 h at 60 °C. It was then centrifuge and the clay particles were collected, washed with distilled water and completely dried at 120 °C. Furthermore, the solid material was calcined at 400 °C for 3 h using a muffle furnace to obtain iron-pillared clay nanocatalyst (ICN).

Characterization of Materials

The specific surface area of the samples were evaluated by obtaining the nitrogen adsorption-desorption isotherm at 77 K using a Protech Korea BET surface area analyzer (Model ASAP 2020). Prior to the measurements, the samples were degassed at 423 K for 4 h to remove any residual moisture. The surface morphology of the pristine clay and the modified clay were captured by

scanning electron microscope (SEM; FE-SEM-Model: SU-70, Hitachi, Japan) equipped with an energy dispersive X-ray spectroscopy (EDX) system and the elemental composition of the materials were also obtained. The X-ray diffraction (XRD) pattern of the pristine clay and modified clay were recorded with an X-ray diffraction instrument (PANalytical, Netherland; Model X'Pert PRO MPD) using Cu K_{alpha} radiation at a wavelength of 1.5418 Å.

Batch Experiments

The degradation of MB using ICN was studied in batch adsorption experiments. Briefly, 50 ml of MB solution was taken in borosilicate glass beaker and 0.1 g of ICN was added in the solution with continuous stirring with magnetic stirrer. The effects of various physico-chemical parameters were studied in the degradation of MB using ICN, including the influence of pH (pH 3 to 11), initial MB concentration (10 to 50 mg/L), contact time (2 to 60 min), and dose of the adsorbents (1.0 to 5.0 g/L). After several interval of time, the suspended ICN samples were separated using a centrifugation instrument (Hanil science industrial co. ltd, South Korea) and the absorbance of MB solutions was measured at λ_{max} 665 nm using uv-visible spectrophotometer (Model: Humas HS 3300). Further, in order to study the mechanistic involved in the degradation of MB by ICN, the effect of scavengers such as NaN_3, 2-propanol and $NaHCO_3$ were employed to scavenge the hydroxyl radicals or superoxide anion.

Reusability Test

In addition, reusability of ICN was evaluated in batch studies. Once after the degradation was completed as described in section 2.4, the spent ICN was separated by centrifugation and then wash with pure water for two times. It was completely dried and again the same material was used for the next degradation experiment.

RESULTS AND DISCUSSION

Characterization of Materials

The X-ray diffraction data of pristine bentonite and ICN were collected and graphically shown in Fig. 1. The pristine bentonite has shown the diffraction peak corresponding to 001 plane at 2θ values of 12.33. After the incorporation of iron and heat treatment, this peak was shifted to the lower angle and appeared at 2θ values of 8.88 and the peak intensity was significantly decreased due to annealing. This observation indicates that iron oxide particles were successfully intercalated between the interlayer's of bentonite clay [14]. Moreover, the sharp peaks obtained at 2θ values of 33.3° corresponds to β-FeOOH [15]. The characteristic peaks obtained at 35.6° and 51.8° are attributed to Fe_2O_3 [16]. The prominent peak shown at 20° and 27° corresponds to SiO_2 [17], whereas a distinguish peak obtained at 61.9° is due to 060 reflection of smectite which indicate the clay phase is dioctahedral [18].

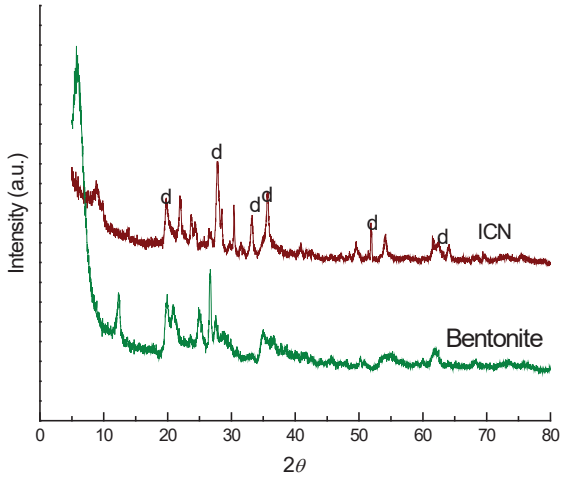

Fig. 1: The X-Ray Diffraction Pattern Obtained for Bentonite and ICN.

The SEM micrograph were obtained for bentonite and ICN and shown in Fig. 2 (a & b). The SEM image showed the ICN possessed more heterogeneous structure and iron oxide particles were aggregated on the surface as well as pore of the clay. The particles are very small in size and randomly distributed on the surface of the bentonite clay. Moreover, the EDX analytical graph (Fig. 2 (c & d)) have shown that a distinct peak corresponding to iron were significantly increased after the incorporation of iron oxide nanoparticles into bentonite. Therefore, SEM-EDX analysis clearly proved that iron oxide nanoparticles are successfully incorporated on the bentonite clay. Further, the surface area of bentonite found to be increased after the incorporation of iron oxide and heat treatment; the surface area of bentonite and ICN were 63.41 and 82.55 m^2/g, respectively. The large surface area of ICN provides an additional advantage that the large number of MB dye molecules can be adsorb and then degrades simultaneously.

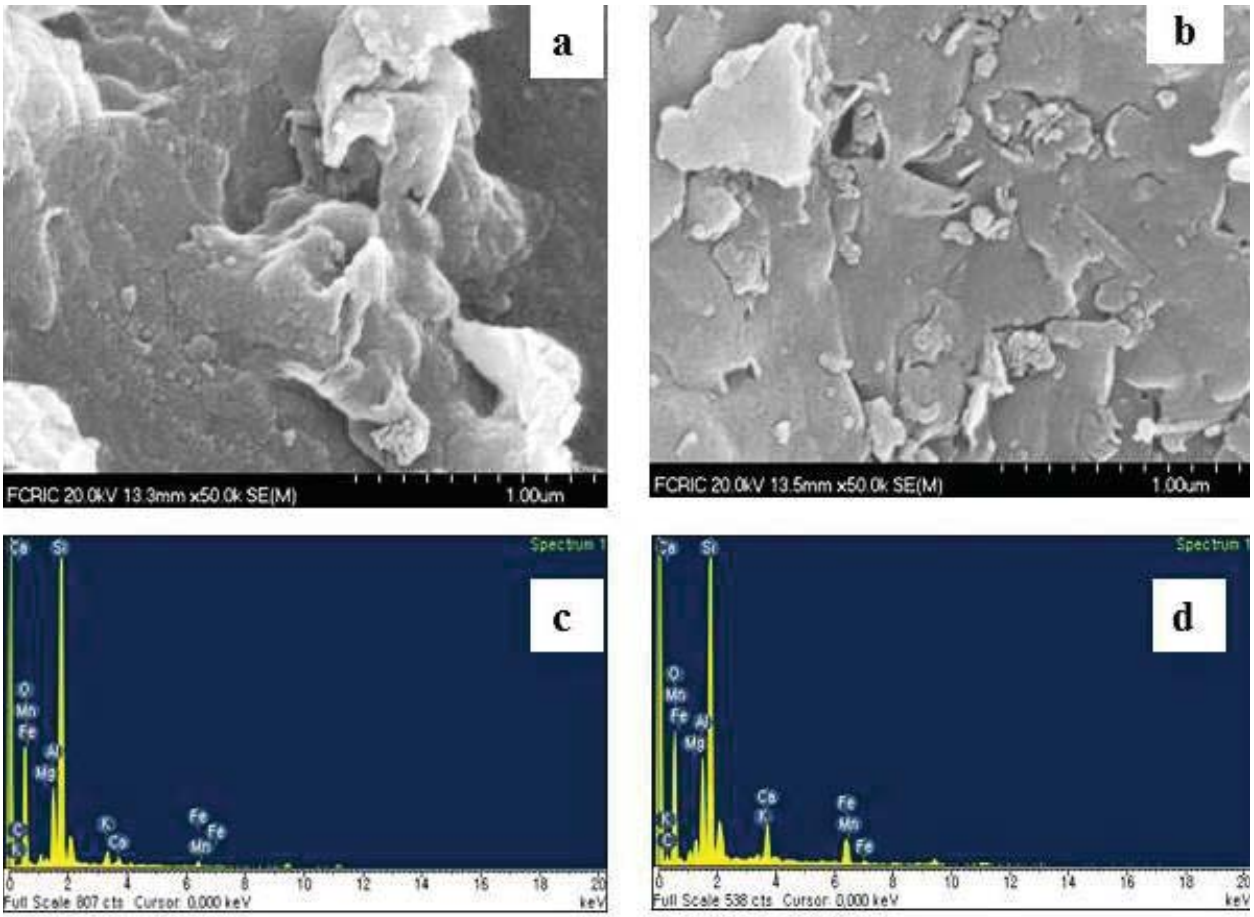

Fig. 2: SEM Micrograph Obtained for (a) Bentonite and (b) ICN and EDX analytical graph obtained for (c) Bentonite and (d) ICN

Batch Experiments

Removal of MB using Pristine Bentonite and ICN

Batch experiments were conducted to study the removal behaviour of MB by pristine bentonite and ICN under the same experimental conditions. The initial concentration of MB was maintained at 20 mg/L and the material dose is 2 g/L. The results obtained are graphically shown in Fig. 3. It is observed that the removals were fast in both cases; however, the removal efficiency of MB by ICN was significantly high compared to the pristine bentonite. Almost 100 % removal was achieved within 20 mins using ICN whereas the bentonite has shown the maximum removal about 75% only. It was observed that some MB colour remained in the solution even after the equilibrium adsorption achieved by pristine bentonite as displayed in Fig. 4. On the other hand, the ICN degrade the MB molecules and a clear solution was obtained within a short period of time. Therefore, these results indicate the suitability of using ICN for degradation of MB in aqueous solutions.

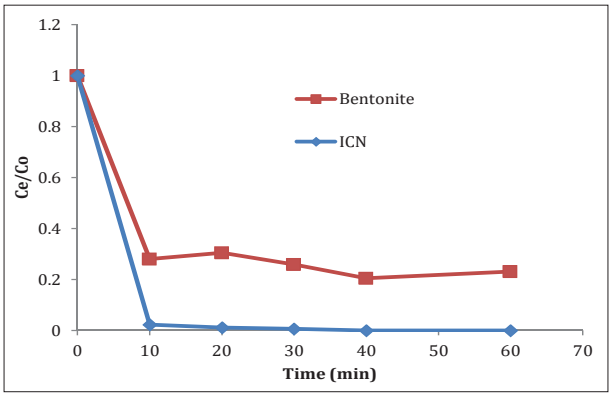

Fig. 3: Removal of Methylene Blue (MB) using Pristine Bentonite and ICN (Concentration: 20 mg/L; Dose: 2 g/L).

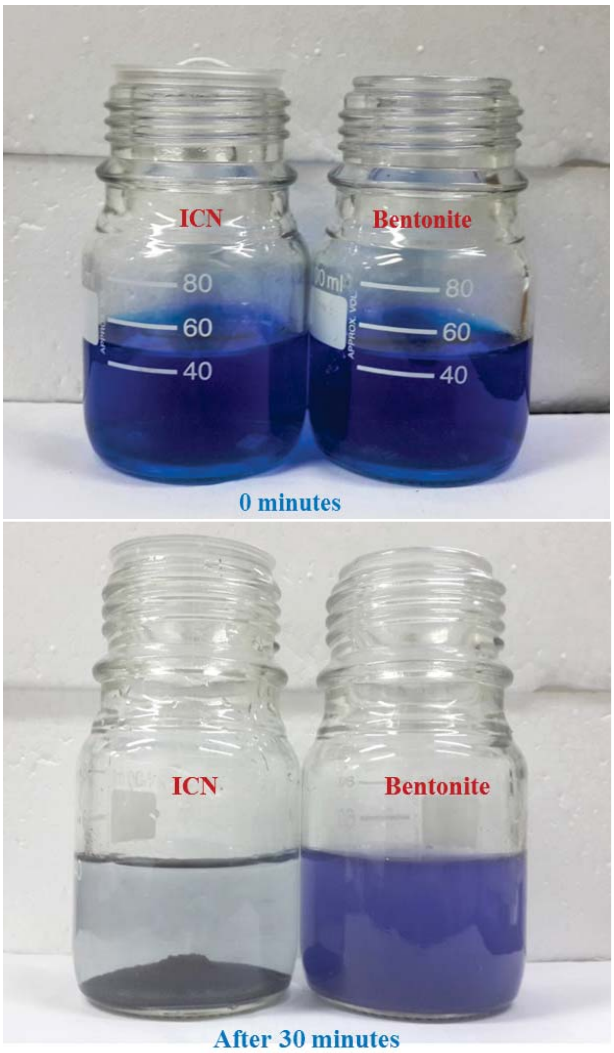

Fig. 4: Picture Showing the Removal Efficiency of Methylene Blue (MB) using Pristine Bentonite and ICN (Concentration: 20 mg/L; Dose: 2 g/L).

Effect of pH

The effect of initial solution pH on the degradation of MB by ICN was studied within the pH range of 3.0 to 11.0 and the initial MB concentration were taken was 20 mg/L. As shown in Fig. 5, rapid degradation of MB was observed within a wide range of pH and the extent of MB removal was similar in all the studied various pH. The extent of degradation was slightly lower at pH 3 and 5 within the reaction time of 10 to 30 min. This difference can be explained with the help of point of zero charge of the ICN material and the speciation of MB in aqueous solutions. The pHpzc of the ICN was found to be pH 6.6. This indicate that the ICN carries net positive charge at lower pH whereas it carries net negative charge at pH higher than the pHpzc due to dissociation of surface functional groups [19,20]. On the other hand, the speciation studies showed that MB exists as the cationic species at higher pH and undissociated/uncharged species at acidic media. At pH 3, MB is present as uncharged species with a small fraction of MB^+ species. The uncharged species is equivalent to cationic species at pH ~4 and then MB^+ species is the dominant beyond this pH [21]. The cationic MB molecules were strongly attracted towards the surface of ICN at higher pH which resulted in rapid degradation of MB. On the other hand, the ICN carries net positive charge at lower pH and the uncharged MB/cationic species were less attracted towards the surface of ICN which cause a slight retardation in degradation of MB. However, this difference diminished as the reaction time was increased up to 60 min. The pH dependence study clearly showed that the ICN can be efficiently employed for the treatment of MB dye within a wide range of pH or these findings suggest that ICN can be directly used in the removal of MB from wastewater without prior adjusting of solution pH.

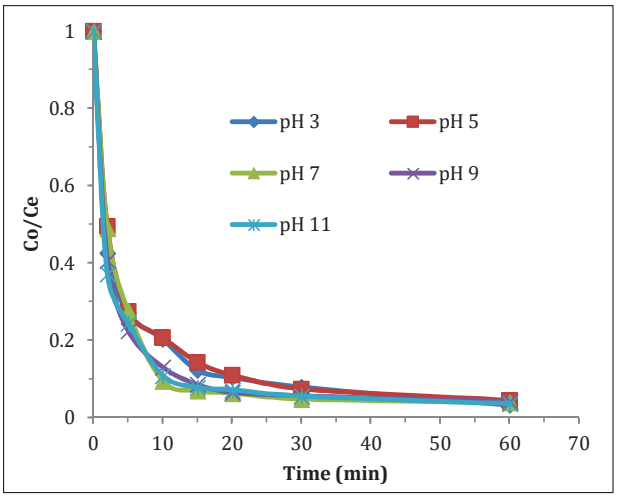

Fig. 5: pH Dependent Degradation of Methylene Blue using ICN (Concentration: ~20 mg/L; dose: 2 g/L)

Effect of Initial Concentrations

The degradation of MB using ICN were performed at various initial concentrations (i.e., 10, 20, 30, 40 and 50 mg/L) and the results are shown in Fig. 6. The time required for decolorization of MB was found to be increased as the initial concentration of MB was increases from 10 to 50 mg/L. As seen in the figure, the kinetic of degradation is relatively faster while the initial concentration were

maintained at 10 and 20 mg/L, and more than 90 % of MB were removed within 10 min and then degradation reaction was slowed down beyond 10 min. The degradation rate was significantly slowed down as the initial concentration of MB was increased to 30 mg/L. Further, this study showed that atleast 60 min is required for complete degradation of 30 mg/L of MB using ICN.

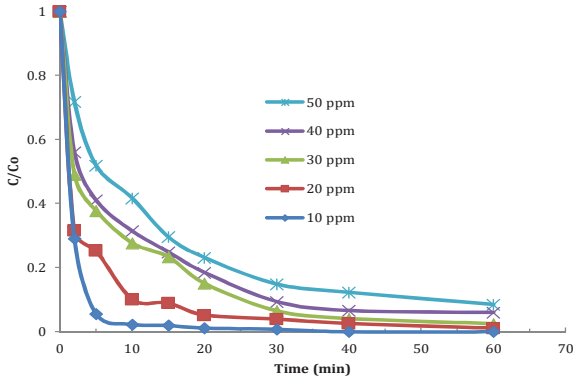

Fig. 6: Degradation of MB using ICN at Various Concentrations (pH: ~7, Dose: 2 g/L)

Further, the kinetics of MB degradation was studied by utilizing the known pseudo first order kinetic equation [22]. The graphs are plotted between the $ln\ C_t/C_o$ and time as shown in Fig. 7. The rate constant (k) of pseudo-first order kinetic are obtained to be 37.0 x 10^{-2}, 10.0 x 10^{-2}, 6.90 x 10^{-2}, 6.00 x 10^{-2}, 5.40 x 10^{-2} min^{-1} for 10, 20, 30, 40 and 50 mg/L, respectively. The rate constant is decreasing as the concentration increases and this result indicate an efficient degradation at lower concentrations of the MB dye [23]. Previous studies also shown that the degradation of MB using SnO-decorated TiO_2 nanoparticle [24], $PbBi_2Nb_2O_9$(Bulk)/TiO_2 (Nano) hetero structured composites [25], NiO–ZnO–Ag nanocomposites [26] and biosynthesized zinc oxide nanoparticles [27] were well defined by pseudo first order kinetic model.

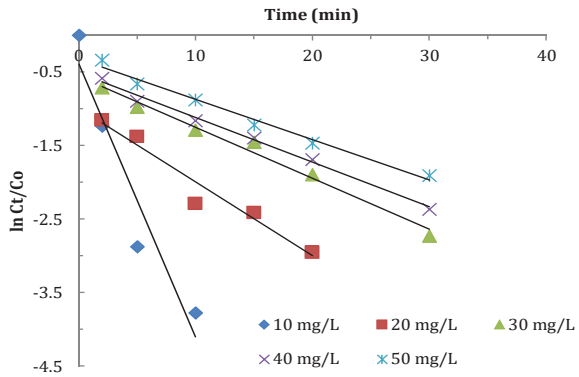

Fig. 7: Plot of ln C_t/C_o Versus Time (min) for the Removal of MB using ICN.

Effect of Dose of ICN

In order to optimize the effect of dose of ICN in the degradation of MB, the experiments was performed by increasing the dose of the ICN from 0.5 g/L to 3.0 g/L with the initial MB concentration of 20 mg/L. The result were plotted as the percentage removal versus dose of the ICN and shown in Fig. 8. The percentage removal is almost same for the dose of 0.5, 1.0, 2.0 and 3.0 g/L; therefore, these findings indicate that even small amount of ICN is efficient in degradation of MB in aqueous solutions.

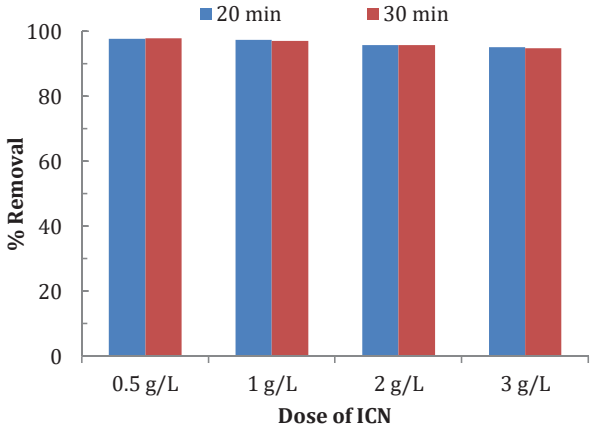

Fig. 8: Percentage Removal of Methylene Blue using Various Doses of ICN (Concentration: 20 mg/L).

REUSABILITY OF ICN

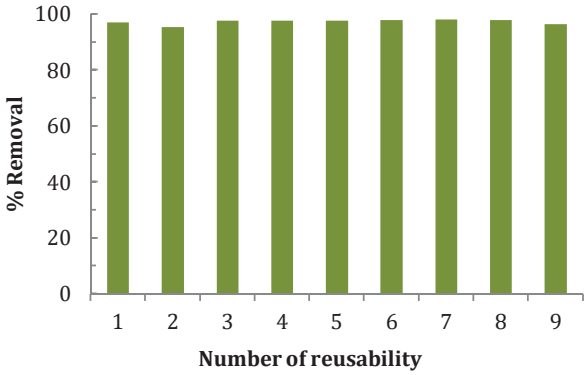

Fig. 9: Reusability of ICN for Degradation of Methylene Blue (Conc. 20 mg/L, pH: ~7, Dose: 2 g/L)

Reusability of a catalyst is an important parameter for practical implication of the study in real waste water treatment technologies. Moreover, the reusability of materials could render the cost-effectiveness of materials for real treatment technology. Therefore, reusability test was conducted at initial MB concentration of 20 mg/L with ICN dose of 2 g/L. A

detail procedure is given in section 2.3. It was observed that the percentage removal of MB remain almost same even after the ICN was reused for 9 times (Fig. 9). Therefore, this study strongly suggests that ICN must be a useful material for the complete degradation of MB in water.

Effect of Scavengers

To study the catalytic action of the synthesized materials in the degradation of methylene blue, the scavengers such as NaN_3, 2-Propanol and $NaHCO_3$ were utilized to scavenge the active radicals. In this study, the degradation of MB was conducted in presence of 1000 mg/L of the scavengers (i.e., NaN_3, 2-Propanol and $NaHCO_3$) and the results obtained are given in Fig. 10. The 2-Propanol and $NaHCO_3$ are good scavengers of OH radicals whereas the NaN_3 is a scavenger for superoxide anion [28,29]. It is interesting to observe that the presence of 2-propanol and $NaHCO_3$ cause to decrease the percentage degradation of MB, whereas NaN_3 did not show significant affect. The results suggest that the double bond in MB molecules are attacked by hydroxyl radical species which results in the degradation of the dye molecules [30,31]. Thus, according to this study, ·OH radicals generated from the ICN are mainly responsible for the degradation of MB in aqueous media.

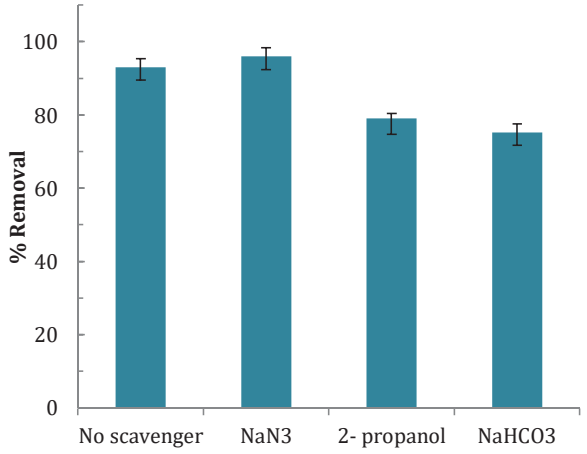

Fig. 10: Effect of Scavengers on the Degradation of MB using ICN (Conc. 20 mg/L, Dose: 2 g/L).

CONCLUSIONS

The iron oxide particles were successfully immobilized into bentonite clay. The changes in clay structure after the incorporation of iron-oxide particles evidently observed with the help of XRD analytical data. The SEM micrographs showed higher heterogeneous structure of the modified clay, i.e., ICN compared to pristine clay and the specific surface area of ICN (82.54 m^2/g) is considerably higher than the unmodified pristine clay (63.41 m^2/g). Further, the EDX analytical data indicate the successful incorporation of iron-oxide into bentonite clay. Batch experiments showed that ICN could degrade MB within a wide range of solution pH (i.e., pH 3.0 to 11.0) and it is efficient even at higher concentrations. The degradation is very fast and more than 90% is removed within 30 mins. A small amount of ICN is effective for degradation of MB in aqueous media and the reusability test showed that ICN can be reuse for several times for the degradation of MB in aqueous solutions. The effect of scavengers studies indicate that the ·OH radicals generated from the ICN are responsible degradation of MB. This study indicates that ICN must be low cost and environmentally friendly catalyst for degradation of MB dye present in aquatic environment.

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