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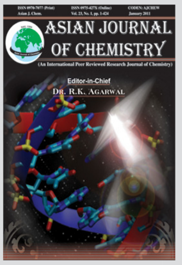

Adsorption of Azo Dye (AR 138) onto Acid Activated Bentonite Layered Cu and TiO_2 Catalyst

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The acid activation bentonite supported TiO_2 and Cu(II) ion as adsorbent-catalyst materials in aqueous solution was prepared. The decomposition of AR 138 dye in presence and in absence of H_2O_2 investigated. Adsorption of acid red 138 from aqueous solutions onto adsorbent under different condition was investigated. This powder adsorbent showed excellent adsorption towards AR 138 dye in acidic media (pH 2) and contact time 90 min. Strong preferential adsorption to A-Ben/TiO_2 was observed. Comparatively, in the absence of H_2O_2, per cent of AR 138 dye removal was lower than in the presence of H_2O_2. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and isotherm constants were determined. The Freundlich model agrees well with experiment data.

Key Words: Azo dye, Adsorption, Activated bentonite, Catalyst.

INTRODUCTION

Wastewaters originated from textile industry contain various pollutants including a high content of organic matter and dyes. Textile dyes can be structurally different. Azo dyes are the most commonly applied among other dyes applied in textile processing[1]. Azo dyes are resistant to biodegradation under aerobic conditions[2]. Many chemical treatment processes have been used extensively to treat textile wastewaters. Although several traditional chemical and biological processes exist for dye removal, the application of these techniques has been restricted due to the essentially nonbiodegradable nature of dyes, which are stable to light and oxidation[3-5]. Adsorption is one of the effective methods to remove coloured textile contaminant from wastewaters. Adsorption phenomenon in solution system plays a vital role in many areas of practical environmental technology, which are mainly in water and wastewater treatment due to several advantages such as high efficiency, simple operation and easy recovery/reuse of adsorbent[6-8]. Therefore, there is a growing need to find low cost and efficient, locally available materials for the removal of dyes. The adsorption of dyes onto clays has had in the past the unique application of being a rather simple way to determine important properties of clays, like the superficial area and the cation exchange capacity[9-11].

Some clay such as sepiolite[12-15], organobentonite[16,17], bentonite[18,19], hectorite[20], alunite[21], kaolinite[22-24], montmorillonite[25] and smectite[26] have been investigated for this purpose. These kinds of clays have a variety of surface and structural properties, high chemical stability, high specific surface area and high adsorption capacity and hence they can be used to remove dye from effluents.

Bentonite clay is one kind of smectite clay which has a very similar structure to montmorillonite. The crystal structure of montmorillonite is deteminated by two layers of siliceous tetrahedrons with an inserted layer of aluminum octahedrons between them; *i.e.*, the bentonite is also aluminum silicate. Its aluminosilicate layers are negatively charged due to isomorphous substitution. When found in nature often the negative charges of these layers are compensated by the cations between the layers. In aqueous state, the negatively charged aluminosilicate layers attract water molecules of the interlayer for charge balance. This charge balance phenomenon allows swelling and cation exchange to take place. Such properties can therefore be used to intercalate a desired cation into the clay lattice[26]. The clay-based metal composites prepared by this ion exchange method have shown their activities in various pioneer works in the field of catalysis. Zirconium intercalated clay as a support for a nickel catalyst worked effectively for methane reforming with CO_2[27]. A mixed Al and Fe pillared laponite clay catalyst showed its performance in wet peroxide oxidation[28]. Utilization of magnetic composites combined the adsorption as catalysts were developed[29-31]. The photodegradation of orange II dye on adsorbents such as montmorillonite and zeolite supported TiO_2 was studied and role of H_2O_2 and O_3 determined[32]. Photocatalytic degradation of indigo carmine dye using TiO_2 impregnated activated carbon also investigated[33].

In this research, the ability of acid-activated bentonite coated Cu and TiO_2 to remove the acid dyes, namely acid red 138 (AR 138) by adsorption and oxidation by H_2O_2, has been studied. This work investigated the parameters that affect the dye adsorption such as acid activation, Cu catalyst, temperature of solution, initial dye concentration, pH of solution and TiO_2 and H_2O_2 concentration.

EXPERIMENTAL

A textile organic dye, acid red 138 (AR 138 $C_{30}H_{38}N_3O_8S_2Na_2$) was used as the model pollutant for this work. AR138 is an anionic monoazo dye that contains OH and SO_3 function groups. It has a maximum absorbance at 515 nm. AR 138 has a molecular weight of 632.5 g. The structure of this dye is shown in Fig. 1.

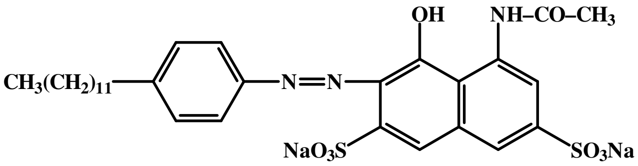


Fig. 1. Chemical structure of acid red 138 (disodium-5-acetyl amino3-(4-dodcylephenyle azo)-4-hydroxynaphtalene-2,7-disulphate) (AR 138 $C_{30}H_{38}N_3O_8S_2Na_2$)

AR138 (disodium-5-acetyl amino-3-(4-dodecylphenyl azo)-4-hydroxynaphtalene-2,7-disulphate) was used without further purification. The dye stock solutions were prepared by dissolving accurately 1 g of dyes in distilled water and diluting to 1 L in volumetric flask. The catalyst was evaluated under the reactions of 0.1 g/L of AR 138.

All materials used in this work were obtained from commercial sources and used without further purification. Hydrogen peroxide is obtained from Merck.

Preparation of adsorbent: Bentonite clay, denoted by Ben supplied by Tavan slices Co. Iran was selected as catalyst support throughout in present studies. The bentonite clay was purifying by acid treatment and the activated bentonite clay is denoted by A-Ben. Acid activation was performed by suspending the bentonite clay in the presence of H_2SO_4. 10 g of natural bentonite clay was suspended in 40 % (w/w) H_2SO_4 for 4 h under vigorous stirring. The activated bentonite clay was the separated by centrifugation and dried in an oven for 24 h. Cu(II) ion and TiO_2 were then deposited onto surface of acid activated bentonite clay. Chemical vapour deposition (CVD) for Cu was carried out at 250 ºC for 1 h and copper(II) acetate as Cu source. The Cu activated bentonite composite was then calcinated at 350 ºC for 24 h. In the preparation of TiO_2:Ben, 1 g of A-Ben and 0.2 g of TiO_2 in the 50 mL water mixed and refluxed for 2 h and then dried in autoclave at the temperature was set to 150 ºC. The resultant product was separated from the solution and washed with double distilled water and then the product was centrifuged and finally dried at 40 ºC.

Analytical method: A UV-vis spectrophotometer (Shimadzu UV-16-A Japan) was used to monitor the degradation of AR138, respectively. pH measurement was done with a Horiba pH meter (M13-Japan). The pH adjusted using 0.1 N NaOH and 0.1 N HCl solutions. Infrared spectra of adsorbents (Ben, A-Ben and A-Cu-Ben) in the FTIR region (4000-400 cm^{-1}) were recorded using a Shimadzu for KBr pellets.

RESULTS AND DISCUSSION

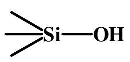
Effect of activation of bentonite: Before the use of heterogeneous catalyst, a pre-treatment was employed to treat the bentonite clay with H_2SO_4 prior to the deposition of Cu. Such a procedure has an activation effect on the bentonite clay and called (referred to as acid activation) A-Ben. The untreated or natural bentonite clay contains various cations that may take up the active sites in the clay structure, resulting in reduction of the catalytic power of the catalyst. It is believed that acid activation is able to provide enough hydrogen ions to displace the cations that compensated the negative charge in the layers. It can be seen that the untreated bentonite clay contains more cations in terms of compared to that of the bentonite clay treated with acid.

The chemical composition of bentonite is given in Table-1, obtained by using EXD indicates the presence of silica and alumina as major constituent along with traces of sodium, potassium, iron, magnesium, calcium and titanium oxides in the form of impurities. XRD results combined with EDX analysis demonstrate that most of the aluminum is in the form of bentonite. XRD also indicated the presence of free quartz in bentonite. It is thus expected that the adsorbate species may be removed mainly by SiO_2 and Al_2O_3.

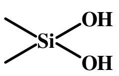
TABLE-1
CHEMICAL COMPOSITION OF BENTONITE
SAMPLES BEFORE AND AFTER ACID ACTIVATION

Component	Weight (%)	
	Activated	Unactivated
SiO_2	70.6	56
Al_2O_3	18.3	16.15
MgO	1.25	1.5
Fe_2O_3	0.7	2.4
CaO	1.71	0.85
Na_2O	0.12	< 0.1
K_2O	1.11	3
TiO_2	0.18	7.25
Loss of ignition	5.63	9.5

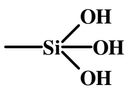
The surface hydroxyl groups of adsorbent have a main effect on the adsorption of acid red 138 onto the bentonite. Therefore it would be useful to review the surface hydroxyl groups. The silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups. Theoretically, it is possible to use a pattern in which one silicon atom bears two or tree hydroxyl groups, yielding silanediol and silanetriol groups, respectively. It is stated as improbable that silanetriol groups exist at the silica surface. The types of silanol groups are shown below[34].



Hydroxyl or silanol groups



Silanediol groups



Silanetriol groups

Fig. 2 shows the effect of acid, Cu and TiO_2 activation of bentonite as a function of concentration of AR 138 dye. It was found the acid activation of bentonite increases up the capacity of adsorbent. It is due the protonation of silanol groups on the surface of sorbent. It is observed that Cu catalyst also increased the per cent of dye removal (Fig. 2). The effect of TiO_2 impregnation on the adsorption capacity was shown that A-Ben: TiO_2 very high efficiency in comparing with untreated bentonite.

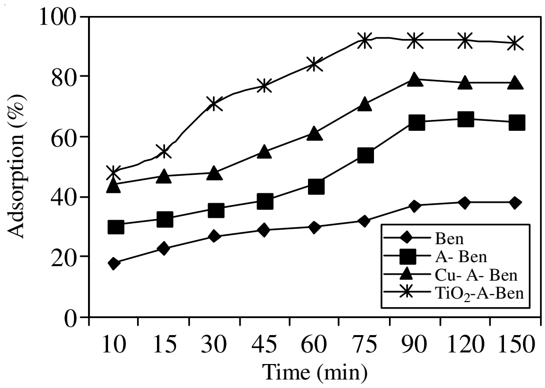


Fig. 2. Effect of bentonite activation with acid and coating with TiO_2 and copper on percentage adsorption of AR 138 in room temperature for different concentration of dye

A massive improvement was recorded that colour removal at 1 h was increased by almost 30 % if acid activation was carried out for the original bentonite clay and for A-Ben: TiO_2 almost 80 % increased. This provides strong evidence that acid activation is indeed an essential preparation step for the Cu- Ben clay catalyst.

It is observed that importance of acid activation of bentonite is highlighted by comparison between Cu-A-Ben and Cu- Ben. It is well known that the surface charges, specific surface areas of clays can be altered by the activations with acid-treated. During acidification of clays, the octahedral ions can be leached out and the specific surface area increase[35].

On comparison of Cu-A-Ben and Cu-B at 15 min, it is found that acid activation improves the discolouration of AR 138 by nearly 32 %, but Cu-A-Ben holds the activity more than 80 %.

FTIR analysis: In order to obtain complementary evidence for the intercalation of hydrogen ions into the silicate lattice, IR spectra were recorded in region of 4000-400 cm^{-1}. IR spectroscopy is sensitive to modification of the clay structure upon acid treatment. As protons penetrate into the clay layers and attack the OH groups, the resulting dehyroxylation connected with successive dissolution of the central atoms can be readily followed by changes in the characteristic absorption bands, attributed to vibrations of OH groups and/or octahedral cations. In the spectra of acid bentonite, the intensity of characteristic absorption bands decrease, compared with before modification. There is a group absorption peaks between 3495 and 3645 cm^{-1}, which is due to stretching bands of OH groups and the band at 1619 also corresponds to the OH deformation of water to observe natural bentonite and acid activated bentonite, but the peak intensities of acid-activated bentonite are lower than that of natural bentonite. This may be acceptable evidence for acid activation occurring on bentonite.

A gradual transformation of the tetrahedral sheer to a three-dimensional framework of protonated amorphous silica can be observed in the region of the stretching vibrations of Si-O groups. The peak at 1060 cm^{-1} due to Si-O stretching band, within the layer, decreased with increasing extent of dissolution, while band at 1090 cm^{-1}, is due to the vibrations of the three-dimensional reaction product, increased. The bands at 468 and 531 cm^{-1} obtained from the Si-O-Al (where Al is an octahedral cation) and bending vibrations, respectively, in the untreated bentonite. After acid treatment the Si-O-Al vibration was only observed at 480 cm^{-1}. The bending vibration of Si-O-Si was not observed. It is the most sensitive indication of the remains of the layers after extensive acid dissolution[19].

In the spectrum of acid bentonite with Cu catalyst, the intensity of characteristic absorption the band of 3645 cm^{-1} decreased and broaded compared with before modification and the bands of 1110 cm^{-1} appear.

Effect of pH: The adsorption isotherms at various pHs are shown in Fig. 3. 50 mL of AR 138 solution at the initial dye concentration of 20 and 50 mg/L was used. It indicates that the removal of AR 138 was strongly dependent on pH. Acidic condition was favourable at pH < 5. In this condition, the removal of AR 138 above 95 % was achieved. It has decreased with increasing pH values. The surface is positive at low pH where reaction (1) predominates and is negative at higher pH when reaction (2) takes over.

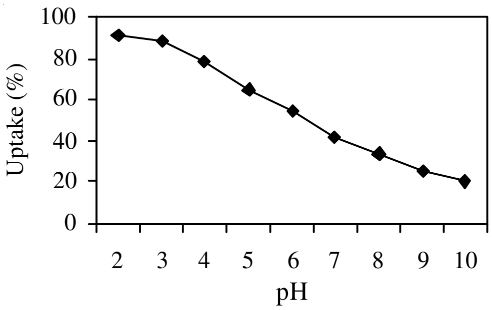


Fig. 3. Effect of pH of solution on the percentage uptake of AR 138 (50 mL of 50 mg/L) onto 1 g A-Ben: TiO_2 at room temperature

$$\text{Si—OH} + H^+ \rightleftharpoons \text{Si-OH}_2^+ \qquad (1)$$

$$\text{Si-OH} + OH^- \rightleftharpoons \text{Si- O}^- + H_2O \qquad (2)$$

As the pH of the dye solutions becomes lower, the association of dye anions with more positively charged bentonite surface were done, because of increasing $Si\text{-}OH_2^+$ groups, can more easily take place.

Effect of Cu: The affect of film thickness on the degradation amount of AR 138 dye was also investigated. The degradation amount of dye increases to 3 ppm of Cu concentration, but increasing of thickness of Cu on bentonite, the degradation amount begins to decrease. This indicates that a thin film catalyst thicker than 1 μm require no additional catalytic power. The main reason for this phenomenon is that a slow diffusion is limiting the number of molecular reaching the interior of the catalyst.

Thin films can add new chemical and physical properties to a substrate material. Unique combinations of properties can thus be obtained through particular combinations substrate and coating[35].

Effect of catalyst of TiO_2 (A-Ben/TiO_2): Experiments were carried out taking different amount of A-Ben:TiO_2, keeping 50 mL of dye (50 mg/L). In order to obtain an optimum condition with respect to the amount of catalyst used at which the photodegradation efficiency is maximum that can save unnecessary use of excess of photocatalyst quantity-wise.

Fig. 4 illustrates the effect of different amounts (10-70 mg) TiO_2 on the decomposition of the dye molecules. It is clear from Fig. 4 that the efficiency increases up to 30 mg of TiO_2/50 mL of the dye, beyond which it shows a gradual reduction in the rate constant. An increase in the efficiency is due to an increase in the number of active sites on A-Ben: TiO_2 available for the reaction, which in turn increases the rate of radical formation. The reduction in the rate constant may be due to the reduction in the penetration of light with surplus amount of A-Ben: TiO_2. The surplus addition of the catalyst makes the solution more turbid and light penetration is retarded. The addition of surplus catalyst also results in the deactivation of activated molecules by collision with ground state molecules. Results also showed that acid activated bentonite has higher efficiency than natural bentonite. 30 mg of TiO_2/50 mL of the dye solution was found to be the optimum condition for treatment, which shows maximum photodegradation efficiency.

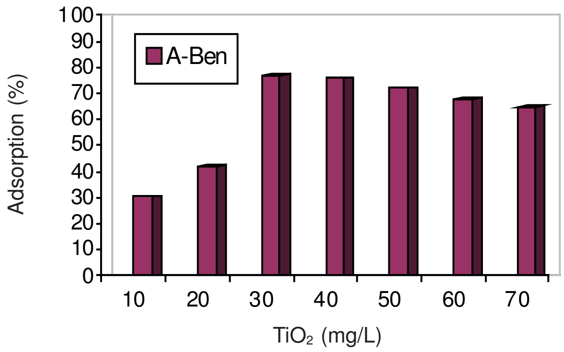


Fig. 4. Effect of TiO_2 dosage on degradation of AR 138 dye (50 mg/L) onto A-Ben: TiO_2

Effect of H_2O_2: Additional oxidant such as hydrogen peroxide was conducted to determine whether small addition of the oxidants can induce complete AR138 dye. This way, the strong adsorptive capacity of the supported catalysts can be combined with the oxidative capacity of additional hydroxyl radicals generated in the solution. The degradation rate by addition of hydrogen peroxide is attributed that it acts as electron acceptor to reduce the recombination rate of photo generated hole-electron pairs:

$$H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + {}^{-}OH$$

The reaction rates of AR 138 dye degradation was found to increase with the addition of H_2O_2 at low dosages (Fig. 5). It was observed that degradation rates of AR 138 decreased with the increase in hydrogen peroxide dosages and in fact were inhibited concentration 0.1 M H_2O_2. This is probably due to the following scavenging reaction:

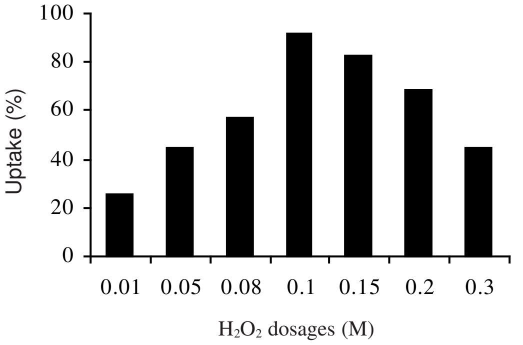


Fig. 5. Effect of H_2O_2 dosage on degradation of AR 138 dye (100 mg/L) onto A-Ben: TiO_2

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2$$

Monitoring of H_2O_2 concentration in solution indicates that competitive adsorption of hydrogen peroxide especially at higher dosages is also one of the reasons for the decrease of catalytic degradation rates.

Conclusion

It is found that activation of bentonite was able to increase the per cent of adsorption of AR 138 dye from aqueous solutions. The molecules of AR 138 dye have such affinity for the acid-activated bentonite surface that they are completely adsorbed from dilute solution. The surface charge on the adsorbent and the solution of pH play a significant role in influencing the capacity of an adsorbent toward acid dye AR 138 dye. Having an excess of positive charge on their surfaces, acid-activated bentonite has a greater capacity to adsorb acid dyes. Copper and TiO_2 supported on acid activated bentonite clay was found to be an effective catalyst for the degradation of AR 138 dye. Approximately adsorption of dye recorded after 90 min. Activation of bentonite with acid increases the oxygen percentage from 53.7-58.4, but supports a layer of A- Ben with Cu ion decrease the per cent of oxygen to 53.9; therefore it can remove the anion and acid dye.

The adsorption property of A-Ben was demonstrated by an adsorption test in the presence of H_2O_2 and TiO_2. This result suggests that A-Ben is a dependable adsorbent for the acid dye in particular AR 138 dye, but the major degradation is from the catalytic oxidation. The importance of H_2O_2 and TiO_2 is explained by comparing the percentage adsorption of AR 138 dye in the presence and absence of H_2O_2 and TiO_2. Monitoring H_2O_2 concentrations in solution indicates that competitive adsorption of hydrogen peroxide at higher dosages is also one of the reasons for the decrease of catalytic degradation rates. Although AR 138 dye concentration in water increased with the addition of H_2O_2 at higher dosages, which indicates the competitive adsorption of H_2O_2 on the catalyst surface releasing AR 138 dye in solution.

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