

Temperature Effects on Adsorption Rate for Azo Dye Removal From Textile Waste Water Using Activated Bentonite Clay

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ABSTRACT

Waste water from the textile industry is one of the major sources of contamination causing serious health problems. In textile waste water, dyes are the main pollutant. In this research work textile waste water was treated with various organic acid-activated clays to remove the dyes. Pink Azo dye was selected as a component to remove from waste water. Adsorbent selected was bentonite clay and was activated by acids such as phosphoric, acetic, oxalic, and citric acids. Adsorbent characteristics have been analyzed through infrared spectroscopy (FTIR) and Scanning Electron Microscope (SEM) while the removal of dye at various temperatures has been analyzed through Ultraviolet (UV) analysis. It was observed that the bentonite clay-treated with phosphoric acid had relatively maximum capacity to remove the dye while the clay treated with oxalic acid got minimum capacity to remove the dye from same waste water.

Keywords: Azo-dye, adsorption, Phosphoric, Acetic, Citric and Oxalic acids, SEM, FTIR, UV.

Introduction

Waste water from textile industries containing dyes is one of the major sources of pollutants causing contamination of water resources [1,5]. Due to large number of textile industries in various areas, effluent dyes are contaminating the water resources and creating a water pollution on massive scale [2,4]. Considering these issues, it is important to control these dye effluents especially for the protection of underground drinking water [3,6]. Various techniques have been developed for reducing the dye contents in waste water. Among different methodologies, dye removal through adsorption is the most effective and economical method [7,8]. There are different classes of dyes present in textile waste water. Among these classes AZO dye is the most common and found in almost in all kind of textile waste water. AZO-dye is the collective term used to describe a group of synthetics that rose to prominence in 1880's and now comprise 70% of all organic commercial dyes. AZO-dyes are being used because these are applied to cloth at low temperatures (60-65°C), while AZO free dyes require (95-100°C). AZO-dyes are also being used in wide range for better color fastness and shining at low cost [9,10].

AZO compounds have the functional group $R-N=N-R'$, in which R and R' can be either aryl or alkyl. Bentonite is categorized as a class of clay mineral which is made up of two consecutive silicate layers and its unit cell consists of two tetrahedral sheets bonded to either side of octahedral sheet. The low valency negative charge is due to the isomorphs replacement of Al^{+3} for Si^{+4} in tetrahedral layer and Mg^{+2} for Al^{+3} in octahedral layer. The negative charge is balanced by the presence of replacement of cations (Ca^{+2} , Na^{+} etc.). The high swell potential, small particle size and high specific surface area are the key factors which make bentonite clay the effective adsorbent for different applications [14,15].

Researches have shown that almost 50% of AZO-dyes go into the waste effluents [12,13]. The AZO-dyes under reduction

conditions produce dangerous substances known as aromatic amines (EU restricted aromatic amines), which are carcinogenic for both aquatic and human life [16]. Many techniques were developed for the recovery of AZO-dyes from waste effluents e.g. filtration, oxidation, adsorption and membrane separation. Among these methods the adsorption was reported to be more satisfactory due to the absence of non-disposable sludge. For enhancing the process of adsorption by using bentonite clay the activation of this clay is required [18]. Different techniques were used for its activation but the safest and most effective mode of surface activation and increasing the specific surface area is by organic acids due to the better safety of labor and equipment as compared to the activation of clay by HCL [17].

Activated bentonite clay (fuller earth) has many applications. It is being used in the removal of color of dyes, for the removal of poisonous and hazardous compounds from water, for increasing the thickness of paints, and in the preparation of porous heterogeneous clay material [19]. When fuller earth is activated the major modification takes place in the clay is the exchange of ions. The cations which are present between the layers of clay are replaced by the ions which are present in the solution [20,21].

The extent to which the fuller earth removes the color of AZO dye from waste water depend upon the type of fuller earth, type of acid, the temperature, and the residence time for activation of clay in acid. Organic and inorganic both acids can activate the bentonite clay. In case of inorganic acids like hydrochloric and sulfuric acid the equipment and human health damages were reported, only phosphoric acid is found as less hazardous. Fumigation of organic acids is relatively low compared to strongest inorganic acids, therefore the use of organic acid, and weak inorganic acid is better. The activation process is a slow process therefore agitation, residence time and temperature are important factors to improve the quality of clay. The degree of activation of fuller earth also depends upon the acid strength.



Low strength acids are not helpful in activating the bentonite clay. High strength acids are also not recommended to activate bentonite clays. Temperature is also an important factor to activate the bentonite clay. The temperature for activation should be in between 30°C to 70°C. Above this temperature the fuming of acids damages the environment whereas below this temperature the activation process become slow. Bentonite clay without activation cannot pick the AZO dye as effectively as it can pick in activated form [22-28].

EXPERIMENTAL SECTION

MATERIAL

Waste water containing AZO dye was collected from local textile mill and was used in experiments without further treatment. The 50 ml of dye solution was used in all experiments for dye removal. All organic acids of analytical grade of Merck (Germany) were used. A standard 1N solution of all acids was prepared by dissolving the acids in distilled water and used for the activation of bentonite clay. Bentonite clay of Engelhard (USA) was used for activation.

SAMPLE PREPARATION

Four samples were prepared by adding 8 g fuller earth in each 50 ml of 1N solutions of different acids such as phosphoric acid, acetic acid, citric acid and oxalic acid. Each sample was put into the shaker at 60°C for 24 hours followed by filtration by ordinary filter paper. The samples were washed by distilled water and then dried in electric oven at 250°C for 3 hours. The activated clay samples were stored in plastic jars for further application.

TREATMENT OF WASTE FOR DYE REMOVAL

Various temperatures and residence times were selected for experimentation. Experiments were carried out in a batch reactor by using 50 ml of waste water with 5 gm of activated clay. A constant agitation of 20 rpm was selected using thermostatic magnetic stirrer with the residence time of 60 min at various temperatures such as 30° 35° 40° 45° 50° and 55°C followed by filtration and drying in oven at 90°C for 6 hours. The dried samples were analyzed by Ultra-violet (UV) spectrometry by monitoring the absorbance changes at the wavelength of maximum absorbance.

METHOD OF CHARACTERIZATION

The FTIR analysis was performed to identify the changes in the structure of the sorbent after activation by comparison between raw and activated clay. The Infra-red spectroscopic analysis was also performed to study the variation of properties of AZO dye before and after treatment. Properties of dye in waste water were also studied using ultraviolet analysis. The absorbance of dye before and after treatment was studied and the effect of temperature was verified. Detailed structural analysis of sorbents was finally analyzed through Scanning Electron Microscope (SEM) for changes in structure before and after treatment at micro level [27].

RESULTS AND DISCUSSIONS

F.T.I.R STUDIES

In fig.1 spectrum behavior of raw clay is more intensive at the beginning. More sharp peaks were found in wavenumber range between 2000 cm⁻¹ to 2500 cm⁻¹ showing greater tendency of adsorption in this region. Alkyl group of carbon triple bond stretch lies in this range which shows greater tendency of unsaturation which ultimately links directly with greater tendency of adsorption.

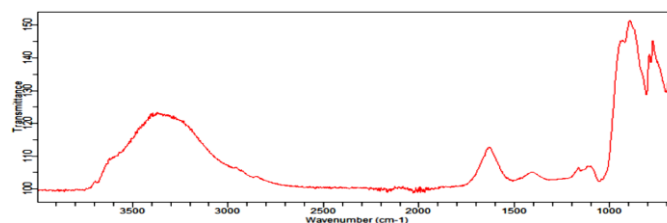


Figure 1: Raw Clay Analysis

Oxalic acid treatment of fig.2 shows more intensive behavior spectrum especially in the range of wave numbers 2100 cm⁻¹ to 3300 cm⁻¹. Spectrum transmittance level is also enhanced in this region. However peak sharpness is relatively low throughout the spectrum. Little sharp peaks are observed in the region between 1900 cm⁻¹ to 2100 cm⁻¹.

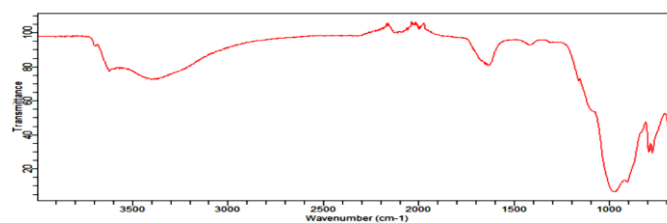


Figure 2 Oxalic acid activated clay analysis

However citric acid treated clay spectra in fig.3 shows greater enhancement and modification of sorbent properties of clay. The intensive behavior and transmittance level is comparatively greater than previous two analyses. Sharper peaks are produced in large range of wavenumbers between 1500 cm⁻¹ to the end. Alkyl triple bond and benzene triple bond groups lie within this range which shows higher degree of unsaturation and therefore greater rate of adsorption.

For the clays treated with acetic acid and phosphoric acid, the spectra generated by FTIR is shown in fig.4. The intensive behavior of spectrum is almost the same as in fig.2 and fig.3 but the relative sharpness of peaks is different within this spectrum and sharpness tendency of peaks exists in various regions. Peak development at various portions of spectrum shows the enhanced adsorption tendency of the activated clays.

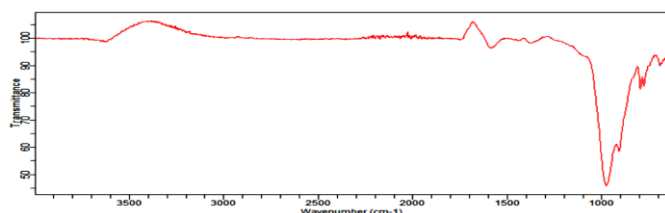


Figure 3 FTIR after Citric Acid treatment

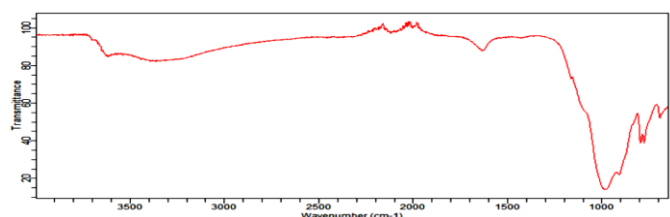
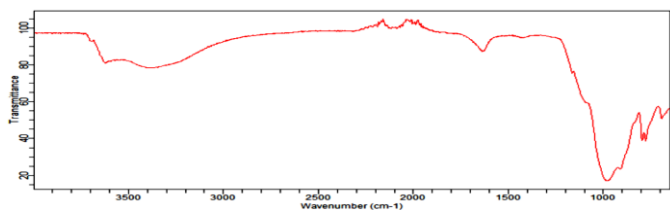


Figure 3: Acetic Acid and Phosphoric acid treated clay FTIR analyses

SEM ANALYSIS

Figure 5 shows the scanning electron microscopic image at 5000 magnifications for phosphoric acid treated clay. From this image, the enhanced porosity of clay is clear. Different porous zones are generated inside the clay structure which can adsorb more material comparatively. Increased distance between the layers shows porous behavior and more availability of space for dye to penetrate between these layers.

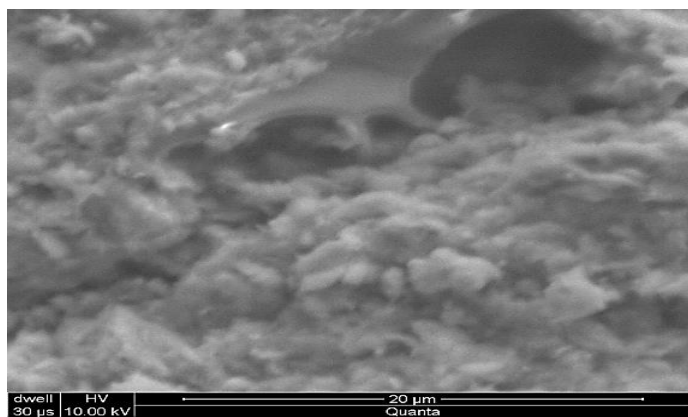


Figure 4 Phosphoric acid treated clay sem analysis

Figure 6 is for acetic acid treated clay at 4000 magnifications. The acetic acid treated clay has also become porous. The different porous zones represent the enhanced surface area available for the dye to absorb. In both cases the enhanced

surface area is favorable for the dyes to be absorbed at the surface with greater quantities. Only large surface area is not sufficient to absorb the dye, it should also have the charge and capability to absorb the dye at reasonable temperature which is not possible to identify in SEM images.

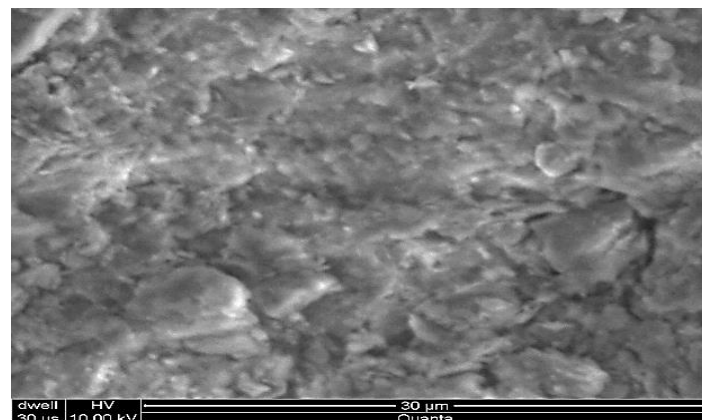


Figure 5 Acetic acid treated clay SEM analysis

Comparing the magnified images of clays treated with phosphoric acid and acetic acid under same conditions the surface area rendered by clay treated by phosphoric acid is larger than the clay treated by acetic acid. A good technique to measure the surface area is the BET technique which tells the surface areas of any particle under consideration. In SEM technique, it is possible to compare the surface area not mathematically but visually. Overall SEM images of phosphoric acid acetic acid showed effective results in terms of enhanced porosity compared to the raw clay. Oxalic acid and Citric acid treated clays showed less surface area increase in SEM images therefore their images are not included in this article.

UV-STUDIES

UV analysis is carried out to find out the light absorbance on treated samples with dyes at different temperatures. Absorbance value of sample indicates the amount of dye removed from the waste water. Table 1 shows the absorbance values of treated clays at different temperatures with same residence time of 1hr.

Table 1: UV-Analysis of Phosphoric Acid clay treated dye sample

Sr. No.	Temp ($^{\circ}$ C)	Time (hr)	Absorbance Value
1	30	1	1.264
2	35	1	1.029
3	40	1	0.527
4	45	1	0.248
5	50	1	1.424
6	55	1	0.873

Absorbance values of phosphoric acid treated clays at different temperatures are obtained at different wavelengths. With increase in temperature, the absorbance values start decreasing which shows decrease in concentration of dye and increase in the efficiency of adsorption. The minimum absorbance value shows maximum dye removal from waste water. Hence the best and optimum value of temperature for maximum adsorption is 45 °C for phosphoric acid treated clay. At 50 °C the absorbance value starts increasing which shows decrease in the efficiency of adsorption process. The overall behavior of clay absorbance at different temperatures is shown in fig.5.

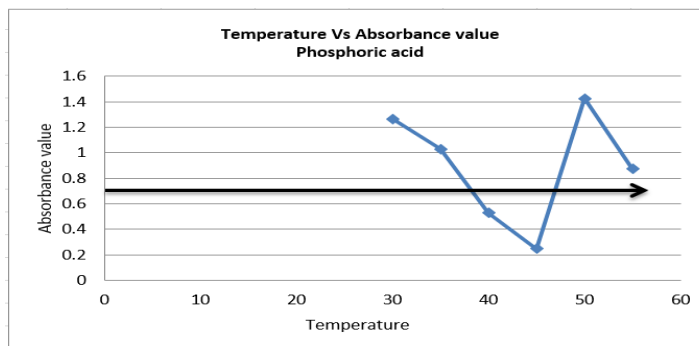


Figure 6: Absorption value of phosphoric acid vs temperature

Table 2: UV-Analysis of Acetic Acid clay treated dye sample

Sr. No.	Temp (°C)	Time (hr)	Absorbance Value
1	30	1	1.328
2	35	1	1.077
3	40	1	1.034
4	45	1	0.258
5	50	1	1.790
6	55	1	0.508

The UV results of clays treated with acetic acid are shown in table 2. The absorbance values of clays treated with acetic acid are higher than the absorbance values of clays treated with phosphoric acid. The trend of both clays is similar. At 45 °C again the absorbance value for acetic acid treated clay is minimum as we observed in case of phosphoric acid treated clay in table 1. Figure 6 shows the trend of absorbance against temperatures for acetic acid treated clays. Low absorbance value means high dye removal. Relatively all absorbance values of acetic acid treated clays are higher than the absorbance values of phosphoric acid treated clays.

Clays treated with citric acid after activation showed poor results as compared to phosphoric and acetic acid treated clays. The UV results of citric acid treated clays are shown in table 3. At each temperature compared to previous two acids the absorbance value is higher. The absorbance values for given 6 temperatures first increases then decreases. For all temperature the absorbance

value is much higher indicating less removal of dyes. At 35 °C the absorbance value is minimum which is more than 3 times higher than phosphoric acid treated clay. The trend of absorbance vs temperature graphically are shown in Figure 7.

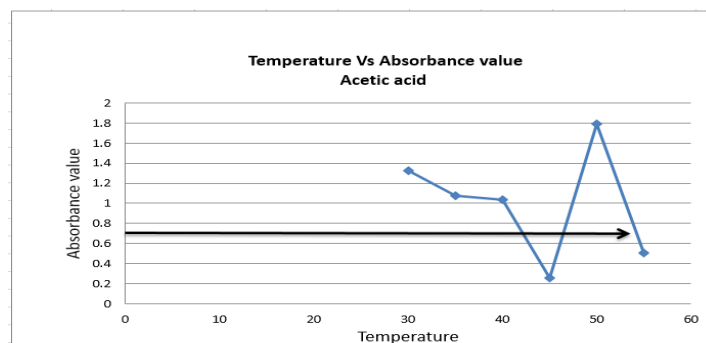


Figure 7: Absorption value of acetic acid vs temperature.

Table 3: UV-Analysis of Citric Acid clay treated dye sample

Sr. No.	Temp (°C)	Time (hr)	Absorbance Value
1	30	1	3.954
2	35	1	3.079
3	40	1	3.733
4	45	1	4.323
5	50	1	3.557
6	55	1	3.843

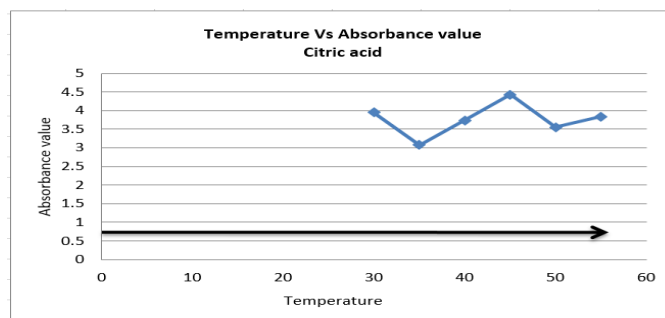


Figure 8: Absorption value of citric acid vs temperature.

Table 4: UV-Analysis of Oxalic Acid clay treated dye sample

Sr. No.	Temp (°C)	Time (hr)	Absorbance Value
1	30	1	3.647
2	35	1	5.645
3	40	1	3.494
4	45	1	4.543
5	50	1	2.540
6	55	1	9.257

Among four acids the dye removal properties of clays treated with oxalic acid showed the least results. For same temperature and same residence time the absorbance values of clays treated with oxalic acid are higher than the clays treated with citric acid. Table 4 shows the absorbance values of clays treated with oxalic acid. In the figure 8 these values are expressed graphically. The absorbance values are not uniform. At one temperature, it's higher and by slight increasing the temperature it increases or decreases. This behavior cannot be explained in simple words but may be concluded that such clays treated with oxalic acid are not fit for dye removal from water.

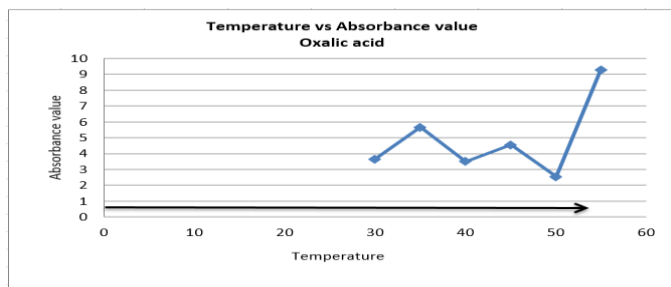


Figure 9: Absorption value of oxalic acid vs temperature.

Conclusions

Bentonite clay activated by organic acids can remove the pink AZO dye from waste water of textile industry containing AZO dyes. Four organic acids were used to activate bentonite clay such as phosphoric, acetic, oxalic and citric acid. All four acids were used to activate the bentonite clay at same temperatures, normality and time. The activated clays then was used to remove AZO dye from waste under similar conditions. Clays were tested for AZO dye removal by FTIR, UV and examined by SEM for surface changes. It was observed that all four treated clays are capable to remove AZO dyes from waste water. Clay treated by phosphoric acid was found to be the most effective among four clays. By increasing the temperature of waste water (45C to 50C) the adsorption increases except the clay treated by oxalic acid. SEM result shows the increase in surface area of all four treated clays. It was observed that increase in surface area of clay adsorbed more dye. FTIR results confirmed the SEM results of surface area of the clays. Among four organic acids the most favorable acids were phosphoric acid and acetic acid. Other two acids had the little effect in removing the AZO dyes.

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