Adsorption of Amido Black 10B by ZnFe$_2$O$_4$-ZnO Nanopowder

M. N. Zulfiqar Ahmed, A. A. Jahagirdar, H. M. Somashekar

Abstract: ZnFe$_2$O$_4$-ZnO nanopowder was synthesized by solution combustion method using zinc nitrate and ferric nitrate as oxidizers and oxalyl dihydrazide as fuel. The nanopowder was characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) surface area measurements. The nanopowder was used as adsorbent for the removal of the dye Amido Black 10B (AB 10) from its aqueous solution. The effect of dosage of the nanopowder and contact time was studied. The results indicated that the nanopowder acted as a good adsorbent for the removal of AB 10. More than 89% removal of the dye was achieved for a catalyst dosage of 0.8 g of the nanopowder per liter of the dye solution. The optimum contact time was found to be 40 minutes. Adsorption isotherms and adsorption kinetic models were applied to the adsorption data to know the mechanism and kinetics of adsorption. The adsorption data fitted well for the Langmuir adsorption isotherm and followed pseudo-second order kinetics.

Keywords: ZnFe$_2$O$_4$-ZnO, solution combustion synthesis, adsorption isotherms, Amido Black 10B.

I. INTRODUCTION

The major pollutants of water include heavy metals, pesticides, dyes, detergents, degreasing agents, volatile organic compounds and chlorophenols [1]. Synthetic dyes are extensively used in the textile industry and are therefore common industrial pollutants [2]. The textile industry releases huge quantities of intensely coloured effluents which are highly toxic in nature besides being resistant to destruction by biological treatment methods [3]. The dyeing process employs various types of dyes based on the type of fabric. These dyes include acidic, reactive, basic, disperse, azo, diazo, anthraquinone based and metal complex dyes [4]. Azo dyes are among the toxic and most recalcitrant classes of compounds to treat due to the presence of one or more azo groups in them which are usually attached to radicals [5].

Each dye contains at least one chromophore and auxochromes which impart intense colour to it which is undesirable and disgusting in wastewater. Several conventional treatment methods such as flocculation, chemical oxidation and membrane separation employed for the removal of dyes from wastewater are not effective. Adsorption is being considered as an important process for the removal of synthetic dyes from wastewater due to its imaginative opportunity to design the chemical composition of the adsorbent surface [6]-[10]. The removal of colour from wastewater is as important as the removal of other pollutants. The decolouration of effluents from textile dyeing and finishing industries is very important due to aesthetic and environmental concerns [11]-[15].

The synthesis of nano metal oxides with high surface area for use as adsorbents in the removal of dyes from wastewaters has attracted the attention of many researchers across the globe. Several nano metal oxides such as MgO, ZnO, α-Fe$_2$O$_3$, TiO$_2$ etc. have been used for the removal of dyes [16]. Nanocomposites are multiphase solid materials in which the average crystallite size of at least one of the phases lies in the nanometer range. These nanocomposites usually exhibit better sorption, catalytic, optical, electrical, and other special properties [17]. In comparison to their individual components, these nanocomposites are high performance materials that exhibit unusual properties in combination and are being regarded by some researchers as the materials of the 21st century [18]. They possess high specific surface area and find potential applications in gas sensors, photocatalysis and photo-electrochemical cells [19]. The synthesis of various nanocomposites such as ZnO/TiO$_2$, ZnO/SnO$_2$, ZnO/CO$_3$O$_4$, TiO$_2$/SnO$_2$ etc. by various methods has been reported in literature. Some of these methods include hydrothermal, chemical bath deposition, chemical vapor deposition, sol-gel and co-precipitation. However, many of these methods suffer from various drawbacks such as long reaction time, requirement of high reaction temperature and so on [20]-[22].

Solution combustion synthesis is an important method for the synthesis of a number of nano metal oxides, ferrites and other nanomaterials. It has several advantages such as low processing time, relatively lower operating-temperature, cost effectiveness, good stoichiometric control and ultrafine particle formation with narrow size distribution [23]-[25]. In the present study, we report the synthesis of the nanocomposite ZnFe$_2$O$_4$-ZnO by solution combustion method. The efficiency of the nanopowder as adsorbent for the removal of the azo dye Amido Black 10B (AB 10) from its aqueous solution was studied. The data was analyzed using adsorption isotherms and adsorption kinetic models.
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II. MATERIALS AND METHODS

A. Synthesis of the ZnFe$_2$O$_4$-ZnO Nanopowder

All the chemicals used were procured from M/s sd Fine Chemicals Limited, India. The fuel oxalyldihydrazide (ODH) was prepared by the reaction between diethyl oxalate and hydrazine hydrate [26]. A 1000 ppm stock solution of AB 10 was prepared using double distilled water. The stock solution was appropriately diluted to give solution of concentration 10 ppm. All the chemicals were of analytical grade and were used without purification. Double distilled water was used throughout the experiment.

Solution combustion synthesis involves combustion reaction between the oxidizer and the fuel. In case of the ZnFe$_2$O$_4$-ZnO nanocomposite, zinc nitrate and ferric nitrate were used as oxidizers and ODH was used as fuel. Appropriate amounts of zinc nitrate and ferric nitrate were dissolved in minimum quantity of double distilled water taken in a cylindrical pyrex dish of approximately 300 cm$^3$ capacity. Appropriate amount of ODH was added to it and the mixture was stirred magnetically for about 10 minutes and then placed on a hot plate when the excess water was evaporated and a pasty mass was left behind. The pyrex dish was then introduced into a muffle furnace maintained at about 350°C. The reaction mixture first dehydrated, ignited at one point and then burnt instantaneously resulting in the formation of the desired nanopowder. It was then cooled to room temperature and ground well (Fig. 1).

The formation of the nanopowder can be represented by 

$$3\text{Zn}(\text{NO}_3)_2(aq) + 2\text{Fe}(\text{NO}_3)_3(aq) + 6\text{C}_2\text{H}_6\text{N}_4\text{O}_2(s) \rightarrow \text{ZnFe}_2\text{O}_4(s) + 2\text{ZnO}(s) + 12\text{CO}_2(g) + 18\text{H}_2\text{O}(g) + 18\text{N}_2(g)$$

(1)

48 moles of gases were released during the formation of one mole of the ZnFe$_2$O$_4$-ZnO nanopowder.

B. Characterization of the Nanopowder

The PXRD data of the nanopowder was used to know its phase purity and crystal structure. The PXRD data was recorded with the help of Philips X’Pert pro X-ray diffractometer. Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) at 40 kV was used. The mean crystallite size of the nanopowder was estimated using (2) known as the Scherer’s equation [27].

$$D = \frac{k\lambda}{\beta\cos\theta}$$

(2)

where, $D$ is the mean crystallite size, $k$ is a constant, $\lambda$ is the wavelength of the X-rays used, $\beta$ is the full width at half maximum and $\theta$ is called the Bragg’s angle.

The identification of various chemical groups present in the nanopowder was done by Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum of the nanopowder was recorded using Perkin-Elmer spectrometer (spectrum 1000) with KBr as the reference.

The surface morphology of the nanopowder was determined by SEM. The SEM micrograph of the nanopowder was recorded using JEOL-2100F (Japan) scanning electron microscope.

The Brunauer-Emmet-Teller (BET) surface area of the nanopowder was determined by nitrogen adsorption using the instrument MICROMERITICS GEMINE 2375. Nitrogen gas was allowed to be adsorbed onto the nanopowder at 77 K. Prior to the analysis, the nanopowder was degassed in an evacuation chamber at a temperature of 523 K under a vacuum of 10$^{-5}$ Torr for 12 hours.

C. Batch Adsorption Studies

Amido Black 10B is an amino acid staining diazo dye used for staining total protein on transferred membrane blots. It also finds applications in criminal investigations for the detection of blood present with the latent fingerprints. It has the molecular formula C$_{32}$H$_{44}$N$_{18}$Na$_2$O$_{10}$S$_2$ and molecular mass equal to 616.49 gmol$^{-1}$. Chemically it is 4-Amino-5-hydroxy-3-[(4-nitrophenyl)azo]-6-(phenylazo)-2,7-Naphthalene disulfonic acid disodium salt. The dye is readily soluble in water and exhibits hazardous effects such as skin and eye irritation. It also exhibits hazardous effects on ingestion and inhalation [28]-[31]. The structure and absorption spectrum of AB 10 are shown in Fig. 2 and Fig. 3 respectively. The maximum absorption was observed at a wavelength of 618 nm.

The adsorption of AB 10 by the ZnFe$_2$O$_4$-ZnO nanopowder was carried out in a batch mode at room temperature. 50 cm$^3$ of the 10 ppm dye solution was transferred to a 500 cm$^3$ beaker followed by addition of appropriate amount of the nanopowder. The mixture was stirred magnetically in the dark for about 30 minutes and centrifuged at around 2500 rpm for about 10 minutes. The absorption spectrum of the supernatant solution was recorded in the wavelength range of 300 to 900nm. The experiments were conducted by varying the dosage of the nanopowder from 0.1 to 1.0gL$^{-1}$.
The powder.

One way of minimizing their observed in the SEM during the complex decomposition. The SEM micrograph. The presence of voids and high porosity make the nanopowder a good adsorbent material. In solution combustion synthesis, the morphological characteristics of the nanopowders are strongly dependent on the heat and gases generated during the complex decomposition. The liberation of large volumes of gases facilitates the formation of tiny particles whereas the heat released is an important factor for crystal growth. The agglomeration of the particles is usually considered as a common way of minimizing their surface free energy [42]-[43].

III. RESULTS AND DISCUSSION

A. Characterization Results

Equation (3) was used to calculate the percentage removal of AB 10 [32].

\[
\text{Percentage dye removal} = \frac{(C_0 - C_e) \times 100}{C_0}
\]

where \(C_o\) and \(C_e\) represent the initial and equilibrium concentrations of the dye solution.

The optimum dosage of the nanopowder was determined by plotting the graph of \(C/C_e\) versus the dosage of the nanopowder.

In order to determine the effect of contact time, 100 cm\(^3\) of the dye solution was taken in the 500 cm\(^3\) beaker and optimum amount of the nanopowder was added to it. The mixture was stirred magnetically in the dark. A small aliquot of the mixture was taken out after every 5 minutes, centrifuged and the UV-Visible spectrum was recorded as discussed earlier. The experiment was conducted up to a contact time of 120 minutes. The optimum contact time was determined by plotting the graph of \(C/C_e\) versus the contact time.

**Fig. 3. Absorption spectrum of Amido Black 10B**

**Fig. 4. PXRD pattern of the ZnFe\(_2\)O\(_4\)-ZnO nanopowder**

**Fig. 5. FTIR spectrum of the ZnFe\(_2\)O\(_4\)-ZnO nanopowder**

**Fig. 6. SEM micrograph of the ZnFe\(_2\)O\(_4\)-ZnO nanopowder**

without any impurity peak. The average crystallite size as determined by Scherer’s formula was found to be around 15 nm.

Fig. 5 depicts the FTIR spectrum of the nanopowder. The peak at around 352 cm\(^{-1}\) was attributed to the Zn-O bond whereas the peaks at around 416 and 542 cm\(^{-1}\) were attributed to the Fe-O bond [37]-[39]. The peaks at around 2361 cm\(^{-1}\) and 3434 cm\(^{-1}\) were ascribed respectively to the vibrational modes of atmospheric CO\(_2\) and the –OH group of water adsorbed on the surface of the nanocomposite [40]-[41].

Fig. 6 represents the SEM micrograph of the ZnFe\(_2\)O\(_4\)-ZnO nanopowder. The particles were agglomerated with a flake like morphology. Voids were also observed in the SEM micrograph. The presence of voids and high porosity make the nanopowder a good adsorbent material. In solution combustion synthesis, the morphological characteristics of the nanopowders are strongly dependent on the heat and gases generated during the complex decomposition. The liberation of large volumes of gases facilitates the formation of tiny particles whereas the heat released is an important factor for crystal growth. The agglomeration of the particles is usually considered as a common way of minimizing their surface free energy [42]-[43].

**Fig. 4. PXRD pattern of the ZnFe\(_2\)O\(_4\)-ZnO nanopowder**

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**Fig. 3. Absorption spectrum of Amido Black 10B**
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Fig. 7 represents the plot for BET surface area of the nanopowder. The BET surface area of the nanopowder was found to be 19.22 m$^2$g$^{-1}$ and the mean pore diameter was found to be 4.6816 nm.

**B. Batch Adsorption Results**

Fig. 8 represents the effect of dosage of the nanopowder on the adsorption of AB 10 by the nanopowder. The amount of dye adsorbed increased with an increase in the amount of nanopowder up to an optimum dosage. This is due to the fact that an increase in the amount of nanopowder increased the number of adsorbent sites which resulted in the adsorption of more number of dye molecules on the surface. The adsorption was maximum for a catalyst dosage of 0.8 gL$^{-1}$. A further increase in the amount of the nanopowder beyond 0.8 gL$^{-1}$ resulted in negligible increase in adsorption.

Fig. 9 shows the effect of contact time on the adsorption of AB10 by the nanopowder. Maximum adsorption occurred for a contact time of 40 minutes. Beyond the optimum contact time, the dye removal was negligible. Under optimum conditions, more than 89% of the dye removal was achieved.

**C. Adsorption Isotherms and Adsorption Kinetics**

The adsorption data was analyzed by Langmuir and Freundlich adsorption isotherms. The linear form of the Langmuir isotherm is given by using (4).

$$\frac{C_e}{q_e} = \frac{1}{Q_0b} + \frac{1}{Q_0C_e}$$  \hspace{1cm} (4)

where $q_e$ (mg g$^{-1}$) is the equilibrium adsorption capacity, $C_e$ (mg L$^{-1}$) is the equilibrium liquid phase concentration, $Q_0$ (mg g$^{-1}$) is a constant related to maximum adsorption capacity and $b$ (Lmg$^{-1}$) is the Langmuir constant related to the adsorption energy.

The dimensionless constant separation factor $R_L$ was calculated using (5).

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (5)

where $C_0$ is the initial dye concentration and $b$ has usual meaning. A value of $R_L$ between 0 and 1 indicated the feasibility of the adsorption process [44]-[45].

The Freundlich adsorption isotherm is a fairly satisfactory empirical isotherm which can be used in case of adsorption involving dilute solutions. (6) represents the linear form of the Freundlich isotherm.

$$lnq_e = lnK_F + \frac{1}{n}lnC_e$$  \hspace{1cm} (6)

where the constant $K_F$ (mg g$^{-1}$) is related to the relative adsorption capacity; the constant $n$ (gL$^{-1}$) is related to the intensity of adsorption. A good adsorbent has a value of $n$ between 1 and 10. The lower the value of $n$, the better is the adsorption. It also indicates the formation of relatively strong bond between adsorbate and adsorbent [46].

The free energy of adsorption ($E$) was calculated by using (7).

$$E = \frac{1}{\sqrt{2K_F}}$$  \hspace{1cm} (7)

A value of $E$ between 1 and 16 kJmol$^{-1}$ indicates that the adsorption is physical in nature whereas a value of $E$ more than 16 kJmol$^{-1}$ indicates that adsorption is chemical in nature [47].

Fig. 10 and Fig. 11 represent the plots of the Langmuir and Freundlich isotherms respectively. From Table I, it is evident that the adsorption obeyed the Langmuir adsorption isotherm indicating multilayer adsorption. The value of $R_L$ was between 0 and 1 which also indicated that adsorption is a favorable process in the removal of AB 10 by the
The value of $E$ below 16 kJmol$^{-1}$ indicated that the adsorption was mainly physical in nature.

Several mathematical models have been reported in the literature which quantitatively describe the kinetics of the adsorption process. The pseudo-first order and the pseudo-second-order models were applied to determine the kinetic of the adsorption process.

In case of pseudo-first order model, the rate constant is determined by using (8) known as the Lagergren equation [48].

$$\frac{dt}{dt} = k_1(q_e - q_t) \quad (8)$$

![Fig. 10. Langmuir adsorption isotherm for the adsorption of AB 10 by the ZnFe$_2$O$_4$-ZnO nanopowder](image)

The linear form of the pseudo-first order equation is given by using (9).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (9)$$

where, $q_e$ and $q_t$ indicate the amounts of dye adsorbed (mgg$^{-1}$) at equilibrium and at time $t$ (min), respectively; and $k_1$ (min$^{-1}$) the rate constant of the pseudo-first order adsorption.

The values of $k_1$ were calculated from the plots of $\log(q_e - q_t)$ versus $t$. The slope of the straight line is $-k_1/2.303$ and intercept $\log(q_e)$.

The pseudo-second order equation based on the adsorption capacity can be expressed by using (10) [49]-[50].

$$\frac{dt}{dt} = k_2(q_e - q_t)^2 \quad (10)$$

where $k_2$ (gmg$^{-1}$min$^{-1}$) is the rate constant of pseudo-second order absorption.

Separating the variables in (10) gives (11).

$$\frac{dt}{(q_e - q_t)^2} = k_2dt \quad (11)$$

The linear form of the pseudo second order equation is represented by (12).

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \quad (12)$$

The values of $k_2$ and $q_e$ were calculated from the linear plot of $t/q_t$ versus $t$. The linear plot of $t/q_t$ versus $t$ shows a good agreement of the experimental data with the pseudo-second order kinetic model. The good correlation coefficients for the pseudo-second order model justify the adsorption mechanism.

Fig. 12 and Fig. 13 represent the plots for the pseudo-first order and the pseudo-second order kinetic models. From Table II, it was evident that the $R^2$ value was higher in case of the pseudo-second order model compared to the pseudo-first order model. It was concluded that the adsorption of AB 10 by the ZnFe$_2$O$_4$-ZnO nanopowder followed pseudo-second order kinetic model.

![Fig. 11. Freundlich adsorption isotherm for the adsorption of AB 10 by the ZnFe2O4-ZnO nanopowder](image)

![Fig. 12. Pseudo-first order kinetic model for the adsorption of AB 10 by the ZnFe$_2$O$_4$-ZnO nanopowder](image)

**Table I: Various isotherm parameters for the adsorption of AB 10 by the ZnFe$_2$O$_4$-ZnO nanopowder**

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$Q_0$ (mgg$^{-1}$)</td>
<td>0.7921</td>
</tr>
<tr>
<td></td>
<td>b (Lmg$^{-1}$)</td>
<td>1.0107</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9946</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$ (mgg$^{-1}$)</td>
<td>0.7081</td>
</tr>
<tr>
<td></td>
<td>n (gL$^{-1}$)</td>
<td>4.4982</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8845</td>
</tr>
<tr>
<td></td>
<td>E (kJmol$^{-1}$)</td>
<td>2.3656</td>
</tr>
</tbody>
</table>
IV. CONCLUSION

ZnFe$_2$O$_4$-ZnO nanopowder was successfully prepared by solution combustion method and characterized by PXRD, FTIR, SEM and BET surface area techniques. The nanopowder was used as adsorbent for the removal of the dye Amido Black 10B from its aqueous solution. The effect of dosage of the nanopowder and contact time on the rate of adsorption was studied. The results indicated that the ZnFe$_2$O$_4$-ZnO nanopowder acted as a good adsorbent for the removal of AB 10. The adsorption was found to obey Langmuir adsorption isotherm and followed pseudo-second order kinetics. It was concluded that ZnFe$_2$O$_4$-ZnO nanopowder can be used as a good adsorbent material for the removal of dyes from textile and paper effluents.

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REFERENCES


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