Utilization of Synthesized Nano-Zinc Oxide in Yellow Basic Dye Decontamination from Industrial Wastewater

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Abstract: ZnO nanorod has been successfully synthesized through the reduction of Zinc chloride salt with ammonia solution in the presence of triethanolamine (TEA) as surfactant agent via hydrothermal technique. The properties of the produced material were determined using different characterization techniques such as X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared spectrum (FTIR). The results showed that the as-prepared ZnO are rod-like morphologies at pH equal to 10. The synthesized nano rod-zinc oxide was employed as adsorbent agent for basic yellow 28 dye decolorization from polluted industrial wastewater. The synthesized nano-ZnO was achieved 93.26% dye decolorization affinity with in 60minutes. The variation in the different processing parameters on the dye sorption process was elucidated using batch technique. The increment in both the dye solution pH and its temperature was association with decline in the decolourization process. The optimum nano-zinc oxide dosage was recorded to be equal to 10 g/L. The adsorption data at equilibrium were analyzed using Langmuir, Freundlich and Temkin equilibrium isotherms. The experimental results confirmed the applicability of synthesized nano-zinc oxide as adsorbent agent for dye decontamination from polluted wastewater.

Keywords: nano-zinc oxide, dye decolourisation, sorption parameters.

Introduction

The residual dyes from different industries (e.g., textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery, and Kraft bleaching industries, etc.) are considered a wide variety of organic pollutants introduced into the natural water resources or wastewater treatment systems. The discharge of dye-containing effluents into the water environment is undesirable, not only because of their color, but also because many of dyes released and their breakdown products are toxic, carcinogenic or mutagenic to life forms mainly because of carcinogens, such as benzidine, naphthalene and other aromatic compounds, Suteu, D. et al (2009). Dye concentrations in watercourses higher of 1 mg/L caused by the direct discharges of effluents, treated or not, can give rise to public compliant. High concentrations of dyes in water bodies stop the reoxygenation capacity of the receiving water and cutoff sunlight, thereby upsetting biological activity in aquatic life and also the photosynthesis process of aquatic plants or algae, Zaharia, C. et al (2009).
The polluting effects of dyes against aquatic environment can be also the result of toxic effects due to their long time presence in environment (i.e. half-life time of several years), accumulation in sediments but especially in fishes or other aquatic life forms, decomposition of pollutants in carcinogenic or mutagenic compounds but also low aerobic biodegradability. Due to their synthetic nature and structure mainly aromatic, the most of dyes are non-biodegradable, having carcinogenic action or causing allergies, dermatitis, skin irritation or different tissular changes. High potential health risk is caused by adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal tract, skin, lungs, and also formation of hemoglobin adducts and disturbance of blood formation, Bornick, H. et al (2006).

One of the powerful treatment processes for the removal of dyes from water is adsorption. Adsorption techniques have been proven successful in removing coloured organics, Erdem et al., (2004). Adsorption is the separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. It is the process that takes place when a liquid known as the adsorbate accumulates on the surface of a solid adsorbent and forming a molecular film.

Among the possible techniques for water decolourization from dye contaminates, the adsorption process by solid adsorbents shows potential as one of the most efficient methods for the treatment and removal of these harmful contaminants in wastewater treatment processes. Adsorption has advantages over the other methods because of simple design and can involve low investment in term of both initial cost and land required.

Since the adsorption process is a surface phenomenon, the extent of adsorption is proportional to the specific surface area which is defined as that portion of the total surface area that is available for adsorption, El-Sheikh, A.H. et al (2004) and Naeem, A. et al (2007). Thus more finely divided and more porous is the solid; the greater is the amount of adsorption accomplished per unit weight of a solid adsorbent, Weber. W (1972). The high surface area to mass ratios of nano-adsorbent materials can greatly enhance the adsorption capacities of these sorbent materials. In this respect, zinc oxide nano-rod will be prepared using the hydrothermal technique to be utilized as adsorbent material. Hydrothermal technique is a promising synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process have several advantage over other materials growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous. The prepared zinc oxide particle properties such as morphology and size can be controlled via the hydrothermal process through adjusting the reaction temperature, time and concentration of precursors. Chen, X. et al (2007).

The purpose of this work is the study of the removal of basic Yellow 28 from aqueous solutions by adsorption process using the hydrothermal prepared nano-zinc oxide. The processing parameters that affect on the dye decolorization process onto the nano-zinc oxide adsorbent material was investigated.
Materials and Methods

Materials and chemicals:

Zinc chloride anhydrous (M.wt 136.29), ammonium hydroxide (NH₄OH), tri-ethanol amine (TEA) M.WT149.19 g/mol, ethanol 99.5%, Distilled water and Basic Yellow 28 dye with 433.52M.wt and its chemical structure was explored in (figure 1).

![Chemical structure of the Basic Yellow 28 dye](image)

Figure 1. Chemical structure of the Basic Yellow 28 dye

Synthesis of nan-zinc oxide adsorbent material using hydrothermal technique

Firstly, add 2.0 g zinc chloride anhydrous in 250ml distilled water under stirring by magnetic stirrer, add specific volume from the tri-ethanol amine surfactant (TEA) to the zinc chloride salt. Adjust the solution pH at 10 through the drop wise addition of ammonia solution (1mole/liter). Insert the reaction beaker onto the autoclave under 500Kpa pressure and 70°C temperature for 300 minutes reaction time. Wash the produced white precipitate several times by distilled water and ethyl alcohol and then dry the white precipitation at 50 °C until complete dryness.

Characterization of the prepared nano-zinc oxide

The prepared white ZnO nano-powder was characterized using different techniques such as X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) techniques to determine their properties.

Scanning electron microscope (SEM)

The SEM is utilized to determine if any material growth has been taken place because the SEM gives information on the morphology of the surface of the sample. The prepared nano-zinc oxide sample was stocked over a holder. Then it was gold-sputtered before examination. The sample was scanned to identify the structure of prepared sample and estimate the particle diameter at different magnifications. The mean diameter of the grains was determined from the SEM pictures by measuring at least 5 crystals for each formulation using the software Image tool.

X-ray diffraction (XRD)

X-ray powder diffractometry was carried out using X-ray diffractometer with Cu Kα radiation beam (λ= 0.154060 nm) in order to determine the structure of the prepared nano-zinc oxide. The finely powdered sample of the nano-zinc oxide was packed into a flat aluminum sample holder, where the x-ray source was a rotating anode operating at 30 kV and 30 mA with a copper target. Data were collected between 10° and 80° in 20°.
Fourier transform infrared (FTIR)

The I.R. spectrum of the prepared nano-zinc oxide was identified. The disc technique using KBr as a matrix was found to be suitable. In this concern, the nano-zinc oxide was thoroughly mixed with KBr and the mixture was ground and then pressed with a special press to give a disc of standard diameter. The I.R. spectrum was scanned over the wave length range 400-4000 cm\(^{-1}\).

Batch procedure for dye decolourization

The synthesized wastewater that was prepared through dissolving the Basic Yellow 28 dye onto distilled water to attain the required waste solution concentrations was utilized to monitor the adsorption efficiency of the prepared zinc oxide. 25 ml of waste solution with 50 ppm dye concentration was mixed with 0.25 g from the prepared nano-zinc oxide sample for 1hr at 400 rpm on the orbital shaker. The solution and solid phase were separated by centrifugation at 15000 rpm for 5 min in centrifuge. The remaining basic yellow 28 concentration were analyzed using a UV-vis double beam spectro-photometer at a wavelength of 470 nm. These experiments were carried out to investigate the effect of contact time (0-2 hr), waste solution pH (2-12), waste solution temperature (25-80 °C), initial concentration of the synthesis dye waste solution (1-500 ppm), and the amount of nano-zinc oxide (0.1-1 g) on the adsorption process.

Results and Discussion

Characterization of the prepared zinc oxide powder sample

The hydrothermal prepared zinc oxide powder material was characterized using different physicochemical technique in order to investigate its properties and structure.

X-Ray Diffraction Analyses

The XRD pattern of fabricated ZnO nano-powder is shown in (Figure 2). All the diffraction peaks can be well indexed to the hexagonal phase ZnO reported in JCPDS card (No. 36-1451, a = 0.3249 nm, c = 0.5206 nm). Strongest 3 peaks were appeared at 2θ = 31.72, 34.39 and 36.22, which correspond to (100), (002) and (101), respectively. No diffraction peaks arising from any impurity can be detected in the pattern confirming that high-purity ZnO powdered material has be obtained.

Figure 2. X-ray diffraction pattern of prepared zinc oxide
Scanning Electron Microscopic Analyses (SEM)
(Figure 3) shows the SEM images of the prepared ZnO nano-powder sample at different magnifications. The morphological structure of synthesized nano-ZnO as illustrated from the figure has rod-morphology. It can be seen from (figure 3) that the prepared rod-like ZnO sample has average diameter size of about 4.5 nm. This result was confirmed that ZnO produced in the nano range. Moreover, the figure investigated that the produced ZnO nano-rods characterized by their length compared with their diameters. These results give prediction that the prepared ZnO nano-rod has high surface area that improves its removal affinity for dye pollutants.

Figure 3. SEM at different magnifications for the prepared nano-zinc oxide

Fourier Transform Infrared Spectroscopy (FTIR)
The FTIR spectrum of the ZnO nano-powder that was acquired in the range of 400-4000 cm\(^{-1}\) was investigated in (Figure 4). The band presence between the wavelengths range of 450-500 cm\(^{-1}\) is correlated to metal oxide bond (ZnO). A broad peak in the wavelength region around the 715 cm\(^{-1}\) was due to metal–oxygen bond, Alberti, G. et al (1966) and Nabi, S. A. et al (2007). The broad peak around 3230 cm\(^{-1}\) corresponds to the presence of interstitial water and hydroxyl groups, Nakamoto, K. (1981) and Davis, M. (1963). A peak at 1614 cm\(^{-1}\) corresponds to the deformation vibration of free water molecules. Accordingly, the FTIR spectrum confirmed that the prepared powder is pure ZnO without any contaminations from the surfactant polymer of TEA utilized at the preparation step.
Basic dye decolourization process onto the synthesized zinc oxide nano-rod using batch adsorption technique

Effect of contact time
The effect of contact time on the adsorption of basic yellow 28 dye (BY 28) onto nano-zinc oxide was shown in (Figure 5). The experiments were carried out at 10 ppm initial dye concentration with 0.25 g adsorbent (ZnO nano-rod) at 400rpm agitation speed at different time intervals ranging from 0 min to 180 min. It was declared that the amount of BY 28 adsorbed was increased with increasing the contact time and reached its maximum value after 30 min. The equilibrium time could be considered to be taking place at 60 min. to ensure the complete dye sorption onto the prepared material. So, the maximum dye removal onto the synthesized nano-zinc oxide was occurred within 60 minutes and thereafter the system has reached equilibrium point.

Effect of nano-zinc oxide dosage
Nanorod zinc oxide dosage is an important parameter because it determines the capacity of the synthesized Nanorod zinc oxide for a given initial concentration of the BY28. The equilibrium sorption capacity and the percentage removal of BY28 using various dosages from prepared Nanorod zinc oxide was illustrated in (Figure 6). It was observed from this figure that the increase in Nanorod zinc oxide dosage has a positive effect on the percentage of BY28 dye removal.
Figure 5. Effect of contact time on basic yellow 28 removal onto nano-zinc oxide (pH= 7; Adsorbent dose=0.25g/L; initial BY28 concentration = 10 mg/L).

Figure 6. Effect of nano-zinc oxide dosage on BY 28 dye removal (initial dye concentration= 10ppm, temperature = 298K, pH=7, contact time= 60 min)

Figure 7. Effect of initial BY 28 dye concentration on the adsorption process (Adsorbent dose= 0.25g/L; temperature=298K; pH=7; contact time= 60 min)
However the amount of BY28 dye removed per gram of Nanorod zinc oxide powder material tend to decrease with increasing its amount. As one was expected, increasing the Nanorod zinc oxide dosage at the fixed BY28 dye concentration of 10 ppm provided more available area for adsorption of dye and thus the extent of BY28 removal was increased. However the decrease in the amount of BY28 dye removed per gram of Nanorod zinc oxide is basically due to the presence of Nanorod zinc oxide sites that remained un-reacted during the dye adsorption process. Furthermore, above 0.25g from the prepared Nanorod zinc oxide dosage, a significant slight increase was observed with the increase in the Nanorod zinc oxide dosages until 1g. Thus 0.25g of Nanorod zinc oxide was chosen as the optimum adsorbent material dosage for earlier studied factors that relating to BY28 removal.

3.2.3. Effect of initial dye concentration

The removed amount and the percentage removal of BY28 dye at equilibrium onto the prepared zinc oxide nano-powder at different initial dye concentrations were illustrated in (figure 7). This figure was elucidated that the percent dye adsorption was decreased with increasing the initial dye concentration. However, the actual amount of dye adsorbed per unit mass of the adsorbent material was improved with increasing the initial dye concentration.
The lower dye uptake onto the synthesized nano-zinc oxide at high dye concentrations resulted from an increase in the ratio of initial adsorption number of moles of the dye to the available surface area of the adsorbent material; hence adsorbent to adsorbate fractional factor is a dependant factor in the adsorption process. The initial dye concentration provides an important driving force to overcome the mass transfer resistance of the dye between the aqueous and solid phases. Therefore, at high initial dye concentration, the number of ions competing for the available sites on the surface of ZnO nano-powder was high enough resulting in improving the basic yellow 28 adsorption capacity onto the powder material. Similar results were also reported by other researchers, Idris M. N. et al (2011) and Mezenner, N. Y.et al (2009).

**Effect of waste solution pH**

The dye solution pH is one of the primary parameters controlling the sorption process due to its impact on both the surface binding sites of the adsorbent and the ionization process of the dye molecules. Where, the hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution.

![Figure 8. Effect of pH on uptake of BY 28 dye onto nano-zinc oxide (initial dye concentration= 10ppm, temperature =298K, adsorbent dosage= 0.25 g, contact time= 60 min)](image-url)
The variation in the adsorption of the dye was studied in the pH range of 1-11, adjusting the solution pH by adding required amount of dilute hydrochloric acid or sodium hydroxide solutions, at same initial concentration, contact time and adsorbent amount this solution were mixed at 400rpm agitation speed. The results were shown in (figure 8), this figure indicates that the percentage of dye removal equilibration with the nano-zinc oxide at various pH values increases with increasing the pH value up to 7, then tend to depletion as the pH value incremented above 7. This may be attributed to at lower pH values, the presence of hydrogen ions (H+) compete with dye cations causing a decrease in the amount of the basic yellow dye adsorbed by nano-zinc oxide. As the pH improved above 7, the surface of ZnO was positively charged due to its amphoteric properties and causes a repulsion force between the positively charged dye cations and positive ZnO surface that decrease the removal affinity of ZnO for dye at higher solution pH. So, the dye solution pH of 7 represents the optimum pH value for dye removal onto synthesis nano-ZnO.

**Effect of waste solution temperature**

The effect of temperature on the dye sorption process is important not only because it affects the rate and extent of sorption but also due to the fact that temperature dependence of sorption provides information about possible sorbate-sorbent interactions, Bajpai, A. K. et al (2003).

The effect of temperature on the adsorption of BY28 onto the prepared nanorod zinc oxide surface at different temperatures (from 25 to 80 °C) was investigated in (figure 9). As the temperature of dye solution was raised from 25 °C to 80 °C, the adsorption capacity (q) was decreased; this finding indicates that the BY 28 dye adsorption process onto synthesized ZnO is exothermic, Zheng, J. (2001).

Regarding to this sorption process is exothermic in nature and the increment in temperature does not favor the extent of dye adsorption. This decrease in adsorption density may be attributed to the weakening of adsorptive forces between the adsobate and adsorbent and also between the adjacent sites of adsorbed phase, Zheng, J. (2001).

Accordingly, the optimum temperature for maximum adsorption was found takes place at 25 °C for the maximum dye removal onto the prepared nano-zinc oxide.

**Adsorption Isotherm Models**

The sorption isotherm is fundamental in the understanding of the adsorption processes since equilibrium studies quantity the capacity of nano-rod zinc oxide sorbent and indicates the affinity of cation dyes to the sorbent material. This isotherm provides a relationship between the concentration of dye in the solution and the amount of dye adsorbed onto the solid phase when the two phases were at a fixed temperature at equilibrium, Duru Bektas, P.E. (2001).
Figure 9. Effect of dye solution temperature on uptake of BY 28 dye onto nano-zinc oxide (initial dye concentration= 10ppm, adsorbent dosage= 0.25 g, pH= 7, contact time= 60 min)

The Freundlich, Temkin and Langmuir isotherms are three kinds of several isotherms equations that were tested to fit the experimental data. The adsorption data obtained at equilibrium conditions have been analyzed using the linear forms of these kinds of isotherms. The applicability of these isotherm equations to the sorption systems was compared by judging the correlation coefficients, $R^2$.

**Langmuir Isotherm Model**

The Langmuir adsorption model assumes that molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule and no transmigration of adsorbate in the plane of the surface. These sites are also assumed to be energetically equivalent and distant to each other so that there are no interactions between molecules adsorbed to adjacent sites. The linear form of the Langmuir isotherm is represented by the following equation, Unlu”, N. & Ersoz, M. (2006).

$$\frac{C_e}{q_e} = \frac{1}{(q \text{ max} \times b)} + \frac{1}{q_{\text{max}}} \times C_e$$  \hspace{1cm} (1)
Where $q_e$ is the amount adsorbed (mg/g), $C_e$ is the equilibrium concentration of the adsorbate ions (mg/L), and $q_m$ and $b$ are Langmuir constants related to maximum adsorption capacity (monolayer capacity) (mg/g) and energy of adsorption (L/mg), respectively.

A plot of $C_e/q_e$ versus $C_e$ should indicate a straight line of slope $1/q_m$ and an intercept of $1/q_m b$. From (Figure 10) the correlation coefficient value of Langmuir fitting equal to ($R^2$ = 0.296) indicates that the adsorption of BY28 dye onto the synthesized nanorod zinc oxide is not adequate for fitting the Langmuir isotherm equation. Langmuir parameters for BY28 dye removal, $q_m$ and $b$, were calculated from the slope and intercept of this figure and tabulated in (Table 1). $R_L$, as an essential feature of the Langmuir isotherm to predict if an adsorption system is “favourable” or “unfavourable”, which is defined as, Metcalf & Eddy (2003):

$$R_L = 1/(1 + b C_i)$$  \hspace{1cm} (2)

The calculating values of $R_L$ equal to (-0.4), This result again confirmed that the Langmuir isotherm was unfavorable for sorption of basic yellow 28 onto zinc oxide nano-rod under the experimental conditions used in this study.

<table>
<thead>
<tr>
<th>Langmuir parameter</th>
<th>$q_m$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BY28 dye sorption onto ZnO</td>
<td>-0.169</td>
<td>-0.50</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

### 3.3.2 Freundlich Isotherm Model

Freundlich isotherm is an empirical equation that encompasses the heterogeneity of sites and the exponential distribution of sites and their energies. The dye sorption data have been analyzed using the
logarithmic form of the Freundlich isotherm as shown below and investigated in (figure 11) CooNey, D.O (1998).

\[
\ln q_e = \ln K_F + \left(\frac{1}{n_F}\right)\ln C_e
\]  

(3)

Where \( K_F \) and \( n_F \) are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When \( \ln q_e \) is plotted against \( \ln C_e \), a straight line with slope \( n_F \) and intercept \( K_F \) is obtained. (Figure 11) illustrated that the Freundlich isotherm obeyed the dye adsorption process onto the prepared zinc oxide nano-powder, where the correlation coefficient of data fitting equal to 0.979. The intercept of the line, \( K_F \), is roughly an indicator of the adsorption capacity and the slope, \( n_F \), is an indication of adsorption effectiveness. These estimated constants of Freundlich equation for dye sorption process onto nano-ZnO were tabulated in (table 2).

![Figure 11. Freundlich isotherm for BY28 dye removal at various initial solution concentrations onto the prepared nanorod zinc oxide (Adsorbent amount= 0.25g, initial dye concentration= 10ppm, pH= 7, solution temperature= 25ºC)](image)

| Table 2. Freundlich sorption parameters for BY28 dye removal onto synthesized ZnO nano-powder |
|----------------------------------|--------|--------|
| Freundlich parameter            | \( n_F \) | \( K_F \) |
| BY28 dye sorption onto ZnO       | 0.674  | -0.50  |

**Temkin Isotherm Model**

The Temkin equation model may be expressed as

\[
q_e = \beta \ln K_T + \beta \ln C_e
\]  

(4)

Where \( \beta \) which is related to the heat of adsorption, and \( K_T \) is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. If the adsorption process obeys Temkin equation, the variation of adsorption energy and the Temkin equilibrium constant can be calculated from the slope and the intercept of the plot \( q_e \) versus \( \ln C_e \). The Temkin fitting of the dye adsorption data onto nano-zinc oxide was investigated at (figure 12). According to the correlation coefficient (\( R^2 \)) value of Temkin fitting data that equal to (0.770), it was demonstrated that the removal of basic yellow dye ions
using the prepared zinc oxide nano-rod not obeyed the Temkin Isotherm. The calculated temkin parameters were tabulated in (table 3).

Table 3. Temkin sorption parameters for BY28 dye removal onto synthesized ZnO nano-powder

<table>
<thead>
<tr>
<th>Temkin parameter</th>
<th>β</th>
<th>Kc</th>
</tr>
</thead>
<tbody>
<tr>
<td>BY28 dye sorption onto ZnO</td>
<td>13.95</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

Figure 12. Temkin isotherm for BY28 dye removal at various initial solution concentrations onto the prepared nanorod zinc oxide (Adsorbent amount= 0.25g, initial dye concentration= 10ppm, pH= 7, solution temperature= 25ºC)

Conclusions
The morphological and crystalline characterized of the prepared ZnO sample were verifying that the nano-powder material was prepared in pure state with good crystallinity and it has nano-rod structure. The adsorption performance of basic yellow 28 dye onto the prepared nano-material was tested. The results relevant that the percentage dye removal increases with increasing contact time and the maximum dye removal occurs within 60 minutes and thereafter the system has reached equilibrium point. The improvement in dye solution temperature from 25°C to 80°C was accomplished by decline in the nano-ZnO adsorption capacity; so, the adsorption process is expected to be exothermic process. Moreover, the percentage dye removal equilibrium with the nano-zinc oxide at various pH values increases with increasing the pH value up to 7, then tend to depletion as the pH value incremented above 7. Finally, the dye adsorption data onto the prepared nano-ZnO was successfully described by the Freundlich isotherms.

References


