Study of the methylene blue adsorption mechanism using ZrO₂/Polyaniline nanocomposite

Naresh Kumar, Tanya Bahl and Rajesh Kumar  
Department of Physics, Panjab University, Chandigarh-160014, India  
E-mail: rajeshbaboria@gmail.com  

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Abstract
ZrO₂ (Zirconia) nanoparticles (NPs), PANI (polyaniline), and ZrO₂/PANI nanocomposites (NCs) were successfully synthesized using CTAB (Hexadecyltrimethylammonium bromide) and SDS (Sodium dodecyl sulfate) surfactants by following the co-precipitation method. The structural phase analysis of as-prepared, annealed nanoparticles, and nanocomposites was done using the XRD (x-ray diffraction) technique. The crystallite size of pure SDS and CTAB assisted ZrO₂ NPs comes out to be 19 and 17 nm, respectively. After the formation of NCs, the size has been reduced to 15.7 and 15.9 nm, respectively for the same samples. The effect of surfactants on the dye adsorption mechanism was studied using XRD and UV–vis spectroscopy. The prepared NPs and NCs were utilized as an adsorbent for the removal of organic dye methylene blue (MB) which is used as a model compound. UV–vis spectra of the supernatant solution were taken and studied to detect the relative decrease in the dye concentration with time. The as-prepared CTAB assisted ZrO₂/PANI NCs show higher adsorption activity than annealed CTAB assisted ZrO₂/PANI whereas a reversal trend in the adsorption activity was observed for SDS-assisted ZrO₂/PANI NCs. Various kinetic models were implemented and correlated to the experimental data to elucidate the working mechanism for dye adsorption and to set up, a relation in the adsorption activity of surfactant modified NPs and NCs.

1. Introduction
The growing population of the world is posing lots of serious consequences of environmental pollution because of the drastically increasing industries for the fulfillment of the needs of such a huge population. Among these issues, water pollution is a serious concern. Due to the limited resources of drinking water, peoples are consuming polluted water which has serious consequences on their life [1–3]. The large-scale development of industries uses toxic chemicals which after use have been flooded into the rivers thereby affecting aquatic life and creates an imbalance in the environment [4]. Among these chemicals, organic dyes are used on a large scale. These organic dyes have a harmful effect on humans as well as on aquatic life. Among organic dyes, methylene blue (MB) is used enormously in medical, paper, leather, plastics, and paints, etc industries on a large scale [5]. There is a huge amount of the dye affected untreated water which is directly mixed in pure water destroying the original structure of water thereby polluting the environment [6].

Since the past few decades, a lot of research has been done on the wastewater treatment for the removal of such organic dyes using various techniques such as sedimentation, sludge treatment, membrane separation, ion-exchange, coagulation, photocatalysis, and adsorption [7–9]. Among these methods, an adsorption study has been done on a vast scale because of its easiness, low cost, effectiveness, and reusability of adsorbent [9, 10]. A large number of organic, inorganic, and bio-adsorbent have been used for the effective removal of dyes from wastewater [6–10]. For example, Pereira et al have studied the adsorption of a range of dyes by using activated carbon as an adsorbent and showed the effect of surface chemistry on the adsorption [11]. Machado and coworker fabricated carbon nanotubes and have gained large efficiency against the removal of alizarin red S dye [4]. Similarly, various metal oxide such as ZnO, TiO₂, MoO₃, WO₃, Fe₃O₄, ZrO₂, etc was employed for the
adsorption of organic dyes from wastewater [2, 3, 10, 12–15]. Despite these materials, from the last few years, a lot of focus has been done on polymer-based adsorbent since the polymer exhibited large surface area, high porosity, and selectivity for the adsorption of the dyes [16]. Among the class of polymer, polyaniline (PANI) has attracted special attention because of its conducting nature and high efficiency of adsorption [17].

The presence of amine and imine groups in PANI is the active species for the dye adsorption. Despite this property, PANI exhibits good mechanical stability, a highly porous structure, and large surface area with low cost, and the easy availability of aniline (monomer of polyaniline) [16, 17]. Ayad et al studied the adsorption of methylene blue using PANI nanotube for the effective removal of dye because of the chemical interaction of PANI with the dye molecule [18]. Similarly, Sharma et al have fabricated crosslinked nanoporous PANI with a large surface area and employed for the removal of both cationic and anionic dye [19]. Although PANI is used on a large scale for adsorption of dyes, there is some obstacle for using it. The poor interaction with dye molecule, difficult separation, and regeneration of adsorbent led to the limited use of it. The increasing research in this field has resolved the problem by producing nanocomposite of the polymer-based compound with metal oxides which leads to the easy separation of the adsorbent material [17].

In this report, we have synthesized PANI, ZrO2 nanoparticles, and ZrO2/PANI nanocomposites. The structural characterization was done using the XRD technique. A particular concentration of MB dye was used as a wastewater source. The effect of different surfactants on ZrO2 nano-particles for MB dye removal has been studied. The adsorption study of MB dye removal was also done using PANI and ZrO2/PANI nanocomposite as adsorbent. Although the efficiency of MB removal was decreased by forming nanocomposite the separation of adsorbent has become easy.

2. Experimental section

2.1. Synthesis of ZrO2 NPs and ZrO2/PANI NCs

The precursor material and additives i.e. Zirconyl chloride octahydrate (ZrOCl2.8H2O), SDS, CTAB, Aniline, Ammonium persulfate (APS), Urea, and Acetone are purchased from Sigma-Aldrich and used without further purification. To synthesize ZrO2 nanoparticles, the co-precipitation method has been used. As prepared CTAB and SDS assisted ZrO2 NPs were named ZC and ZS while the annealed ones were named ZC6 and ZS6, respectively. The synthesis route of ZrO2 NPs has been represented in figure 1.

The polymerization of aniline was performed at ice temperature. For this, 1.71 g of APS dissolved in a mixture of 30 ml DI water and 10 ml of 1 M HCl with continuous stirring for 15 min at 0 °C temperature. Similarly, a separate solution of aniline was prepared by dissolving 1 ml aniline in 50 ml of 1 M HCl with continuous stirring at 0 °C for 1 h. These two solutions were then mixed and stirred continuously for 30 min at ice-cold temperature. The appearance of green-black precipitates was started in the initial 5 min of reaction. After 30 min of reaction, the solution was kept at room temperature for 21 h and then filtered and washed several times with acetone and DI water. These precipitates were then dried at 60 °C temperature for 1 h to get polyaniline powder.

The ZrO2/PANI nanocomposite was fabricated by using the co-precipitation method. During the polymerization of aniline, 10 ml of PANI solution was separated in which 0.2 g of as-prepared SDS/CTAB assisted ZrO2 was mixed along with 5 ml of 1 M HCl. The solution was stirred continuously for 15 min after that.
solution was kept overnight before washing with acetone and DI water. The obtained precipitates were then air-dried to get as prepared nanocomposite. These NCs were named as PZS (for SDS assisted PANI/ZrO$_2$) and PZC (for CTAB assisted PANI/ZrO$_2$). Similarly, PZS6 and PZC6 were the names given to the samples when annealed ZrO$_2$ NPs were used for the synthesis of SDS assisted PANI/ZrO$_2$ and CTAB assisted PANI/ZrO$_2$ NCs, respectively.

2.2. Dye adsorption experiment

To study the dye adsorption phenomenon, MB dye was used as a modal compound because of its large scale usage in industries. For the relative adsorption experiment, 15 mg l$^{-1}$ initial dye concentration was chosen and a 60 ml solution was prepared in DI water. The amount of adsorbent was selected as 30 mg. The adsorption experiment was performed at the natural pH of the solution and at 30 $^\circ$C temperature. After the adsorption experiment, the supernatant solution was collected and measurement was made to detect the relative amount of residual dye concentration at a wavelength of 664 nm using LAMBDA UV–vis Spectrometer.

3. Results and discussion

3.1. XRD

XRD spectra of NPs and NCs were taken using Cu–K$_\alpha$ radiation on Rigaku miniflex 600 diffractometer over a 2$\theta$ range of 10 to 80$^\circ$ with a scanning speed 5$^\circ$/min. The detailed structural phase and crystallite size analysis were done using PDXL2 and X’PERT high score analysis software.

Figure 2(a) shows the XRD spectra of samples formed at 400 $^\circ$C temperature which was named as-prepared. Phase analysis of these samples shows that CTAB assisted sample consists of an orthorhombic and cubic phase with their respective JCPDS card 01-083-0809 and 00-027-0997 [20–22] whereas SDS assisted sample shows the combination of monoclinic and cubic phase with reference JCPDS card 00-013-0307 and 00-049-1642, [23, 24] respectively. The crystallite size was calculated using Debye Scherer’s formula and comes out to be around 10 nm and 6 nm for ZC and ZS, respectively. From figure 2(b), it has been found that the ZC6 sample is a mixture of cubic and monoclinic phases corresponding to their respective JCPDS card 00-027-0997 and 01-086-1451,
respectively [20, 21]. The major peak at 2 theta value 30.6° corresponds to the cubic phase. Similarly, mixed phases have also been found in ZS6 NPs. But the crystallinity, in this case, has been improved as the peak corresponding to (−111) and (111) of the monoclinic phase grows higher in intensity. Some new peaks corresponding to (012) and (112) of the monoclinic phase have emerged which were absent in the case of ZC6. The crystallite size was calculated to be approximately 17 nm and 19 nm for ZC6 and ZS6, respectively. The trend in the crystallite size was reversed for annealed samples as compared to as-prepared samples. The crystallite size of ZS6 grows higher than ZC6 whereas for the as-prepared sample crystallite size of ZC was higher than ZS. This is because SDS has a relatively lower boiling point than CTAB. On annealing, SDS evaporated earlier and faster than CTAB and therefore particle agglomeration in the case of SDS assisted sample becomes more prominent. Figure 2(c) shows the XRD spectra of pure PANI and ZrO2/PANI NCs. The XRD spectrum of PANI shows its characteristics peaks at 2 theta values 19.5° and 25.7° [25]. On comparing the peak positions and lattice planes of figures 2(b) and (c), it has been observed that NPs retains its original phase in synthesized NCs. No new peaks were observed in the NCs eliminating the possibility of any structural change occurrence. A slight difference in the orientation has been observed for different surfactants which are due to the different acting mechanisms of surfactants. The crystallite size in the fabricated NCs has been reduced to 15.9 and 15.7 nm for PZC6 and PZS6, respectively.

3.2. Dye adsorption using ZrO2/PANI nanocomposites

Figure 3 shows the UV–vis spectra of MB dye adsorption using pure polymer PANI and ZrO2/PANI nanocomposites and their comparison of adsorption rate. It can be seen in figure 3(a) that PANI alone itself is a good adsorbent. It had adsorbed about 53% of initial dye concentration in just 55 min. On the other hand, by utilizing composites, the adsorption performance decreases which can be seen in figure 3(d). The comparison of adsorption for PZC and PZS samples shows that about 37% and 6% dye was adsorbed in 55 min respectively. The necessity of the formation of nanocomposites was that PANI alone when used as an adsorbent it cannot be separated from the dye easily. But by inculcating the metal oxide nanoparticle along with it, the problem can be resolved. The ZrO2 nanoparticles react with polymer matrix via electrostatic and van der Waal bonding. Due to
this, the properties of the polymer matrix may get changed [26]. Also, the initial surface area of the polymer which was present for dye adsorption reduces thereby lowering the adsorption capability. The introduction of nanoparticles into the polymer chain may change the resistance of the matrix [26, 27]. It may alter the crack growth path of the matrix and affects the micro porosity in the polymer which is responsible for the low adsorption of MB in the ZrO$_2$/PANI nanocomposites in this particular case [27, 28]. As the nano filler ZrO$_2$ nanoparticles are used it had altered the surface energy of the nanocomposites and also the hydrophobicity of the materials which results in the easy separation of materials after the adsorption experiment. From the comparison of MB adsorption with different surfactant-assisted ZrO$_2$/PANI nanocomposites, it has been found that with a larger size of filler material the composite was showing better adsorption than with the lower size of the filler.

Figure 4 shows the adsorption results of NCs prepared using surfactant-assisted annealed ZrO$_2$ NPs. On comparing the adsorption rate of PZC6 and PZS6 as shown in figure 4(c), it has been observed that PZS6 gives better adsorption activity than PZC6 which is in reverse trend as that was obtained in as-prepared ZrO$_2$/PANI NCs where PZC was having better adsorption than PZS.

This reversal in the dye adsorption activity can be attributed to the fact that the crystallinity of the material was improved on annealing. Also, there was a trend in the crystallite size of the materials as that in as-prepared samples, where CTAB assisted ZrO$_2$ gives larger nanoparticles of size around 10 nm while SDS assisted ZrO$_2$ nanoparticles were of the order of 6 nm. But on annealing, the opposite trend can be seen in crystallite size where CTAB assisted nanoparticles were of a smaller size than SDS assisted samples. Since ZrO$_2$ nanoparticles were used as filler materials in the polymer matrix of PANI in ZrO$_2$/PANI, the bonding of filler materials with polymer affects the MB adsorption. It can be seen that in as-prepared samples, the difference in size for SDS and CTAB assisted sample was around 4 nm whereas in the annealed sample this difference was about 2 nm. This effect of filler size has been observed for dye adsorption as the percentage of adsorption in CTAB and SDS for the as-prepared sample was around 31% whereas in the annealed sample it was around 6% only in 55 min which can be seen from the table below. From the adsorption rate comparison, it has been found that 18% and 24% dye was adsorbed in 55 min for PZC6 and PZS6, respectively. The schematic of dye adsorption has been depicted in figure 5.
The mechanistic pathways that do follow by PANI and ZrO2/PANI nanocomposites were studied using different kinetics models such as pseudo-first-order, pseudo-second-order, intra-particle diffusion model, elovich model, and bangham model and are represented in figure 6 [29]. Analysis of the experimental results shows that all five samples follow either intra-particle diffusion (IPD) or Elovich model for dye adsorption. The IPD model equation is given as [30]

\[ q_t = k_i \sqrt{t} + C \]  

(1)

Where \( q_t \) (mg/g) is the amount of dye adsorbed at time \( t \), \( k_i \) (mg/g min\(^{1/2}\)) is the rate constant of the IPD model, and \( C \) is the intercept. According to the IPD model, uptake of the dye onto the nanoparticle (\( q_t \)) when plotted against the square root of time giving linear fitting should pass through the origin if Intra-particle diffusion is the rate-controlling mechanism. Deviation of the graph from the passage of origin in the case of PZC6 is a sign of the fact of some degree of boundary layer control. It means other kinetic models may have some effect on the adsorption of MB dye [31]. From the kinetic fitting of these five different samples, it has been observed that Pure
Similarly, the ZrO$_2$ monoclinic structural phase. The crystallinity of the SDS assisted sample was better than CTAB assisted sample.

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4. Conclusion

ZrO$_2$ nanoparticles were successfully synthesized using SDS and CTAB as surfactants using the co-precipitation method followed by annealing at 650 °C temperature. The annealed samples show mixtures of cubic and monoclinic structural phase. The crystallinity of the SDS assisted sample was better than CTAB assisted sample. Similarly, the ZrO$_2$/PANI nanocomposite was fabricated using the co-precipitation method. It has been observed that ZrO$_2$ nanoparticles retain their structural phase even after forming nanocomposites. All prepared samples were employed for the dye adsorption experiment and the results obtained suggest that even PANI itself is a very good adsorbent but it inherits the problem of separation. After forming composites the problem was resolved by sacrificing some adsorption capability of PANI. The reversal in the adsorption activity was observed in a surfactant-assisted sample showing the different acting mechanisms of different species in synthesis. The kinetic study reveals the diffusion and chemisorption of organic dye onto the nanocomposites materials.

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PANI and PZC6 follows IPD kinetic model whereas the remaining samples follow elovich model whose linearization as well as non-linear equations are defined as equations (2) and (3), respectively [32]:

\[
q_t = \frac{lna_t b_t}{b_e} + \frac{1}{b_e}nt
\]  \hspace{1cm} (2)

\[
q_t = \frac{1}{b_e}ln(1 + a_e b_et)
\]  \hspace{1cm} (3)

Where $q_t$ (mg/g) is the uptake of MB dye at time $t$, $a_{et}$ is the initial adsorption rate (mg/g min), and $b_e$ (g/mg) is related to the chemisorption and surface coverage extent.

The parameters that are calculated by the appropriate fitting of the experimental data to the kinetic models (for fixed time i.e. 55 min) are summarized in table 1 given below:

By the appropriate fitting of the data for these five samples shows that IPD and elovich models are followed by these samples. The PANI itself follows the IPD model with multiple working mechanisms. The piecewise multiple linear fitting shows that the rate constant is different in each step. The largest value of rate constant $k_2$ for pure PANI as seen from the table shows that the adsorption is very fast in this period. After that, the adsorption becomes nearly saturated and the rate constant is also decreased. The negative value of intercept $C_1$ and $C_2$ results from the joint effect of the film diffusion process and surface reaction control [33]. Similarly, PZC6 also does the IPD models up to some extent. The $R^2$ obtained from IPD models was better than other kinetics models. The straight-line fitting does not pass through the origin confirms that there may be other kinetics mechanisms that control the adsorption process in this case [33, 34]. It has been found from the kinetics study that diffusion of MB dye into the nanocomposites is the phenomenon that is responsible for adsorption. For the rest of the three samples, the adsorption of MB has been explained using elovich models having $R^2$ value >0.94 which is higher than other kinetics models. The data presented in the table shows that the rate of adsorption follows the order as PZC > PZS6 > PZS which is also confirmed from the tables as a percentage of dye adsorption for these samples.

Again, the possibility of non-linearisation fitting of elovich model to the experimental data was checked by plotting graph between $q_t$ and $t$ as represented in figure 7 below:

On comparing the linear and non-linear $R^2$ value for PZC, PZS and PZS6, it has been found that fitting has improved for only PZS6 sample as it gives an $R^2$ value of 0.97084 which was 0.949 for linear fitting. Otherwise, for the remaining two samples, linear fitting gives a better $R^2$ value. All the corresponding data related to the non-linear elovich model are summarised in table 1.

This kinetics fitting shows that at first diffusion of dye molecules have taken place into the nanocomposites materials and after that surface reaction has taken place which may be the electrostatic interaction of adsorbate and adsorbent. The chemical bonds may be formed between these two species and thereby follows the chemisorption phenomenon for adsorption. A comparison of relative adsorption using different adsorbent materials using literature has been summarized in table 2.

4. Conclusion

ZrO$_2$ nanoparticles were successfully synthesized using SDS and CTAB as surfactants using the co-precipitation method followed by annealing at 650 °C temperature. The annealed samples show mixtures of cubic and monoclinic structural phase. The crystallinity of the SDS assisted sample was better than CTAB assisted sample. Similarly, the ZrO$_2$/PANI nanocomposite was fabricated using the co-precipitation method. It has been observed that ZrO$_2$ nanoparticles retain their structural phase even after forming nanocomposites. All prepared samples were employed for the dye adsorption experiment and the results obtained suggest that even PANI itself is a very good adsorbent but it inherits the problem of separation. After forming composites the problem was resolved by sacrificing some adsorption capability of PANI. The reversal in the adsorption activity was observed in a surfactant-assisted sample showing the different acting mechanisms of different species in synthesis. The kinetic study reveals the diffusion and chemisorption of organic dye onto the nanocomposites materials.

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Table 1. Kinetics parameter corresponding to different adsorbents.

| Adsorbent | Dosage (mg) | Dye Conc. (Co) | Vol. (ml) | \(k_1\) (mg/g min^{-1}) | \(k_2\) (mg/g min^{-1/2}) | \(k_3\) (mg/g min^{-1}) | \(C_1\) | \(C_2\) | \(C_3\) | \(R^2\) (IPD model) | \(R^2\) (Elovich model) | Time (min) | % ads |
|-----------|-------------|----------------|-----------|--------------------------|---------------------------|--------------------------|--------|--------|--------|----------------|-------------------------|------------|-------|
| PANI      | 30          | 15             | 60        | 0.87376                  | 4.36441                   | 0.47888                  | -0.45033 | -16.567 | 15.724 | 0.93084        | 0.98096                  | 0.99917    | 55    | 53    |
| PZC6      | 30          | 15             | 60        | 0.9424                   | -0.6605                   | 0.5989                   | 9.5034  | 0.9183  | 0.9111 | 55              | 18                        |            |       |
| PZC       | 30          | 15             | 60        | 1.0519                   | 0.2806                    | 0.1883                   | 0.0763  | 0.9795  | 0.9747 | 55              | 37                        |            |       |
| PZS       | 30          | 15             | 60        | 0.4053                   | 0.1050                    | 0.3887                   | 0.2371  | 0.9747  | 0.9183 | 55              | 6                         |            |       |
| PZS6      | 30          | 15             | 60        | 0.9245                   | 0.5244                    | 0.3890                   | 0.2759  | 0.949   | 0.9708 | 55              | 24                        |            |       |
Data availability

The data that support the findings of this study are available upon request from the authors.

ORCID iDs

Rajesh Kumar  @ https://orcid.org/0000-0003-1962-3243

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