



Effect of pH on Adsorption and Photocatalytic Degradation Efficiency of Different Catalysts on Removal of Methylene Blue

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The present study investigates the efficiency of adsorption and photodegradation catalyzed by TiO₂, ZnO, CdS and Co₃O₄ on the removal of methylene blue dye, in different pH values (4, 6, 9 and 11). The photocatalytic degradation of methylene blue dye in aqueous catalysts TiO₂, ZnO, CdS and Co₃O₄ suspension follows apparent after 0.5 h of photodegradation a first-order kinetics. The photodegradation efficiency of methylene blue was fast in the present condition (pH 11, pH 6, pH 6 and pH 4) and slower in (pH 4, pH 11, pH 11 and pH 11) of ZnO, TiO₂, CdS and Co₃O₄, respectively. The highest adsorption capacity as follow: TiO₂ > ZnO ≈ CdS ≈ Co₃O₄, while the photocatalytic activity: ZnO > TiO₂ > CdS > Co₃O₄.

Keywords: pH, Adsorption, Photocatalytic degradation, Methylene blue, TiO₂, ZnO, CdS and Co₃O₄.

INTRODUCTION

The textile dyes, with largest groups of organic compounds, are mainly dumped directly in the environment^{1,2}. These dyes are toxic to microorganism, aquatic life and human beings, by constituting a serious concern to the ecosystem³. Therefore, many efforts have been devoted to remove these dyes from the waste water. Recently, the advanced oxidation processes (AOPs) have drawn much attention in the wastewater purification and other environment application⁴⁻⁷. Reactive species based oxidation processes are usually performed as effective photocatalytic medium through the photoexcitation of the semiconductors through the solution pH⁸⁻¹¹. In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photocatalysts (*e.g.*, TiO₂, ZnO, CdS, Co₃O₄, WO₃) an energetic light source and an oxidizing agent such as oxygen or air. To best of our knowledge only photons with energies greater than the band-gap energy (ΔE) can result in the excitation of valence band (VB) electrons which then promote the possible reactions with organic pollutants¹². The absorption of photons with energy lower than ΔE or longer wavelengths usually causes energy dissipation in the form of heat. The illumination of the photocatalytic surface with sufficient energy, leads to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band (CB). The positive hole oxidizes either the pollutant directly or water to produce hydroxyl radical OH[•],

whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst. In the photocatalytic degradation of pollutants, when the reduction process of oxygen and the oxidation of pollutants do not advance simultaneously, there is an electron accumulation in the conduction band, thereby causing an increase in the rate of recombination^{13,14} of e^- and h^+ .

In this work, methylene blue was selected for study. The main objective of this work is adsorption and photocatalytic degradation of methylene blue dye by four types of semiconductors (TiO₂, ZnO, CdS, Co₃O₄) and examining the influence of various pH values of solution on the adsorption and photocatalytic efficiency.

EXPERIMENTAL

Methylene blue used in this work was purchased from Sigma-Aldrich. The methylene blue was chosen in this study because of its known strong adsorption onto solids. Chemical structure of methylene blue dye was shown in Fig. 1 and the maximum wavelength of this dye is 663 nm.

All semiconductors (TiO₂, ZnO, CdS and Co₃O₄) where supplied (Sigma-Aldrich) were used as purchased. Adjustment of pH of the dye solutions prior to degradation was carried out with NaOH or HNO₃ from Merck. Distilled water was used in all experiments.

Adsorption studies: Kinetic studies on the adsorption of methylene blue dye by semiconductors (TiO₂, ZnO, CdS and

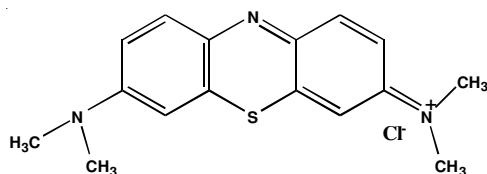


Fig. 1. Chemical structure of methylene blue dye

Co₃O₄) were carried out in the dark for 60 min. Batch equilibrium adsorption experiments were conducted in the dark of initial concentration [20 g/L], over different pH of solution (4, 6, 9 and 11) with a fixed weight (1.5 g/L) of the catalysts. The suspension was placed in 250 mL reaction vessel and mechanically shaken by magnetic stirrer at constant temperature (25 °C). After reaching equilibrium, 3 cm³ of reaction mixture was collected and centrifuged (6000 rpm, 15 min) in a Hettich centrifuge. The supernatant was carefully collected in a syringe with a long pliable needle and centrifuged for a second time, at the same speed and for the same period of time. This second centrifugation was found necessary to remove the fine particles of semiconductors that found effective on the result of analysis by UV-visible spectrophotometer. The amount of adsorbed dyes per gram of catalyst at equilibrium, q_e (mg/g), was obtained¹⁵.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of methylene blue dye. V (L) is the volume of the solution and W (g) is the weight of catalyst used.

Measurement of photocatalytic activity: The photocatalytic experiments were conducted under ambient atmospheric conditions at different pH solutions using Philips mercury lamp UV (A) 365 nm, contains four lamps off 15 W for each one as the light source. The incident photon flux (2.2 mW cm⁻²) was determined by UV-meter (Dr. Honle). For each run, 0.3 g of catalyst powders was dispersed in 200 mL of aqueous solution of methylene blue with a concentration of (20 mg L⁻¹). Prior to the beginning of irradiation, the mixture was allowed to equilibrate in the dark with stirring for 60 min. At certain irradiation intervals, aliquots of about 3 mL solution were withdrawn from the suspension and then centrifuged. The photocatalytic performance of the sample was subsequently gauged by measuring intensity changes of the optical absorbance peaks at 663 nm, of aqueous supernatant aliquots containing methylene blue, using a UV-visible spectrophotometer. The efficiency of the photodegradation process was calculated with the relation¹⁶:

$$\text{Efficiency (\%)} = \left(\frac{C_{MB}^0 - C_{MB}}{C_{MB}^0} \right) \times 100 \quad (2)$$

where: C_{MB}^0 is the initial concentration of methylene blue and is the concentration of methylene blue at a certain irradiation time. The variation of methylene blue concentration as a function of irradiation time, under UV-A light, was determined using the UV-visible spectroscopy based on a calibration curve. The kinetics of the degradation process of methylene blue was studied. The rate constant, k , was obtained by plotting of the ratio between initial concentration and the concentration at a

certain irradiation time of methylene blue versus irradiation time assuming a first order reaction¹⁶:

$$\frac{C_{MB}^0}{C_{MB}} = e^{kt} \quad (3)$$

RESULTS AND DISCUSSION

Adsorption of methylene blue dye: Adsorption processes are important for the description of how adsorbate will interact with an adsorbent and are critical in optimizing the use of adsorbent. During adsorption, the adsorption capacity is highly influenced by the pH variations of the solution^{17,18}. The plot of pH variation against the adsorption capacity of different catalysts surfaces are shown in Fig. 2.

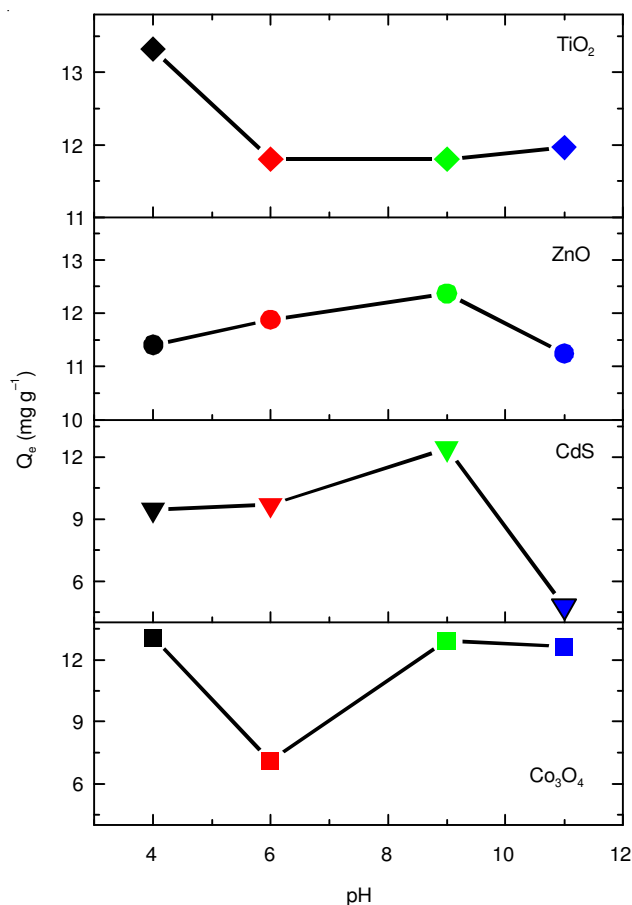


Fig. 2. Effect of pH on adsorption capacity of methylene blue on TiO₂, ZnO, CdS and Co₃O₄ catalysts

Fig. 2 shows that the adsorption capacity increases at higher (pH 4) for the TiO₂ and at (pH 9) for both CdS and ZnO, while Co₃O₄ at all pH under study expect pH 6, these variations in adsorption capacities of different catalysts highly dependent on the zero point charges¹⁹⁻²¹. Because of the amphoteric behaviour of most of the semiconductor oxides, an important parameter in the reaction taking place on the semiconductor particle surface is the pH of dispersions, since it influences the surface charge properties of photocatalyst. On the other hand, the anionic dye molecule is negatively charged, so low pH favors adsorption on the catalyst surface.

Photocatalytic degradation of methylene blue dye: The solution pH appears to play an important role in the photocata-

lytic process of various pollutants²¹. The effect of pH on the photodegradation of methylene blue was studied in the pH range 4–11. The pH of the solution is adjusted before adsorption and it is not controlled during the course of the reaction.

An important parameter in the photocatalytic reactions taking place on particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms²². Hence, pH plays an important role both in the characteristics of dyes and in the reaction mechanisms that can contribute to dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band. In the presence of photocatalyst, it is presumed that the photocatalytic processes are probably result from the electron-hole pairs formed on the surface of the semiconductor by the irradiation of the UV-light²³. Then the holes with the high oxidative potential either direct oxidize the reactive dye or react with the OH[−] to form hydroxyl radical. The total reaction between the photocatalyst and the reactive dye could be written as follows²³.



Or



The point of zero charge (pzc) of the TiO₂ (Degussa P25)²⁴ is at pH 6.8. Thus, the TiO₂ surface is positively charged in acidic media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8).

In the presence of TiO₂ (Fig. 3a), the photodegradation was significantly enhanced at medium pH (pH = 6). The degradation rate of some azo dyes increases with decrease in pH as reported elsewhere²⁵. At pH < 6, a strong adsorption of the dye on the TiO₂ particles is observed as a result of the electrostatic attraction of the positively charged TiO₂ with the dye. At pH > 6.8 as dye molecules are negatively charged in alkaline media, their adsorption is also expected to be affected by an increase in the density of TiO[−] groups on the semiconductor surface. Thus, due to coulombic repulsion the dyes are scarcely adsorbed²⁶. On the contrary, different optimal pHs (6–7) have been observed for the photocatalytic degradation of other azo dyes and a decrease of degradation in both acidic and alkaline pH was reported²⁷. The inhibitory effect seems to be more pronounced in the alkaline range (pH 11). At high pH values the hydroxyl radicals are rapidly scavenged and they do not have the opportunity to react with dyes.

In the presence of ZnO (Fig. 3b), the photodegradation was significantly enhanced at high pH (pH = 11). While the lowest at low pH is due to the photodecomposition of ZnO to Zn²⁺ takes place in acidic and neutral solutions and that efficient formation of hydroxyl radicals occurs in alkaline solution²⁸.

In the presence of Co₃O₄ (Fig. 3c), the photocatalytic degradation efficiency slightly reduced at high pH (pH 11), similar trends were observed for CdS (Fig. 3d) when compared to Co₃O₄.

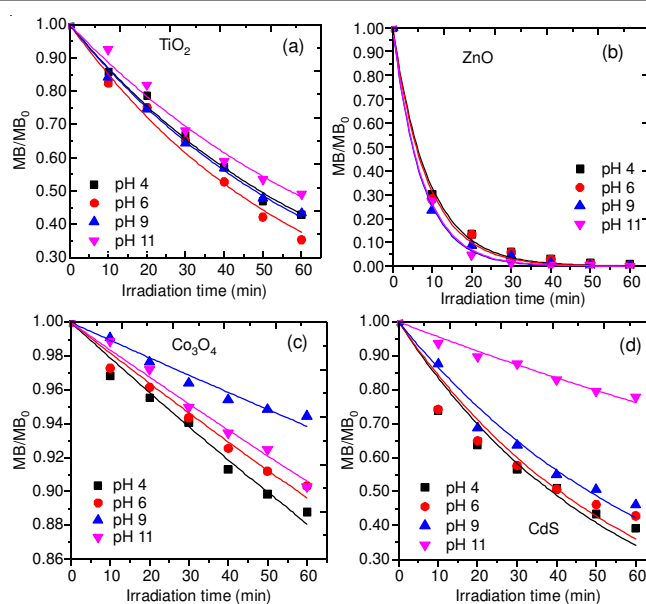


Fig. 3. Photocatalytic degradation of methylene blue in the presence of different pH of solution; (a) TiO₂, (b) ZnO, (c) Co₃O₄ and (d) CdS

Thus, the effect of pH on the photodegradation was versatile depending on the catalyst present in solution (TiO₂, ZnO, CdS, Co₃O₄). Low pH (pH 4) also favored the photodegradation of methylene blue in the presence of CdS and Co₃O₄. While higher pH (pH 11) favourable of ZnO.

Comparison of different photocatalysis: In view of the advantages of different semiconductors in the heterogeneous photocatalysis, we tested the photocatalytic activity of four different commercially available photocatalysis on the degradation rate of methylene blue.

The degradation rates for the decomposition of the dye with initial concentrations of 20 mg L^{−1} in the presence of different types of photocatalysis are shown in Fig. 4. The photocatalyst of ZnO and TiO₂ was found to be more efficient in degradation of the dye and other exhibits negligible catalytic activity compared to the other catalysts used in this study. by depending on zero point charge, The zero point charge is a condition where the surface charge of semiconductor is zero or neutral that lies in the limited pH range, depending on the catalysts used^{29,30}.

This phenomenon is attributed to the band gap energy of catalyst, redox potentials and rates of these redox reactions. For desired reaction, the energy separation (band gap) between e[−] and h⁺ must be larger than the energy required and the redox potentials of the e[−] and h⁺ (thus the position of conduction band and valence band) must be suitable for inducing redox processes³¹. In addition, the rates of these redox reactions must be faster than or at least fast enough to compete with the e[−] and h⁺ recombination³².

Conclusion

The pH-dependent surface charging of metal oxides and related materials remains an active field of research. Many experimental studies were carried out for the materials whose surface charging behavior is already well known.

In this study, adsorption and photocatalytic decolorization of an azo reactive textile dye, methylene blue dye, was investigated by the use of TiO₂, ZnO, CdS and Co₃O₄ powder catalysts

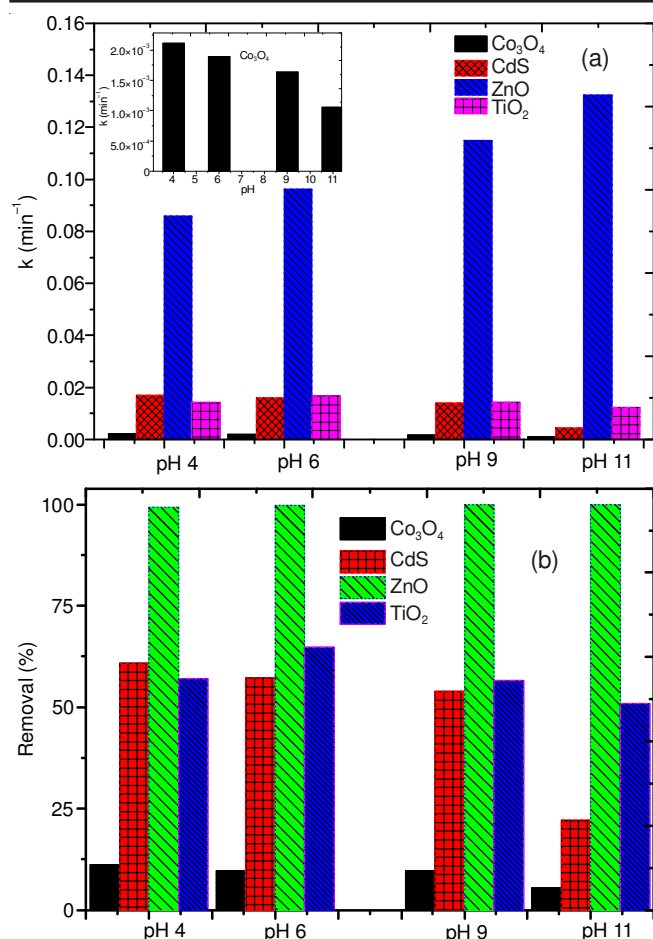


Fig. 4. A comparative case in presence of pH for different catalysts; (a) rate constant of photocatalytic degradation, (b) percentage of removal

in different pH of solution as a comparative study. The photocatalyst of ZnO was found to be more efficient for the degradation of the dye as compared to other catalysts used in this study. After 90 min reaction, the relative decomposition order established was: UV/ZnO > UV/TiO₂ > UV/CdS > UV/Co₃O₄.

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