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# Solar photocatalytic efficiency of impregnated Bentonite for textile dye degradation

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***Abstract*— The solar photo-degradation of Solophenyl Red 3BL is studied on the impregnated Bentonite with ZnO. ZnO-Bentonite is characterized by X-ray diffraction (XRD) which indicates mixed phases of nanocomposites. The scanning electron microscopy (SEM) and X-ray fluorescence (XRF) are also reported. The optical properties confirm the presence of ZnO phase with an optical gap of 3.27 eV. The physical parameters for the photoactivity such as: catalyst dose (0.25–1 $gL^{-1}$), pH solution (4–11) and initial dye concentration (5–75 mg/L) are optimized. 92 % of the degradation during 160 min of treatment is achieved for a concentration of 5 mg/L and a catalyst dose of 0.75 g $L^{-1}$ at free pH under solar light. The data are well fitted by the Langmuir-Hinshelwood model; the SR 3BL disappearance obeys to a first-order kinetic with an apparent rate constant of $10^{-2}$ $mn^{-1}$.**

***Keywords*— Solar irradiation, Algerian Bentonite, ZnO, Photocatalysis, Textile wastewater**

## I. INTRODUCTION

The conventional techniques for the wastewater treatment are expensive and not enough destructive. Accordingly, the search of low cost alternatives techniques is a topic of high priority [1, 2]. In this respect, the advanced oxidation processes (AOPs) such as photocatalysis, are low cost effective procedures for removing recalcitrant compounds. The main advantage of AOPs is the conversion of organic pollutants to less toxic molecules [3]. The photocatalysis is a successful strategy for the degradation and mineralization of organic compounds in water [4].

Solophenyl Red 3BL (SR 3BL), chosen for the photocatalytic tests, is a poly azo dye widely used in the textile industry. It is not biodegraded because of the complexity of the chemical structure [5] and its presence in water is harmful to the human health [6].

Our study deals with the synthesis of the hetero-system ZnO/Bentonite; ZnO was supported on the clay using zinc acetate as precursor. The hetero-system has been tested successfully for the degradation of SR 3BL under solar light. The Bentonite is inexpensive, presents environmentally friendly characteristics, good adsorption properties, it has been successfully applied for the immobilization of some photocatalysts [7, 8, 9] and is locally available. It is used in the food industry, animal feed, adhesives, ceramics and drilling muds [10]. On the other hand, ZnO is suitable for the photocatalytic applications because of its advantages like activity in the ultraviolet range, non-toxicity, thermal and chemical stabilities [16], strong oxidation ability and a large free-exciton binding energy [17]. The influence of the catalyst dose, pH and initial SR 3BL concentration are investigated.

## II. EXPERIMENTAL

### A. Photocatalytic preparation and characterization

The preparation procedure consists of the Bentonite purification followed by its impregnation with ZnO. The Bentonite was washed with water and dried at 80 °C. The hetero-system ZnO/Bentonite was prepared by impregnation: 1 g of $Zn(CH_3CO_2)_2$, $2H_2O$ was dissolved in 125 mL of DMF in presence of 5 g of the purified Bentonite; the mixture was stirred overnight and evaporated at 100 °C. Then, the powder was calcinated at 200 °C for 3 h, homogenised in an agate mortar and identified by X-ray diffraction over the 2θ range (5-120°).

The surface morphology of the samples was analyzed by Scanning Electron Microscope (Fei Quanta 600 SEM). The chemical analysis of the catalysts was performed by the X-ray fluorescence (XRF) using Horiba XRF. The diffuse reflectance spectrum was plotted with a UV-Visible spectrophotometer (Specord 200 plus) using PTFE as reference. The point of zero charge (pzc) is obtained by measuring the equilibrium pH of an aqueous solution containing a suspension of finely powdered catalyst.

### B. Batch experiments

SR 3BL was selected for the photocatalytic tests, its chemical structure and UV-Visible absorption spectrum are illustrated in Figure 1. A quantity of the catalyst powder was dispersed in 250 mL of SR 3BL solution at variable concentrations in an open borosilicate reactor exposed to sunlight in a clear day under magnetic stirring (350 rpm). The aliquots were withdrawn at regular time intervals and centrifuged twice (2000 rpm, 10 mn) to separate the catalyst particles from the solution. A double beam spectrophotometer was used to determine the residual concentration of SR 3BL at $\lambda_{max}$= 540 nm. The photodegradation yield (R) is calculated from the relation:

$$R(\%) = \frac{(C_0 - C_t)}{C_o} * 100$$

$C_o$ and $C_t$ are the initial and equilibrium concentration of SR 3BL in the solution respectively.

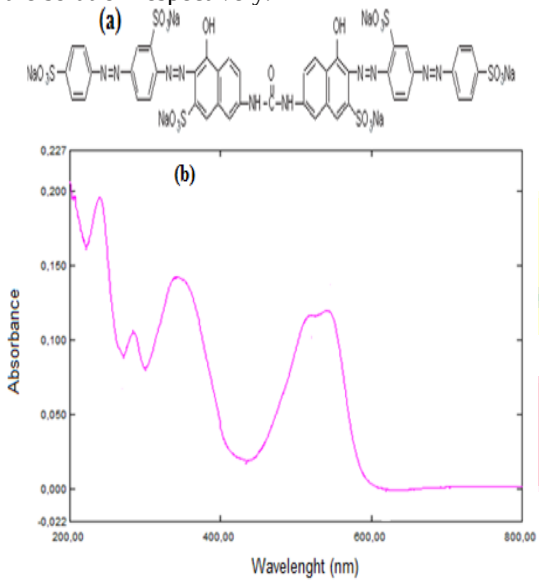


Fig.1 (a) Chemical structure of Solophenyl Red 3 BL. (b) The absorption spectrum ($C_o$ = 10 ppm)

## III. Results and Discussion

### A. Photocatalyst characterization

Figure 2 shows the X-ray diffraction pattern of both the raw Bentonite and the impregnated Bentonite. The latter indicates mixed phases and contains peaks of ZnO and Bentonite, indicating clearly the successful of the impregnation. In addition to the XRD peaks of the Bentonite, new peaks appeared, attributed to ZnO (hexagonal wurzite) at 31.77, 34.42, 36.25, 47.53, 56.60, 62.86, 67.96 and 69.10 respectively for the reticular plans (100), (002), (101), (102), (110), (103), (112) and (201) in agreement with the JCPDS card N° 36-1451.

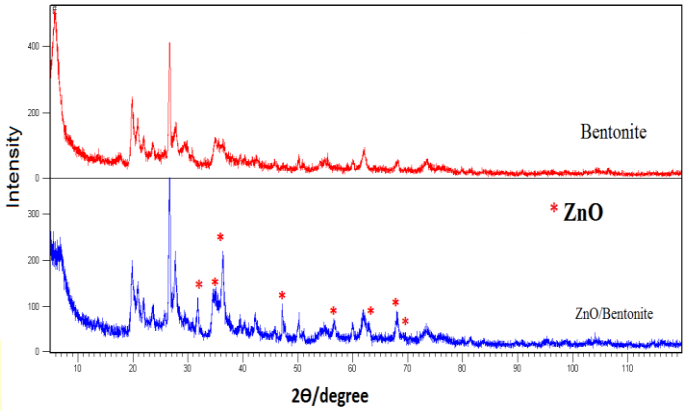


Fig.2 X-ray diffraction patterns of Bentonite and ZnO/Bentonite

The optical gap ($E_g$) of the catalyst is crucial for the solar energy conversion. The gap of the hetero-system ZnO/Bentonite is obtained by extrapolating the linear part of $(\alpha h\nu)^2$ to the abscissa axis according to the Pankov relation [19]. A value of 3.27 eV is obtained (Figure 3), attributed to ZnO with an intensity of ~ 20. The zoom in the low energy region indicates a second transition at 2.21 eV with a weak intensity (~ 0.1), due to the hematite phase $Fe_2O_3$, in conformity with its small percentage in the clay (ppm order).

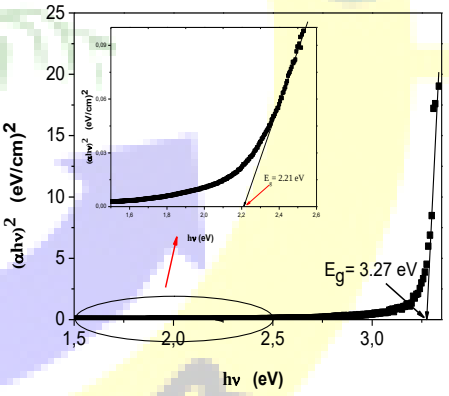


Fig.3 *The optical transitions of the hetero-system ZnO/Bentonite*

### B. Photoactivity of the hetero-system ZnO/Bentonite

It is worthwhile to outline that the Bentonite alone exhibits neither adsorption nor photodegradation for SR 3BL while the impregnated bentonite shows a high removal under solar light. The Bentonite support plays a more active role by increasing the dispersion of ZnO particles which increases the active surface area, thus enhancing considerably the photocatalytic performance.

1) *Effect of catalyst dose*: The influence of the catalyst dose on the photodegradation efficiency was investigated over the range (0.25-1 $gL^{-1}$), the results are illustrated in

Figure 4. The activity increases with raising the dose and the maximal degradation occurs for an optimal dose (mass of catalyst/volume of the solution) of 1 g $L^{-1}$. This is simply due to the increasing number of active sites of catalyst which lead to a higher reception surface for incident photons and in this way to an increasing number of ($e^-/h^+$) pairs. Above 1 g $L^{-1}$, the scattering effect predominates and inhibits the photocatalytic process, accounting for the regression of the photoactivity. It is worthwhile to outline that the optimal conversion occurs for dose of 1 g $L^{-1}$ (77 %) is not far from that of 0.75 g$L^{-1}$ (74 %). So, the tests were continued with the last dose for economic reasons and in order to decrease the turbidity of the solution.

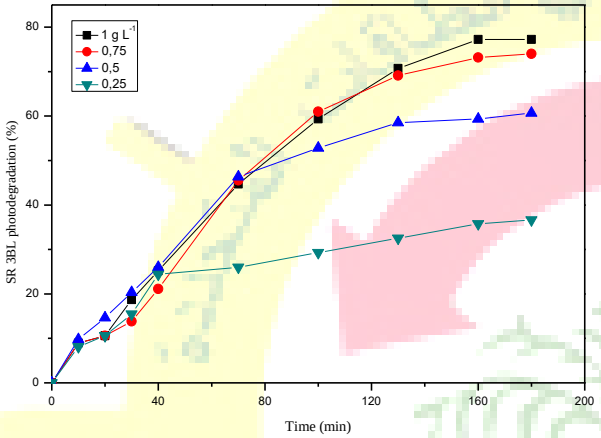


Fig.4 *Effect of the catalyst dose on the photodegradation of SR 3BL ([SR] = 10 ppm, free pH)*

2) *Effect of pH*: The effect of pH on the efficiency of decolorization process is an important parameter to investigate. The generation of hydroxyl radicals is function of pH [12]. SR 3BL is chemically stable over a wide pH range (4-11) and Figure 5 shows a strong influence of pH, the photodegradation yield increases with raising pH up to pH ~ 6.7 and then decreases. The best efficiency occurs at free pH (6.7), close to that of the natural aquatic environment. The mechanistic aspect involved at the solid/solution interface for the SR 3BL adsorption onto the hetero-system ZnO/Bentonite is determined from the pH study, closely related to the point of zero charge (pzc). The pzc of the catalyst is found to be 9.20. The surface catalyst is positively charged below pzc and negatively charged above pzc. SR 3BL molecules have negative charges (anionic dye) in a wide pH value range. Therefore, when the SR 3BL solution pH value is below the PZC, the adsorption (first step in photocatalysis) of SR 3BL anions on the surface of catalyst particles is favored through electrostatic attraction ally and in this way the SR 3BL photooxidation. A similar behavior was obtained in the study carried out by Changchun *et al*. [13].

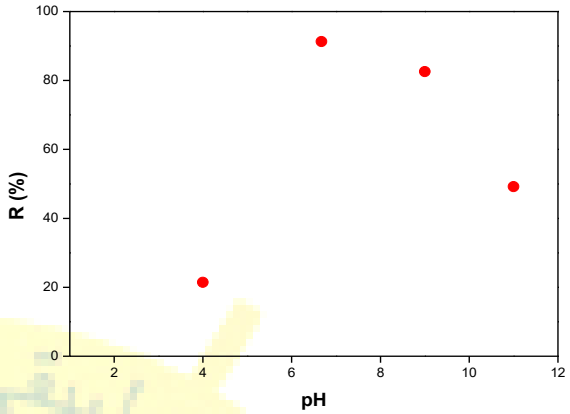


Fig.5 *Effect of pH on the removal of SR 3BL ([SR 3BL] = 10 mg/L, catalyst dose = 0.75 g $L^{-1}$)*

3) *Effect of initial dye concentration*: The dyes are thrown in the aquatic environment at concentrations up to 20 mg/L and inhibit dramatically the aquatic life by blocking the photosynthesis with serious consequences on the eco-system. So, it is interesting to study the photodegradation by varying the initial SR 3BL concentration ($C_o$) while all other parameters were kept constant at their optimal values; five concentrations ranging from 5 to 75 mg/L were selected; Figure 6 shows that the photodegradation efficiency of SR 3BL decreases with raising $C_o$. For high concentrations, more dye molecules are adsorbed on the catalyst surface, and the generation of active radicals on the catalyst surface is reduced since the active sites are occupied by the dye molecules. In addition, the light penetration is strongly attenuated as the concentration $C_o$ increases; consequently fewer photons reach the catalyst surface and the photodegradation decreases significantly [14]. Hence, the optimal concentration is found to be 5 mg/L with a degradation yield of 92%.

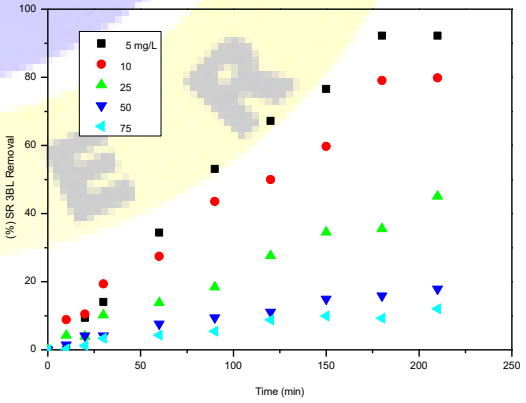


Fig.6 *Effect of initial concentration on the removal of SR 3BL (free pH, catalyst dose = 0.75 g $L^{-1}$)*

*C.* Kinetic analysis as a function of dye concentration

The kinetic of SR 3BL photodegradation under solar light is investigated. The surface adsorption has a direct effect on the photoactivity, through the increasing number of photocatalytic sites [15]. As mentioned above, the SR 3BL molecules are adsorbed on the hetero-system by electrostatic interaction of azoic groups. The disappearance rate of SR 3BL depends on the initial concentration $C_o$ and the mechanism is well described by the pseudo-first order kinetic.

To elucidate the photodegradation kinetic; the graphs -Ln ($C/C_o$) versus time for different concentrations $C_o$ were plotted (Figure 7).

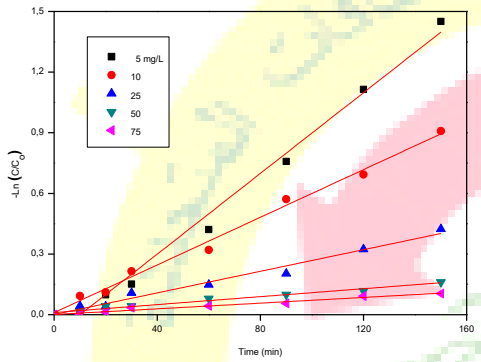


Fig.7 *Kinetics of SR 3BL photodegradation; linear transform -Ln (C/Co) versus time at different concentrations (free pH and catalyst dose = 0.75gL$^{-1}$).*

The kinetic model fits well the experimental data and the rate constant $k_{app}$ decreases with increasing $C_o$ (Table 1). Consequently the pseudo first-order kinetic can really be used to describe the photodegradation of SR 3BL onto the hetero-system ZnO/Bentonite.

*Table I*
*First-order kinetic constant ($k_{app}$) and $R^2$ for different initial concentrations*

| **$C_o$ (mg/L)** | **5** | **10** | **25** | **50** | **75** |
|---|---|---|---|---|---|
| $K_{app} \times 10^2$ (min$^{-1}$) | 1 | 0. 5 | 0.2 | 0.1 | 0.07 |
| $R^2$ | 0.989 | 0.992 | 0.979 | 0.975 | 0.970 |

The Langmuir–Hinshelwood (L–H) model is successfully used to describe the kinetic of the photocatalytic degradation of organic compounds and is expressed by the following equation:

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1+KC}$$

Therefore, the SR 3BL photodegradation is described by a pseudo-first order kinetic, which is rationalized in terms of L–H model to accommodate the reactions.

## IV. Conclusions

The photocatalytic elimination of the SR 3BL dye on the hetero-system was successfully achieved under solar light. The X-ray diffraction, optical properties, SEM images and XRF analysis showed that the Wurtzite ZnO is well impregnated and homogeneously supported on the Bentonite, forming a novel and efficient hetero-system for the photocatalytic applications. The catalyst dose, pH solution and initial dye concentration were optimized. It has been found that the photodegradation increases with decreasing the SR 3BL concentration and the equilibrium is reached within 160 min. The experimental data are suitably described by the Langmuir-Hinshelwood model and the photodegradation follows a first-order kinetic. The best photoactivity is obtained for a concentration of 5 mg/L and a catalyst dose of 0.75 gL$^{-1}$ at natural pH.

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