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SIGNIFICANT ENHANCEMENT OF PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE BY EXTRACTED ANTHOCYANIN PIGMENT AND SOLAR LIGHT

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Abstract

Sensitized zinc oxide semiconductor was prepared using different masses of anthocyanin stain (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1)g. Each mass of dye mixing with 1g of zinc oxide using a Pyrex reactor with capacity of (100 cm^3), the suspension solution was irradiated with a solar lamp at 298K. Prepared sensitized zinc oxide was used as a photo catalyst for the treatment of waste water, malachite green stain was used as a model compound. Many experiments were used to optimize the experimental factors. First set of experiments include studying the effect of sensitized zinc oxide masses were used with a constant concentration of malachite green. It was found that 94.78% of sensitized zinc oxide gave the highest photo degradation rate. The second set of experiments sensitized zinc oxide concentration was constant at 0.16g with different concentration of malachite green, the optimum rate constant was obtained at 50mg/L of malachite green. The photodegradation of malachite green decreased in the presence of high concentrations of malachite green. The highest photodegradation rate was obtained at pH = 9.

Key words: Zinc oxide, Malachite green dye, semiconductor, photodegradation

Introduction

Hibiscus sabdariffa Linn. is also known as Roselle or Rosella an annual herb belonging to Angiosperms, Dicotyledons, Malvales, and the family Malvaceae (Mahadevan *et al*., 2009), It is a plant with a height of up to two meters, simple or branched, leaves roundish to elliptic in outline, the uppermost digitate, 3-7 lobed or reduced to single lobe, Flower solitary, axillary, Calyx 5 dentate or partite, persistent in fruit; Petals 4-5, yellowish with a deep purple spot at the base, stamina column short, ovary 5-locular, stylar column 5-branched above, stigma capitate; fruit a loculicidally dehiscent 5-valved capsule (Townsend *et al*., 1980).

Many of the researchers believe that the origin of the plant in India and Saudi Arabia and some believe that its native habitat is Central and West Africa (Sudan, Ghana, Nigeria) and Asia, where it is cultivated mainly in the Philippines, In Iraq its only found in desert region especially in 15 km south of Diwaniya. Hibiscus has several species of different economic importance, Two botanical types are recognized: *Hibiscus sadbariffa* var. *sadbariffa*, this variety is generally branched and pigmented, and are grown for the purpose of obtaining red leaf containing anthocyanin and vitamin C and many Phenolic compounds, flavonols, terpenes and other medically active compounds, the second variety is Hibiscus sabdariffa var. attissma, its long vegetation reaches a height of 2m and is very low branching and is used in the production of fiber(Eltayeib *et al*., 2014 and Huda *et al*., 2016).

Anthocyanin is the biggest group of water-soluble natural pigments, concentrated in regions such as flowers and fruits. Roselle is rich in anthocyanins and protocatechuic acid concentrated in the calyxes and giving them a bright red color. Anthocyanins possess a high thermo stability and contribute towards antioxidative, antiinflammatory, cardioprotective and hepatoprotective activities (Azevedo *et al*., 2010 and Huda *et al*., 2016)

In the last decade, heterogeneous photo catalysis processes are using semiconductor oxides metal oxide

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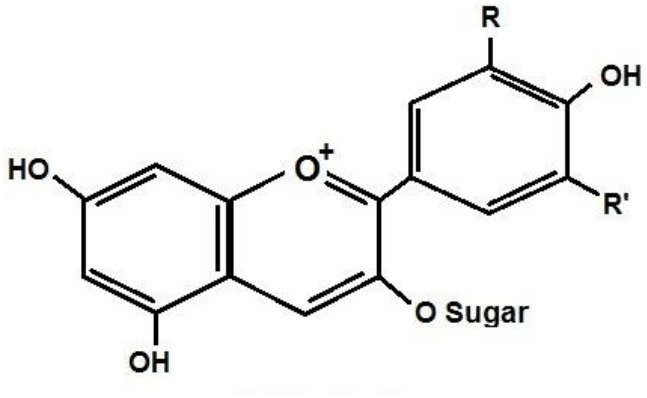

Structure of Anthocyanin

and solar lamp, to removed organic and inorganic pollutants into carbon dioxide and water. Zinc oxide (ZnO) is one of the most important semiconductors, because zinc oxide is a highly stable, inexpensive metal oxide, nontoxic material and environmentally friendly material (Akpan *et al*., 2009).

The mechanism of formation (electron-hole) pairs are as follows:

$$ZnO + hv \longrightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O \longrightarrow H^+ + OH^- \quad (2)$$

$$e^- + O_2 \longrightarrow O_2^{\bullet -} \quad (3)$$

Free radicals created from this reaction are highly reactive to attack organic and inorganic molecules and degrade them to produce water and carbon dioxide (Molly *et al*., 2016).

The aim of this study is to extend the activity of zinc oxide toward the visible region by using Anthocyanin, and then investigate the efficiency of sensitized zinc oxide for the degradation of malachite green dye in aqueous solution.

Materials and Methods

Materials

Zinc oxide (ZnO) was obtained from Sigma-Aldrich (St. Louis, USA). Sodium hydroxide (analytical grade), hydrochloric acid (analytical grade) and malachite green dye were supplied by Fluka (Buchs, Switzerland). All chemicals were employed without any further purification.

Raw materials and Extraction preparation

The aqueous extraction was carried out according to the method (Harborne, 1984). The floral calyces of H.sadbariffa var. sadbariffa (local Iraqi) was obtained from the local markets of Hilla city (Souq Al-Ammar), which identified according to a morphological characteristic in the flora of Iraq (Townsend *et al*., 1974). Samples were transported at home for cleaning by washing with tap water to remove dust and insects, then immersed 250 g of floral parts in 500ml of boiling water at 100°C for 48 hours at room temperature with continuous mixing to allow solubility of active substances in the solvent used. The extract was then first applied with a soft cloth and then in Whatman No.1 filter paper. Solvent from the extract was removed by using rotary vacuum evaporator and put it in the oven at 50°C. Finally, the powders were collected and used for the experiment.

Synthesis of sensitized zinc oxide

The sensitized zinc oxide with anthocyanin were prepared by mixing of 1g of zinc oxide metal oxide and different masses 0.1, 0.2. 0.4, 0.6, 0.8, 1.0g of anthocyanin aqueous suspension solution. The process is accompanied by continuous stirring for three hours in photolysis cell using solar lamp at 298K.

Photocatalytic experiments

The degradation process of malachite green dye has been tested in glass photoreactor. Photo degradation of malachite green stain reactor consisted of two parts. The first part of cooling the suspension solution in which the running water was passed through it. The second part called the reaction vessel solution with (100 ml) capacity. The removal of malachite green dye was conducted under solar light. All experiments were performed by mixing 0.16 g of the catalyst with 50 mg/L of the dye solution. In order to ensure adsorption equilibrium between surface of catalyst and dye, the suspension solution was kept under stirring in the dark for 30 minutes. The solution of dye was bubbled with air (10mL/min) during the irradiation. A 2ml of suspension reaction mixture was withdrawn every 10 minutes, then centrifuged at 4000

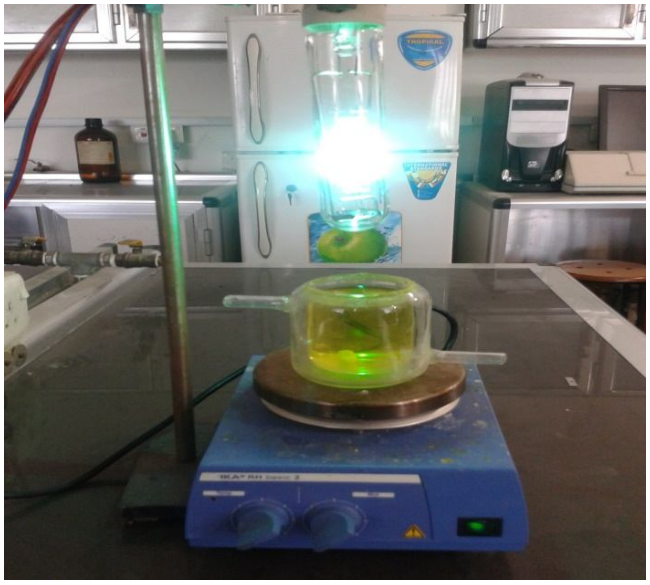

Fig. 1: Main compartments of the photocatalytic degradation cell used in removal of malachite green stain

rpm to remove any residual sensitized zinc oxide particles. All samples taken were analysed at a maximum absorption band by UV-vis spectrophotometer. The instrument picture of photochemical reaction shown in fig. 1.

Results and Discussion

The effect of sensitized zinc oxide loaded masses

A set of experiments was carried out to study the effect of sensitized zinc oxide mass on the degradation of malachite green dye. All experiments were performed using 50mg/L malachite green dye, 10 mL/min of an air bubble and four different masses of sensitized zinc oxide 0.03, 0.08, 0.16 and 0.85 g at room temperature. As observed from fig.2, the removal dye increases with increase the amount of sensitized zinc oxide until 0.16g. The reason may due to increase the number of active sites which are responsible for the generation of highly reactive radicals. However, the degradation efficiency of malachite green dye was decreased at 0.85g sensitized zinc oxide, may be attributed to decreasing in the penetration of the photon in the solution, therefore decreases the photocatalytic degradation rate (Ajmala *et al*., 2016, Hazim *et al*., 2017and Yaghub *et al*., 2016).

Effect of malachite green dye concentration

Photocatalytic degradation of malachite green dye was conducted using different initial dye concentration

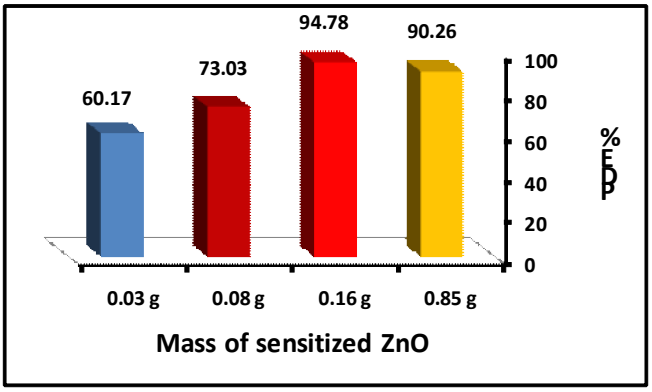

Fig. 2: Effect of sensitized zinc oxide mass on removal of malachite green dye, dye concentration is 50 mg/L.

range (50-100 mg/L). All experiments were performed at range (0.16gm/100 ml) of sensitized zinc oxide, the suspension solution was irradiated with 8.22mW/cm^2 intensity of light, flow rate of air 10 ml/min, at 298k and 0.16 gm/100 ml of sensitized zinc oxide as a catalyst. The results are shown in fig. 3. It can be noted from the figure that the photo degradation of dye was depended on the concentration of malachite green dye. Photo degradation of dye decreases with increasing concentration of dye, because the fact that as the initial concentration of malachite green dye increases, the malachite green dye molecules are adsorbed on the surface of sensitized zinc oxide particles, but the number of hydroxyl radicals and super oxide radical radicals formed on the surface of sensitized zinc oxide particles and the exposure time are fixed. Therefore relative number of $^{\bullet}OH$ and $^{\bullet-}O_2$ radicals available for attacking malachite green dye molecules becomes less, and consequently photo degradation efficiency decreases. On the other hand as the initial malachite green stain concentration increases, the path length of photons entering the suspension solution decreases, resulting in lower photon adsorption on catalyst particles and, consequently, a lower photo catalytic degradation rate (Hazim *et al*., 2016, Peidong *et al*., 2016 and Jianguo *et al*., 2016).

Effect of initial pH

A set of experiments was performed to investigate the influence of initial pH, on the photocatalytic degradation process of malachite green dye range (3–10). The initial

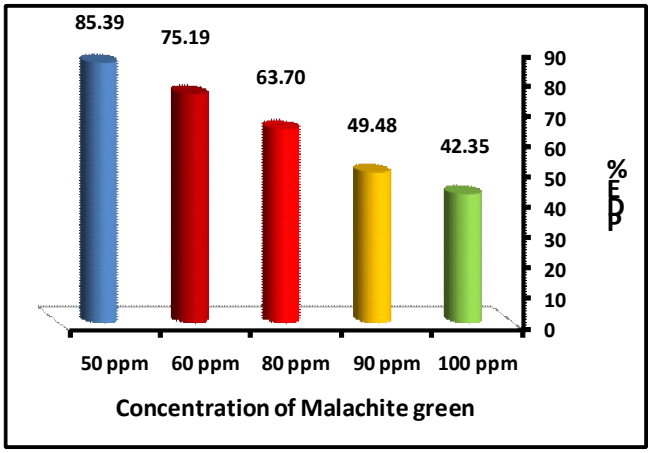

Fig. 3: Effect of malachite green stain concentration on photocatalytic process in the presence of 0.16g of sensitized zinc oxide.

pH was adjusted using 0.01mol/L of hydrochloric acid and sodium hydroxide. All experiments were performed in the presence of 0.16 g of sensitized zinc oxide and 50 mg/L of malachite green dye under 10 ml/min flow rate of air. As shown in fig. 4 the photocatalytic degradation efficiency of malachite green stain was as low as in very acidic medium compared to other moderate acidic and basic medium. It was observed that the removal of malachite green stain was 20.19% at pH 3. The highest removal of dye was at pH 9 which is 90.89%. However, at basic conditions, the removal of dye was 80.23%, this variance of dye behavior at different pHs value could be explained by the availability of the active site on the sensitized zinc oxide surface (Hazim *et al*., 2016, Yadollah *et al*., 2012, Rosari *et al*., 2014, and Clament *et al*., 2013).

Conclusion

Photocatalytic degradation of a malachite green stain was tested by sensitized zinc oxide as a catalyst. Removal efficiency was affected by the pH of solution, exhibiting

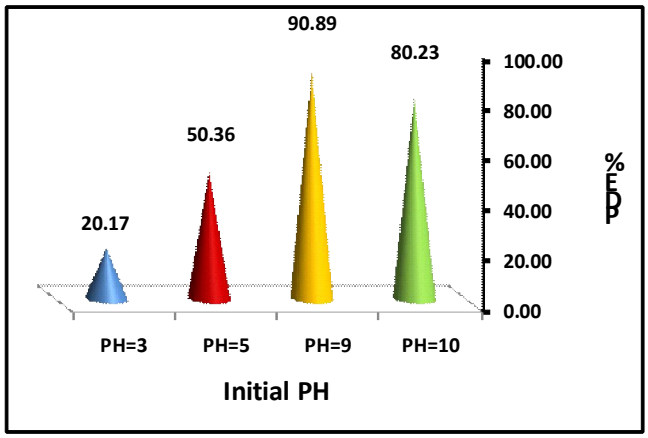

Fig. 4: Influence of initial pH on the photo degradation of malachite green dye. 50mg/L of dye and 0.16g of sensitized zinc oxide.

high removal percentage was observed at pH 9. The removal of malachite green stain was increased with the increasing of sensitized zinc oxide mass up to 0.16g. Initial dye concentration was also investigated; the removal of dye was decreased with increasing the initial dye concentration. Malachite green dye was degraded almost completely at 50mg/L.

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