Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 9 (2) 95-102: summer 2012
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Application of Electroactive Nano Composite Coated onto Wood Sawdust for the Removal of Malachite Green Dye from Textile Wastewaters

M. H. Fekri[1], M. Banimahd keivani[2, 3,*], M. Darvishpour[4] and H. Banimahd keivani[5]

[1] Department of Chemistry, Islamic Azad University, Khorramabad Branch, Khorramabad, Iran
[2] Iranian Academic Center for Education Culture & Research (ACECR), Guilan Branch,Rasht, Iran
[3] Department of Chemistry, Payam Noor University, Rasht, Iran
[4] Department of Chemistry, University of Razi, Kermanshah, Iran
[5] Department of Chemistry, Islamic Azad University, Ghaemshahr Branch, Ghaemshahr, Iran

Received December 2012; Accepted December 2012

ABSTRACT

In this research, the removal of malachite green dye from Textile Wastewaters using polyaniline coated onto sawdust (PAni/SD) has been investigated. Ammonium peroxodisulphate was used as chemical oxidant for polymerization of polyaniline directly on the surface of sawdust. The effects of some important parameters such as pH, initial concentration, sorbent dosage, exposure time and temperature on uptake of malachite green dye were investigated.Adsorption studies have shown that pH of the malachite green solution has influence on the dye removal capacity of PAni/SD. It was found that effective dye removal is occurred under neutral or acidic conditions. The treatments of data were carried out using both Freundlich and Langmuir adsorption isotherms.

Keywords: Polyaniline, Malachite green dye, Sawdust, Adsorption, Nano composite, Textile

INTRODUCTION

Synthetic dyes have been increasingly used in the textile, paper, rubber, plastic, cosmetics, pharmaceutical and food industries because of their ease of use, inexpensive cost of synthesis, stability and variety of colour compared with natural dyes [1-3]. The Textile industry is in the forefront in the use of dyes in its operations with more than 9000 types of dyes incorporated in the colour index [4]. Similarly, it has been reported that more than 70000 tons of approximately 10000 different types of dyes and pigments are produced annually worldwide, of which 20-30% are wasted in industrial effluents during dyeing and finishing processes in the textiles industries [5]. The discharge of coloured waste is not only damaging the aesthetic nature of receiving streams, but is also toxic to the aquatic life [6].

Azo dyes generally have been known to be carcinogenic for over 60 years and are linked, particularly, to bladder cancer [7]. Synthetic dyes used for doing different cases in many commercial and industrial techniques. The structure of malachite green is shown in Fig. 1.

The toxic nature of the dye is still not quantified much but its high content in living systems can prove to be harmful. Thus, the safe removal of such a dye is the prime aim of our present research and this

*Corresponding author: mbk_ir@yahoo.com

is accomplished by using a novel adsorbent. Polyaniline (PAni) is a poly aromatic amine that can be easily synthesized chemically from bronsted acidic aqueous solutions. It is one of the most potentially useful conducting polymers and has received considerable attention in recent years [8-12]. Chemical polymerization of aniline in aqueous acidic media can be easily performed using of oxidizing agents such as $(NH_4)_2S_2O_8$ as shown in the following (Fig. 2).

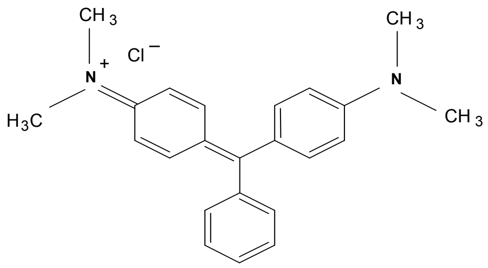

Fig. 1. Chemical structure of malachite green.

Recently it has been reported that chemically synthesized polyaniline and polypyrrole can be used for removal of some organic dyes (acidic and basic) from their aqueous solutions effectively. Polyaniline behaves as a charged surface upon post-synthesis treatment of the polymer with acid and base. The dye removal efficiency was found to be greatly controlled by pH of the treated solution [13, 14, 15].

In this paper we have introduced an application of polyaniline that is the principle is based on the switchable chemical structure and ion exchange properties of conducting polymers. Adsorption properties of the PAni/SD were investigated with the malachite green dye as target pollutant from Textile Wastewaters as a function of dye contact time by sorbent and experiment temperature using pseudo-first and second-order kinetics models.

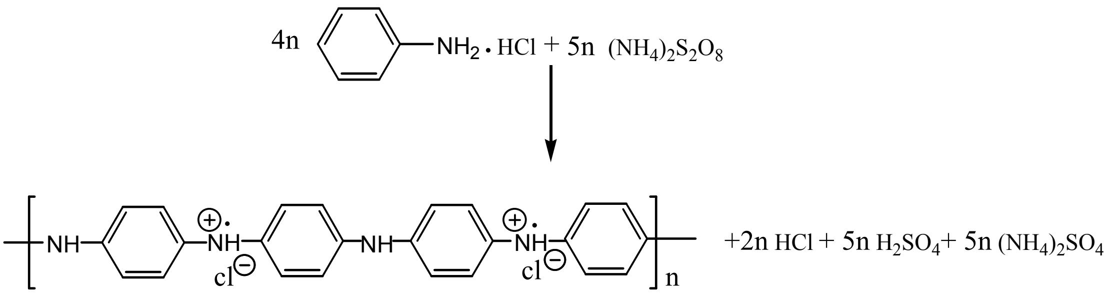

Fig. 2. Chemical polymerization of polyaniline.

EXPERIMENTAL

Materials and equipments

Materials and equipments All chemicals used were analytical reagents grade and prepared in deionized water.Aniline was obtained from Merck and distilled before use. Wood sawdust sample (termed as SD) prepared by walnut obtained from a local carpentry workshop. A solution of malachite green was prepared in dionized water, used as stock solution. Absorbance measurements were carried out on a single-beam Perkin–Elmer UV–vis spectrophotometer with a 1-cm cell. A Metrohm pH meter (model 827) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for determining pH. The surface morphologies of polymer samples were studied using scanning electron microscopy (SEM; Model VEGA).

Determination of malachite green (MG)

The measurement of malachite green was carried out in aqueous media spectrophotometrically (λmax=620). Quantitatve analysis of this dye was carried out using a calibration graph obtained from the standard solutions prepared of the standard malachite green in dionized water in the concentration range from 0.0-5.0 ppm.The calibration curve shows that Beer,s law is obeyed in this concentration range (Fig. 3. and Fig. 4).

Preparation of the adsorbent

Aniline (Merck) was doubly distilled before polymerization. Polymerization was carried out in aqueous solution. In order to prepare polymer coated onto sawdust (PAni/SD), 5.0 g sawdust (35-50 mesh, 10 % humidity) immersed in 50 mL of 0.20 M freshly distilled aniline in HCl 1M solution for 12 hours before polymerization. The excess of the monomer solution was removed by simple decantation. 50 mL of 0.5 M $FeCl_3$ as the oxidant solution was added into the mixture gradually, and the reaction was allowed to continue for 4 hours at room temperature. The polymer coated sawdust (PAni/SD) was filtered, washed with distilled water, dried in an oven at about 60 ^oC and sieved before use.

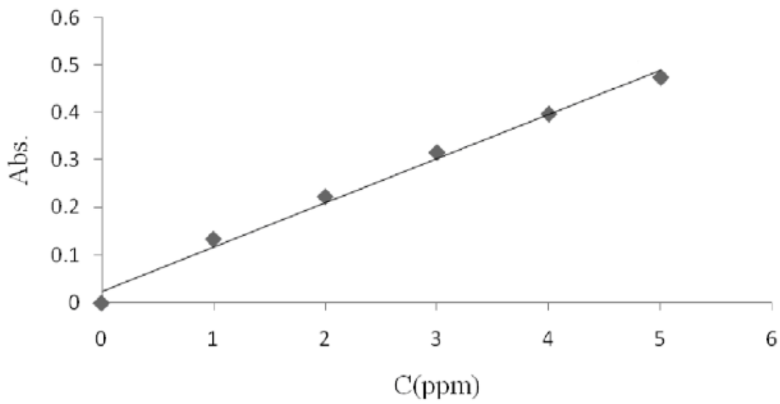

Fig. 3. Calibration curve of absorbance against oncentration of malachite green.

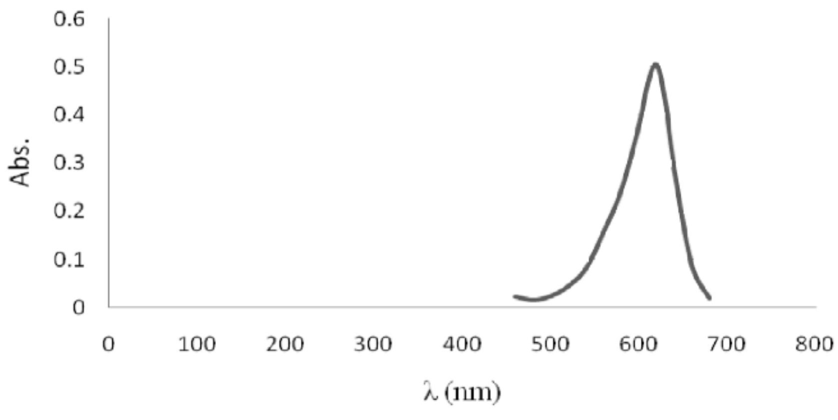

Fig. 4. Absorption spectrum of malachite green.

Adsorption Experiments

Batch mode studies were conducted using 0.2 to 1.0 g of the adsorbents, taken separately. Each adsorbent was shaken in 50 ml aqueous solution of MG of varying concentrations (20-100 ppm) at room temperature for definite time periods. At the end of pre-determined time intervals, the adsorbent was removed by simple filtration. The filtrates were analyzed for the residual (unadsorbed) MG, spectrophotometrically. Adsorption experiments were carried out at room temperature using batch system. All experiments were carried out at least for three times with respect to each condition and mean values are presented. The maximum RSD was less than 2%. The following equations were used to calculate the percentage of sorption and the amount of adsorbed methyl orange, respectively:

$$\%Sorption = \frac{(C_o - C_e)}{C_o} \times 100$$

$$\frac{x}{m} = \frac{(C_o - C_e)V}{m}$$

where, C_0 and C_e are the initial and equilibrium concentrations of the malachite green, respectively (mg L^{-1}), x/m is the amount of malachite green adsorbed onto unit amount of the adsorbent (mg g^{-1}) at equilibrium, and V is the volume of the solution used in the adsorption experiment (L).

RESULTS AND DISCUSSION

Sorption of MG by PAni/SD

A series of experiments has been performed to optimize the adsorption conditions for removal of MG dye using the treated and untreated sawdust. The pH of an aqueous medium is an important factor that may influence the uptake of the many adsorbates such as dyes, so the influence of pH on dye adsorption by the selected adsorbents was studied first.

Effect of pH

In order to find out the effect of pH, 0.5 g of the dried PAni/SD and SD sorbents were treated separately with 50 mL of 50ppm MG at various pH values (from 1 to 12) accompanied by mild shaking at room temperature at constant contact time (1 h).

As our data show (Fig. 5) increasing solution pH increases the extent of dye removal. Lower adsorption percentage of MG on PAni/SD at highly acidic conditions (pH ≤ 3) is probably due to the presence of high concentration of H+ ions on the surface of adsorbent competing with malachite green (a cationic dye) for adsorption sites in the adsorbent (Fig. 1). With an increase in the solution pH, the electrostatic repulsion between the positively charged malachite green (Fig. 1) and the surface of adsorbent is lowered. Consequently removal efficiency is increased.

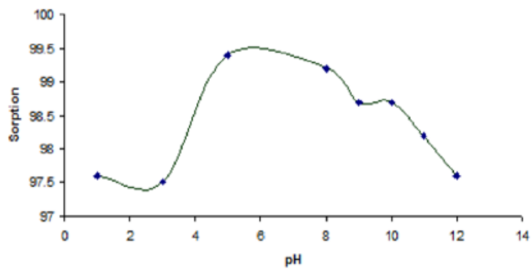

Fig. 5. Effect of solution pH on adsorption percentage of MG by PAni/SD.

Effect of adsorbent dose

For investigating the effect of adsorbent mass on the adsorption of malachite green dye, a series of adsorption experiment was carried out with different adsorbent dosages (0.10-1.0 g). In order to differentiate the sorption capacity of the employed adsorbents, we chose 25 mL of 50 ppm MG solution as test probe in this investigation. Adsorption experiments for uncoated sawdust was carried out at pH 6 (the natural pH of MG solution) and for PAni/SD, the experiments was performed at pH 12. The results obtained have been shown in Fig. 6 .

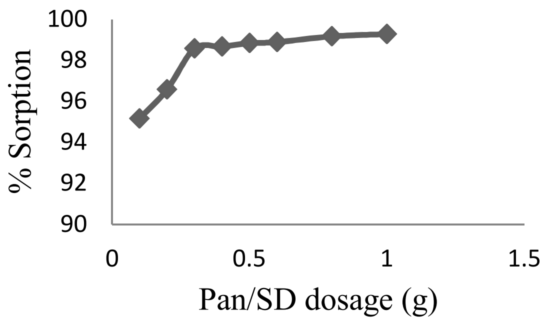

Fig. 6. Effect of amount of adsorbent on removal percentage of MG by PAni/SD.

Effect of initial concentration

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 10 to 50 ppm. For performing this experiment, fixed amounts (0.3 g) of PAni/SD adsorbent was treated with 25 mL of 10-50 mg L^{-1} of MG solution. The period of contact time was 10 minutes accompanied by a mild mechanical shaking at room temperature. The results obtained are summarized in Table 1. Results from this study show that the adsorption process is highly dependent on the initial concentration of the dye in solution and % removal of MG decreases as its initial concentration increases. However, the total amount of dye (X/m) uptake is increased gradually.

Table 1. Effect of initial MG concentration on its sorption percentage onto PAni/SD.

MB concentration (mg/L)	**10**	**20**	**30**	**40**	**50**
% Sorption	97.2	98.3	98.5	98.0	98.0
x/m (mg/g)	0.5	1.0	1.0	2.0	2.5

Effect of contact time

For performing this experiment, 0.5 g of sorbents (PAni/SD), were treated with 25 mL of 50 ppm malachite green for different periods (10-60 min) accompanied by stirring at room temperature. From the analysis of filtrate solution for unadsorbed malachite green in Fig. 7, it was found that about 98% of dye removal was occurred with 40 min. Therefore, removal of malachite green is not very time dependent process and sorption occurs very quickly.

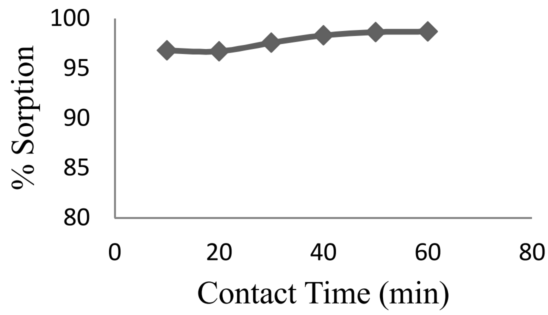

Fig. 7. Effect of contact time on the removal of MG by PAni/SD.

Adsorption Isotherms

The equilibrium adsorption isotherms are of fundamental importance in the design of any adsorption system. In this study Langmuir and Freundlich isotherms were employed for treatments of the equilibrium adsorption data [16, 17]. The Langmuir adsorption isotherm is the best known linear model for monolayer adsorption and most frequently utilized to determine the adsorption parameters. Longmuir model is represented by the following equations:

$$q_e = \frac{K_L C_e}{1 + bC_e} = \frac{Q_o b C_e}{1 + bC_e} \quad \text{(Nonlinear form)}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right) C_e \quad \text{(Linearised form)}$$

where C_e is the equilibrium concentration of MG in solution (ppm), q_e is the amount sorbate adsorbed per unit mass of adsorbant (mg g^{-1}), Q_0 is the maximum amount sorbed (mg g^{-1}) when the monolayer is complete, b is Langmuir's constant related to the affinity of binding sites and is a measure of the energy of adsorption(L mg $^{-1}$). A linearized plot of C_e/q_e against C_e gives Q_0 and b values. Values of Q_0 and b were calculated from the slopes (1/ Q_0) and intercept (1/b Q_0) of the linear plots.

The Langmuir model deals with monolayer adsorption and constant adsorption energy. Another widely used equation in adsorption processes is the Freundlich equation. The Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. The model is represented by the following equations:

$$q_e = \frac{x}{m} = KC_e^{\frac{1}{n}} \quad \text{(Nonlinear form)}$$

$$\log\frac{X}{m} = \log K + \frac{1}{n}\log C_e \quad \text{(Linearised form)}$$

where, X/m is equilibrium adsorption capacity (mg g^{-1}), C_e is the equilibrium or residual concentration (mg L^{-1}) of MG dye in solution, and K and 1/n are empirical Freundlich constants indicating sorption capacity of adsorbent and intensity of adsorption (mg g^{-1}), respectively. The Langmuir model assumes monolayer surface coverage on equivalent sites, the Freundlich model, on the other hand, assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The plot of C_e/q_e against C_e in Fig. 8 gave straight lines for all the concentrations, implies that the adsorption for adsorbent well fitted to Langmuir isotherm. The high correlation coefficient obtained for PAni/SD (R^2 = 0.948) indicates high affinity between adsorbent surface and MG which plays the major role in the adsorption mechanism. The Freundlich isotherm (linear forms) obtained for the adsorbent employed in this research is shown in Fig. 9. From the high correlation coefficient obtained for Pani/SD (R^2 = 0.951) indicates high affinity between adsorbent surface and MG . it could be concluded that the adsorption isotherm of methylene blue using PAni/SD give a better fit to the Freundlich model.

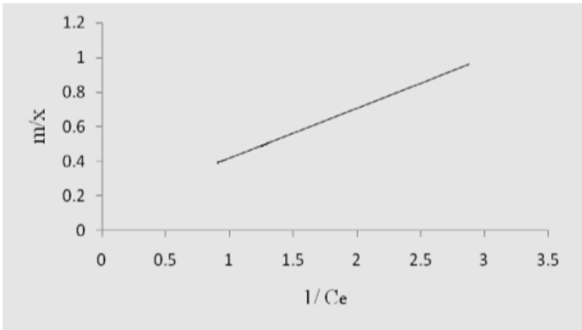

Fig. 8. Langmuir adsorption isotherm for the sorption of MG by PAni/SD.

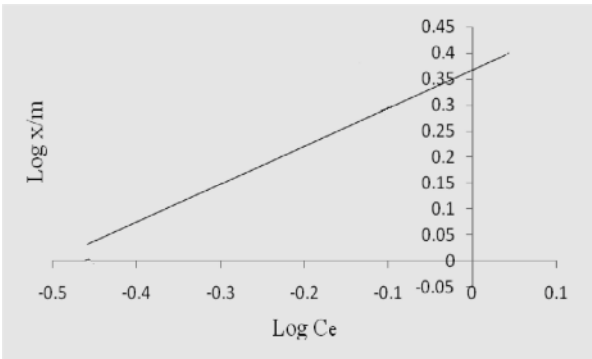

Fig. 9. Freundlich isotherm for the sorption of MG by PAni/SD.

Table 2. Freundlich and Longmuir Isotherms constants for MG adsorption onto PAni/SD (using batch system).

Adsorbent	n	k	b	X_m
PAn/SD	1.37	2.33	0.24	7.75

The morphology of the adsorbent

Different levels of nano-composites were scanned by scanning electron microscope and this images are shown in Fig. 10-12. Different levels in states with no coverage and the coverage is clearly visible.

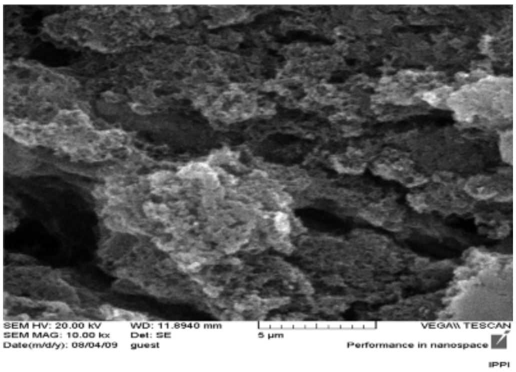

Fig.10. SEM picture from SD.

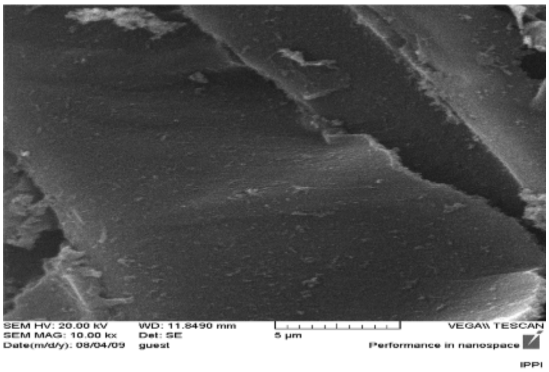

Fig.11.SEM picture from PAni/SD.

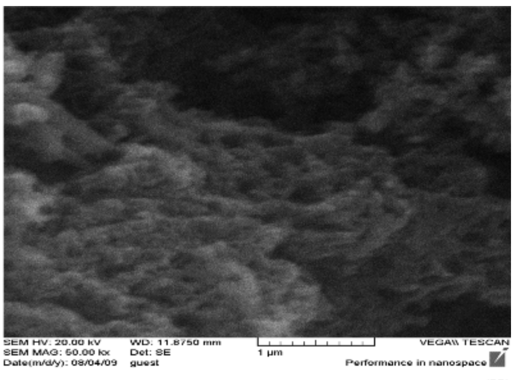

Fig.12. SEM picture from PAni/SD/MG.

CONCLUSIONS

Presence of color and colered derivaties in different effluent, have been caused environmental disturbance and its contamination.The use of sawdust a very cheap matter and compatible with environment is appropriate for coveri it to provide a effective adsorbent by poly aniline for removal of pigments, such as malachite green from Textile Wastewaters. According to benefits such as the system simply, no need advanced equipments, easy to prepare, low cost, efficiency, capacity and high absorption rate of introduced absorpent.

In this work (PAni/SD) for eliminate pigments, it seems to be used it for of industrial wastewater decolorization for example textile industries.

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