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Adsorption Kinetics for Removal of Congo Red Dye from Textile Waste Water using Al-TiO_2/PANI Nanocomposites

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ABSTRACT
In this paper we report the fabrication of Al doped TiO_2 nanofibers by electrospinning and preparation of electrospun Al-TiO_2/polyaniline (PANI) nanocomposites by in-situ chemical oxidation polymerization and its application for the removal of Congo red dye from aqueous solution. The morphology of the prepared nanocomposites was studied by scanning electron microscopy. Adsorption kinetics of synthesised nanocomposites was studied by UV-visible spectroscopy. Percentage of removal of Congo red dye using Al-TiO_2/PANI was found to be 76%. In order to evaluate adsorption kinetics, the pseudo first order model, pseudo second order model, and intra particle diffusion model were studied. The pseudo second order model was found to me more linear than other models which indicate that the adsorption of dye is a surface phenomenon and it depend on both concentration of dye and concentration of material. Experimental data suggested that adsorption is one of the best methods to remove Congo red dye from waste water disposed by textile industries.
Keywords: Polyaniline, Nanocomposites, Titanium dioxide, Aluminium, UV-Vis spectroscopy, Congo red dye.

I. INTRODUCTION

In this modern era where population is expanding day by day and the essential need water scarcity can be removed by the help of nanotechnology. The nanotechnology can provide the solution of removal of dyes from textile [1]. Dye is the substance used to add colour or to change the colour. The use of these dyes led to water pollution. Most of them are azo dyes, more than half of the commercial dyes belong to this class. These azo dyes can cause various health related issues. So, we require a method for the removal of these dyes [2]. There are various technologies for removing dyes from textile industry like reverse osmosis, ion exchange, precipitation biodegradation, coagulation and adsorption. Among which adsorption is fine, fruitful and manageable technique [3]. Congo red dye is an azo (anionic), water soluble, yielding a red colloidal solution and a pH indicator dye [4]. TiO_2 is accepted as photocatalyst due to its stability, non-toxicity highly photoactive and cost effective [5]. Photocatalytic activity can be enhanced by using conducting polymer such as polyaniline (PANI), polypyrole (PPY) etc. PANI has many properties such as low cost, good environmental stability, good electrical conductivity also it provides better binding site for the adsorption of the dye molecule. There are many methods to go to Nano-range like sol gel, phase separation, self-assembly, electrospinning. However, electrospinning process is deemed technically sound, environment friendly cost-effective and viable method for synthesising Al doped TiO_2 nanofibers [6].

II. EXPERIMENTAL

2.1 Fabrication of Al -TiO_2 nanofibers

Solution A was prepared by dissolving 1g of titanium isopropoxide (TiP) in acetic acid and ethanol of 2 ml each, 3 wt% aluminium nitrate nonahydrate which was followed by magnetic stirring for 10 min. The solution A was mixed with the solution B which was made up of 0.2 g polyvinyl pyrrolidone (PVP) in 3 ml of ethanol and 0.5 ml N-N dimethyl formamide (DMF). The resultant solution was magnetically stirred for 24 hours. The prepared solution was filled into 10 ml syringe then it has been subjected to electrospin. The flow rate was adjusted to 0.6 mlh^{-1}. Voltage was kept at 18 KV and distance between needle tip and collector plate was kept at 15 cm then these nanofibers have been collected. These samples were calcinated at 600 ^{o}C for 3 hours to remove PVP and other moieties.

2.2 Preparation of PANI-Al-TiO_2 nanocomposites

In-situ polymerization method was carried out for preparation of PANI-Al-TiO_2 nanocomposites. Solution A was prepared by dispersing Al doped TiO_2 nanofibers for 30 min by ultrasonication in 25 ml de-ionised water, 1 M HCl and 0.25 M aniline and then magnetically stirred for 15 min. Solution B was made in 25 ml distilled water, 1 M HCl and 0.25 M ammonium peroxydisulfate (APS) and then magnetic stirred for 15 min. Solution B was added drop wise with continuous stirring for 6 hours into solution A. The nanocomposite of PANI with Al-TiO_2 nanofibers was obtained as precipitate. This precipitate was isolated by filtration, washed with distilled water several times and dried at 80 ^{o}C overnight.

III. RESULTS AND DISCUSSION

3.1 Scanning electron microscopy (SEM)

Morphology of as-fabricated Al-TiO_2 nanofibers and PANI/Al-TiO_2 nanocomposite was studied by SEM. Fig.1 shows SEM images of (a) Al-TiO_2 nanofibers and (b) PANI/Al-TiO_2 nancomposite. Fig.1(a) clearly showed that Al-TiO_2 nanofibers have been successfully fabricated by electrospinng and Fig. 1(b) showed that polyaniline have been encapsulated over Al-TiO_2 nanofibers and confirmed the formation of nanocomposites due to which adsorption will be more and Congo red dye will be reduced easily.

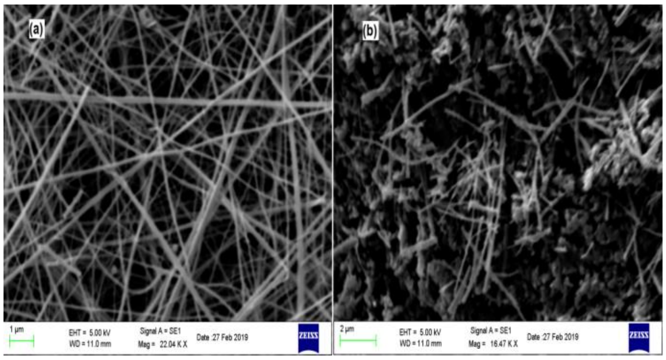

Figure 1. SEM images of (a) Al-TiO_2 nanofibers and (b) PANI/Al-TiO_2 nanocomposite

3.2 UV-Visible Spectroscopy

Photodegradation experiment was carried out by using UV-Visible absorption spectroscopy. Dye concentration was taken as 50 mg/L in de-ionized water and the mixture was magnetically stirred and reading were taken after every 15 min interval and the experiment was carried up to equilibrium. So, when a beam of ultraviolet rays falls on PANI/Al-TiO_2 nanocomposite electron and hole pairs are generated. This electron will combine with oxygen to form O_2^{-} (super oxide anion) and hole will react with H_2O to form $OH^{\cdot}$ (hydroxy radical). Now this $OH^{\cdot}$ and O_2^{-} will directly react with Congo red dye and give decolourisation product [7]. Kinetic studies have been done by pseudo first order, pseudo second order and intra particle-diffusion model. Fig. 2(a) shows the absorbance of dye by PANI/Al-TiO_2 in different time interval.

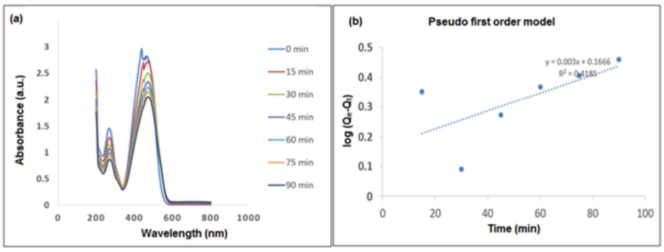

Figure 2(a). Absorbance of dye by PANI/Al-TiO_2 and **(b)** Pseudo first order model of PANI/Al-TiO_2

The percentage of removal of dye was calculated by the equation (1)

$$\%\ \text{dye removal} = \frac{(C - C_e)100}{C} \qquad \text{.........}\ (1)$$

Where, C= initial concentration and C_e= final concentration. The percentage of removal of dye by using PANI/Al-TiO_2 was found to be 76%. Fig. 2(b) shows Pseudo first order model, Fig. 3(a) shows the pseudo second order and Fig. 3(b) shows intra particle diffusion model of PANI/Al-TiO_2 for the study of removal of Congo red dye. These models have been studied by using equation (2), (3) and (4) respectively.

$$\log(Q_e - Q_t) = \log Q_e - \frac{Kt}{2.303} \quad \text{........ (2)}$$

$$\frac{t}{Q_t} = \frac{Q^2{}_e}{k} + \frac{t}{Q_e} \quad \text{........ (3)}$$

$$Q_t = kt^{0.5} + C \quad \text{......... (4)}$$

Where, Q_e = initial concentration, Q_t = concentration at time t and k = rate constant

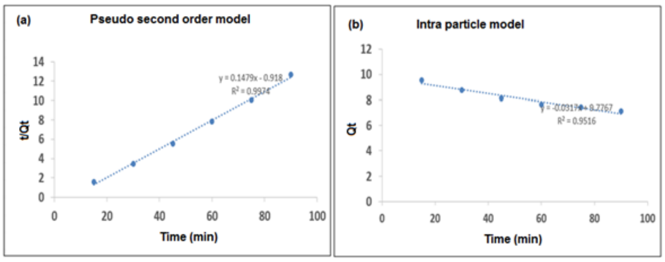

Figure 3(a). Pseudo second order and **(b)** Intra particle diffusion model of PANI/Al-TiO_2

The rate constant k was found to be 2.74 $mole^{-1}min^{-1}$ obtained from pseudo second order model. From these models we can infer that the second order model reaction shows more linearity. This gives the validity of pseudo second order reaction [8].

IV. CONCLUSIONS

Al-TiO_2 nanofibers and PANI/Al-TiO_2 nanocomposite have been successfully synthesised by electrospinning and in-situ chemical oxidation polymerization. Photocatalytic degradation of Congo red dye by using PANI/Al-TiO_2 nanocomposite was achieved under UV-visible light irradiation. Percentage removal of dye for PANI/Al-TiO_2 was found to be 76%. Thus PANI/Al-TiO_2 can be used for photocatalytic decolorization of various pollutants and are expected to play an important role in solving environmental pollution challenges due to their relatively high oxidative power, photostability and non-toxicity.

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