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Research Article

Removal of Acid Orange 74 from wastewater with TiO_2 nanoparticle

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ABSTRACT

The use of nanomaterials in wastewater treatment has gained importance. Nano-structured adsorbents have good adsorption potential due to their properties such as large surface area. In this study, removal of AO74 (Acid Orange 74) from the waters with TiO_2 nanoparticles were investigated. TiO_2 nanoparticles were synthesized by sol–gel method. The X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and Ultraviolet–visible spectroscopy (UV–VIS) spectrometer techniques were used to characterize the synthesized products. Stability analysis was performed by zeta potential analysis. The anatase phase of the TiO_2 nanoparticles was confirmed by XRD analysis. The SEM micrographs revealed the spherical-like morphology with average diameter of about 32 nm which agrees with XRD results. FTIR spectra show the vibrational mode of TiO_2 around 600 cm^{-1}. Absorption peak in the UV region at 320 nm are observed. This peak is characteristics of nano-sized TiO_2nanoparticles. If the measured zeta potential absolute value is greater than 35 mV, it can be said that the produced nanofluid is stable. The zeta potential value greater than 35 mV in all measurements in this study, so that the synthesized TiO_2 nanoparticle is stable in the fluid medium. pH (2-5), contact time (10-120 min) and initial dye concentration (20-100 mg / L) were investigated to determine the adsorption potential of TiO_2 nanoparticles. The optimum parameters for adsorption of AO74 were determined as pH and contact time, respectively: 5 and 75 minutes. The adsorption system is compatible with Langmuir and Freundlich isotherms. As a result, TiO_2 nanoparticles were identified as suitable adsorbent for removal of AO74.

1. Introduction

Dyes are generally used in textile, leather, plastic, paper industry, paints, cosmetics, color additives and biomedical area [1]. The dyes are very stable against light and oxidation due to their complex chemical structure. Due to these properties, their biodegradation is very difficult [2,3]. Textile wastes are one of the most important and dangerous environmental contaminants. Because many dyes are toxic and carcinogenic, they cause damage to the aquatic life and people.[4]. For this reason, it is very important to remove waste from the environment and dye elimination from wastewaters before their release into the environment is very substantial [2,5]. Basic dyes, acid dyes, azo dyes and disperse dyes are commonly used in the textile industry. [6,7]. Most of these dyes such as Acid orange 74 is an azo dye and used for dyeing wool, fibers, silk and carpet (Figure 1).

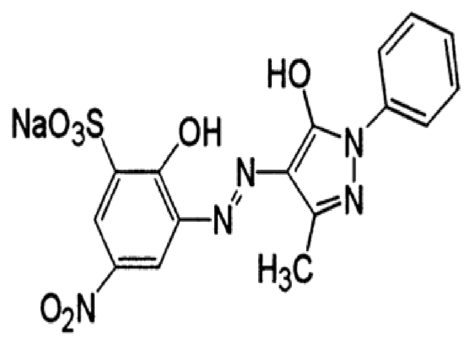

Figure 1. Acid orange 74 molecular structure

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In recent years, many methods such as adsorption, biological treatment, chemical oxidation, photocatalysis, coagulation/flocculation, etc. have been improved for separating organic pollution from water and wastewaters. Among these methods, adsorption process has been demonstrated as a highly effective removal method due to its simplicity, applicability and this technique also generally preferred in terms of cost. Several natural and synthetic adsorbents such as zeolites, polymers, resins, activated carbon, chitin and some nanoparticles like TiO_2, Al_2O_3, etc. have been used to remove contaminants from waste waters. Particles between 1-100 nm are defined as nanoparticles. Their at least one dimension less than 100 nm. Nanoparticle research is presently an area of deep scientific research because a wide variety of potential applications in medicine, energy and electronics, manufacturing and materials, environmental applications. The use of nanoparticles in environmental applications with the developing technology has become widespread. [8]. Nano materials used in water treatment are produced with small size, large surface area and renewable properties. [9]. The reason for the wide use of nanoparticles is the small size and high surface area. Among the nanoparticles, TiO_2 nanoparticles have commercial interests for their nontoxicity, low cost, hydrophilic, photocatalytic activity, large specific surface area, long service life, high efficiency.

In this study, the synthesis of TiO_2 nanoparticles and the AO74 removal potential from aqueous solutions were investigated. TiO_2 nanoparticles were synthesized by sol–gel method. The X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and Ultraviolet–visible spectroscopy (UV–VIS) spectrometer techniques were used to characterize the synthesized products. Adsorption potential of TiO_2 nanoparticles; pH, contact time and initial dye concentration were determined.

2. Materials and Method

2.1 Synthesis and characterization of TiO_2 nanoparticle

Ethanol, iso-propanol and Titanium (IV) butoxide were mixed in a ratio of 160 ml:20ml:20ml and the mixture was sonicated. To prepare a white precipitate, a solution containing 2 g of cetyltrimethyl ammonium bromide (CTAB) in 100 ml of water was added. The mixture was kept at 80 ^{0}C for 4 hours. Excess water in the mixture was removed by evaporation under constant stirring in a water bath. The synthesized material was first dried at 110 ° C for 12 hours and then calcined at 500 ° C in a muffle furnace for the get high degree of crystallization [10].

In this study, TiO_2 were used as the nanoparticles and deionize water (DIW) were chosen as the base fluid. The morphologies of TiO_2 were characterised by the XRD pattern. X-ray diffraction (XRD) analysis was conducted on a Rigaku DMAX IIIC using CuKα radiation at Department of Geological Engineering of Cumhuriyet University in Sivas, Turkey. Scanning electron microscope (SEM) analysis was carried out on TiO_2 nanoparticles by TESCAN MIRA3 XMU electron microscope. To determine the functional groups of TiO_2, FTIR(Bruker: Tensor II) analysis was done in the range 4000-400 cm^{-1}.UV-Vis spectrophotometer (UV-1280, Shimadzu, Japan) was utilized to record the spectra of prepared TiO_2-DIW nanofluids range from 200 to 800 nm. Zeta potential of the TiO_2 nanoparticles in aqueous phase was measured using a malvern Zetasizer Nano Z. The electrophoretic mobility of the particles is determined by this instrument automatically and converts it to the zeta potential [11].

2.2. Adsorption experiments

AO74 (Sigma-Aldrich) stock solution was prepared at 1000 mg / L concentration.AO74 in the desired concentrations was obtained by dilution from stock solution. Adsorption experiments were performed in batch system. The parameters affecting the adsorption were investigated (pH, contact time, starting dye concentration). The experiments were carried out in glass flasks with a working volume of 250 ml. The adsorptive quality of the TiO_2 nanoparticles were tested as a function of pH (2–5), contact time (10–120 min) and initial dye concentrations (20–100 mg/L).The pH of the dye solutions was adjusted with NaOH(0.1-0.01 M) and HCl(0.1-0.01M). After the adsorption system reached equilibrium, the adsorbent was separated by centrifugation. AO74 (λ_{max}455 nm) concentration in the solution was determined by spectrophotometer. The amount of dyes adsorbed (qe; mg/g) was determined by Eq (1) and the percent dye adsorption (%) was determined by Equations (2).

$$q_e = \frac{(C_o - C_e)*V}{m} \tag{1}$$

$$(\%)adsorption = \frac{C_o - C_e}{C_o} x100 \tag{2}$$

C_o is the initial dye concentration, C_e is the final dye concentration (mg/L).m is the mass of adsorbent (g) and V is the volume of the dye solution (L).

3. Results and Discussion

3.1 XRD results

XRD characterized the crystal structures of TiO_2 sample, and Figure 1showstheresults.Well-defined (1 0 1) peak at 25.42^0 and 37.89^0, 48.12^0, 55.16^0, 62.79^0 were displayed by the XRD pattern of TiO_2. These peaks belong to the typical anatase phase TiO_2 [12].

The average crystallite size of TiO_2 nanoparticles using the Scherrer equation [13] was calculated from the XRD patterns (Figure 2). The average crystallite size of the TiO_2 nanoparticles was found to be about 12 nm.

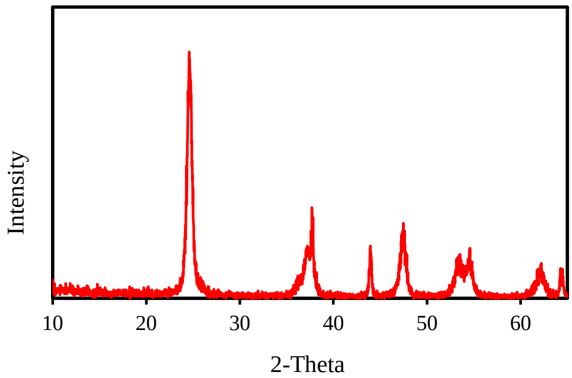

Figure 2. XRD pattern of the sol-gel TiO_2 nanoparticles.

3.2 SEM results

According to the scanning electron microscopy data (Figure 3), TiO_2 nanoparticles are well dispersed systems. As can be observed from the below mentioned micrograph, the particles are spherical. From SEM images, the average particle size was evaluated to be around 32 nm for TiO_2 nanoparticles which is consistent with the XRD results.

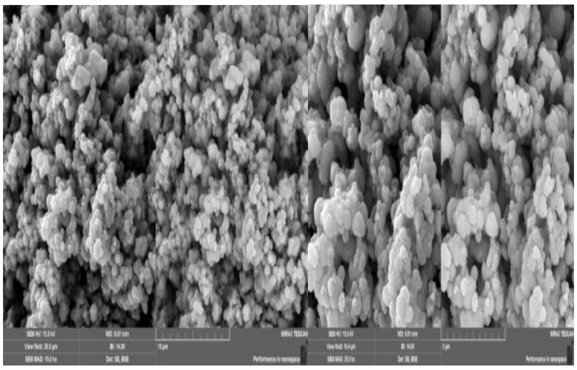

Figure 3. SEM micrographs of sol-jel TiO_2 nanoparticles.

3.3 FTIR results

The FTIR spectrum of TiO_2 nanoparticles was displayed in Figure 4. 700cm^{-1}band is available and it is conformed to the Ti-O stretching vibration and is present in TiO_2.

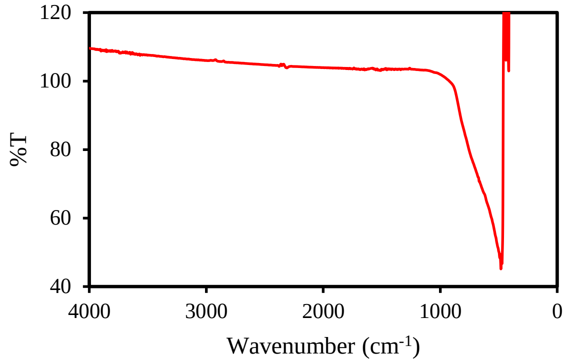

Figure 4. FTIR spectrum of sol-jel TiO_2 nanoparticles.

3.4 UV-Vis results

UV-Vis absorbance spectrum of TiO_2 nanoparticles is shown in Figure 5. Absorption band in the UV region at 320 nm are observed in Figure4. This is characteristics of nano-sized TiO_2 nanoparticles [14].

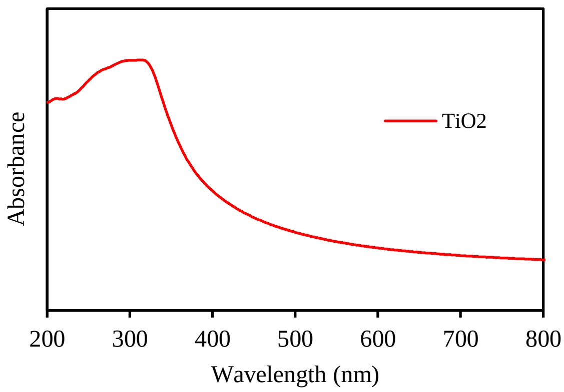

Figure 5. UV-Vis absorbance spectrum of sol-jel TiO_2 nanoparticles.

A Zeta Potential Analyzer was utilized for the purpose of examining the Zeta potential measurement of nanoparticles in the nanofluid. Zeta potential is defined as the electrical potential existing between the nanoparticle surface and the base fluid, and the zeta potential absolute value is related to the nanoparticle stability. If the measured zeta potential absolute value is greater than 25 mV, it can be said that the produced nanofluid is stable. The zeta potential value greater than 35 mV in all measurements in this study. The zeta potential is related to the stability of nanofluids; higher the absolute value of the zeta potential, the higher its stability. It was concluded that the zeta potential of TiO_2-water nanofluid prepared in this study is very stable.

3.5 pH results

pH is an important parameter in adsorption processes. For this reason, AO74 adsorption at different pH values was investigated. The studies were carried out at room temperature and at constant TiO_2 concentration (10 g / L) and pH values were measured at 2-5. The results obtained from pH experiments are given in Figure 6. The concentration of AO74 adsorbed with increasing pH increased and the maximum adsorption was determined as 52% at pH 5. The optimum pH value for AO74 adsorption was determined as 5.

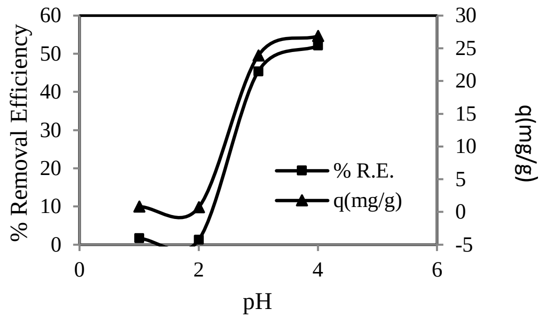

Figure 6. Effect of pH (Co: 50 mg/L, amount of TiO_2 nanoparticles: 10 g/L, T: 23°C)

3.6 Contact time results

Experiments were conducted at different contact times to determine the optimum adsorption time in the adsorption of AO74 with TiO_2 nanoparticles (10-120 minutes). After 75 minutes from the start of the adsorption experiment, the amount of adsorbed dye was determined to reach equilibrium and the optimum contact time for AO74 dye adsorption was determined as 75 minutes (Figure 7).

In another study for AO74 dye removal, activated sludge was used and the removal time was determined to be 240 minutes. In this study, removal time with TiO_2 nanoparticles was determined to be 75 minutes [15]. With TiO_2 nanoparticles, removal was achieved in a shorter time.

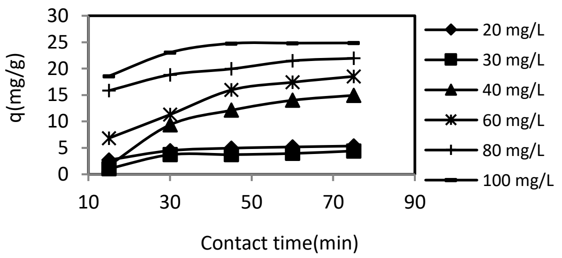

Figure 7. Effect of contact time (pH:5, amount of TiO_2 nanoparticles: 10 g/L, T: 23°C)

3.7 Initial dye concentrations results

Initial dye concentrations results from 20 to 100 mg/L are given in Figure 8. To investigate the effect of initial dye concentration on adsorption, dye concentration was investigated in the range of 20-100 mg / L. An increased concentration of dye was observed with increasing initial dye concentration. Adsorption at 20 mg / L and 100 mg / L dye concentrations was determined as 9.47 mg / g and 30 mg / g respectively.

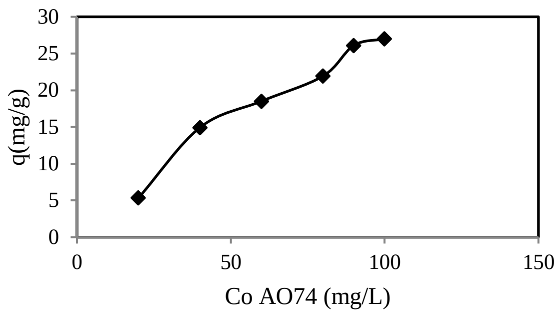

Figure 8. Effect of initial dye concentration (pH: 5, contact time: 75 min, TiO_2 nanoparticles: 10 g/L, T: 23°C)

3.8 Adsorption isotherms

Langmuir and Freundlich isotherm models were calculated by nonlinear regression method using Excel software. The Langmuir model determines the maximum adsorption capacity by assuming that every adsorption site is equivalent in monolayer and energetically. Non-linear Langmuir isotherm equation is given in Equation 3 [16]:

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{3}$$

Here q_e is the amount of equilibrium adsorption capacity and Q_o is the maximum adsorption capacity (mg/g). C_e is the equilibrium solution concentration (mg/L); b is the Langmuir constant (L/mg).

The Freundlich model is applied to adsorption on heterogeneous surfaces [17]. Non-linear Freundlich equation is given in Equation 4.;

$$q_e = k_F C_e^{1/n} \tag{4}$$

k_F is the adsorption capacity (L/g), n is the adsorption intensity.

Langmuir adsorption capacity was determined as 37.03 mg / g for AO74 dye. The results show that the TiO_2 nanoparticles are an effective adsorbent for AO74 removal (Table1).

When using activated sludge in AO74 dye removal, the maximum adsorption capacity was determined to be 142.85 mg /g [15]. Lower results were obtained with TiO_2 nanoparticles in this study.

Table 1. Adsorption isotherm parameters (T=23°C)

Langmuir			Freundlich		
Q^0 (mg/g)	b (L/mg)	R^2	K_F (L/g)	n	R^2
37,03	0.023	0.93	0.65	1.66	0.94

3.9 Adsorption kinetic

The data obtained from the adsorption experiment were analyzed using the pseudo-first order kinetic model, pseudo second-order kinetic model and intraparticle diffusion model [18].

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \quad (5)$$

Where q_t (mg/g) is the at a given moment, the adsorbent adsorbed pollutant concentration and k_1 (min^{-1}) is the rate constant of pseudo first order kinetic model.

The second order kinetic model is explained by the following equation by Equation 6 below:

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{1}{q_e} t \quad (6)$$

where k_2 (g/mg/min) is the rate constant of pseudo second order kinetic model.

The particle diffusion model is given by Equation 7 below:

$$q_t = k_d t^{0.5} + C \quad (7)$$

where k_d ($mg/g/min^{0.5}$) is diffusion rate constant and C is intercept.

Kinetic data from TiO_2 nanoparticle and AO74 adsorption data are presented in Table 2.

Table 2. Adsorption isotherm parameters (T=23°C, Co: 40 mg/L, q_e : 37.03mg/g)

Pseudo first order	k_1	q_1(mg/g)	R^2
	0.011	3.97	0.90
Pseudo second order	k_2	q_2(mg/g)	R^2
	0.0008	24.39	0.97
Intraparticle diffusion	k_i	C (mg/g)	R^2
	2.09	3.68	0.89

According to the results of adsorption kinetics given in Table 2, the adsorption process conforms to the pseudo second order kinetic model. The experimental q_e (37.03mg/g) values were also compatible with adsorption capacities (q_2) obtained from the pseudo second order model.

4. Conclusion

Here in, we report for synthesis TiO_2 nanoparticles via sol–gel technique. Nano-size TiO_2 powders were synthesized using sol-gel method. The synthesized material was characterized by XRD, SEM, FTIR and UV-Vis spectroscopy techniques. The XRD pattern of synthesized sample confirms the formation anatase phase with very good crystallinity. Also, SEM image displayed the uniform morphology in the form of nano clusters and spherical shape. FTIR spectra show the vibrational mode of TiO_2 around 600 cm^{-1}. Strong and sharp peak was observed between 200-700 nm in the UV-Vis region optical absorption study. Absorption peak in the UV region at 320 nm are observed. This peak is characteristics of nano-sized TiO_2 nanoparticles. The zeta potential value greater than 35 mV in all measurements. A route of sol gel method was performed for synthesis pure anatase TiO_2 nanoparticles with high quality production. As a result, TiO_2 nanoparticles were successfully obtained by sol gel method by indicating different characterization analysis results.

In this study, TiO_2 nanoparticles were used for AO74 dye removal from aqueous solutions. pH, contact time and initial dye concentration were determined in order to determine the optimum parameters in the adsorption process. The optimum pH and contact time were determined as pH 5 and 75 min at AO74 dye adsorption. With increasing AO74 dye concentration, it was observed that the amount of adsorbent adsorbed to AO74 per unit weight increased. The Langmuir adsorption capacities for AO74dye was 37.03 mg/g. The results show that the TiO_2 nanoparticles are an effective adsorbent for AO74 removal.

Thus, these results verify the encouragement that titanium nanoparticles propose new dimensions toward reliable and economically applicable water treatment of colored effluents. TiO_2 nanoparticles synthesized by sol-gel method were determined to be useful in removing dyes from aqueous solutions.

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