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Experimental study and modeling of photocatalytic reduction of Pb^{2+} by WO_3/TiO_2 nanoparticles

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ABSTRACT

A pure nanocomposite photocatalyst was prepared from WO_3/TiO_2 using a modified sol–gel technique. The prepared material was characterized using XRD, SEM, BET and XPS. XRD results revealed the presence of anatase, rutile and tungsten oxide with a mass ratio of rutile to anatase of 58.1:41.9. SEM and XPS results demonstrated that the prepared nanocomposite particles have spherical shape with an average size of 7.6 nm when the percent loading of tungsten onto the surface of TiO_2 nanoparticles was 2.7 wt%. BET isotherms showed a specific surface area and an average pore volume of 112 m^2/g and 0.0248 cm^3/g, respectively. Photocatalytic experiments for Pb^{2+} conversion into metallic atoms in synthetic aqueous solution revealed a reduction capacity of 52.2% when pure TiO_2 was used in 50 mg/L of initial lead concentration. This percentage has increased to 74.7% when the catalyst was doped with 2.7 wt% WO_3. This reduction capacity has increased with increasing the mass of the catalyst in the solution and with decreasing the initial lead concentration. Thermodynamic analysis showed that the interaction of Pb^{2+} onto the nanocomposite surface has an exothermic nature with an average ΔG of 14 J/mol K, ΔH of −4.5 J/mol K and ΔS of −65.3 J/mol K. A kinetic model was developed to simulate the experimental data. It was found that the reaction constant increases and reaches a maximum value of 3.95×10^{-4} cm^2/J with decreasing the kinetic parameters. However, the mass transfer coefficient showed an opposite trend, with an estimated maximum value of 8.24×10^{-4} cm/s.

1. Introduction

The industrialization has brought some benefits to human beings but at the same time it has also caused some adverse effects on the environment. One of such negative outcomes of industrialization is water pollution, which is a common problem associated with several industries. Water pollutants are a wide spectrum of materials that have been generated from different processes/activities. One of the most harmful and difficult to treat pollutants in water is the class of heavy metals. Discharging water which has been contaminated with heavy metals into water bodies leads to major changes in water aquifers and other resources. One of the highly undesirable heavy metals, even at small levels, in water is lead. Lead has been classified by the Agency for Toxic Substances and Disease Registry (ATSDR) as the second top water hazard that requires urgent remediation [1]. The source of lead in contaminated water is either the anthropogenic activities such as household plumping and industrialization harmful by-products or the nature throughout acid rock drainage. Prolong exposure to lead can cause several human health problems ranging from gastric upsets to brain damage. The maximum safe level of lead in drinking water is 15 ppb according to the Environmental Protection agency (EPA); the World Health Organization (WHO) is even more strict on lead level in drinking water which has been set to a maximum of 10 ppb [2,3].

In an attempt to treat water contaminated with heavy metals in downstream processes, a number of treatment methods have been proposed in the literature [4,5]. However, these generate harmful by-products [7], require pretreatment [8], have longer residence time [9], or/and expensive [6], To overcome such limitations, photocatalytic processes have been developed in recent years. The continuous improvement in photocatalytic activity and low energy requirement made these photocatalytic processes one of the most interesting and promising methods for treating water contaminated with heavy metals. One of the limitations of such processes is that the photocatalytic activity of titanium dioxide, which is one of the most important and widely photocatalyst, is limited to the UV region Fortunately, this limitation can be overcome by doping foreign transition metals in its crystalline structure, which leads

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to shifting its band gap closer to the visible range. Tungsten doped-TiO_2 has been tested for degradation of several organics and dyes from aqueous solution. The TiO_2 activity was enhanced with WO_3 coverage as a result of increasing its specific surface area and enhancing its optical absorption in the visible region [12,13]. Moreover, TiO_2 nanoparticles coupled with WO_3 form a stable suspension in aqueous solution with less agglomerated particles [14–16].

Despite the fact that many research efforts have focused on the degradation of a wide range of pollutants by WO_3/TiO_2, there is still a window to optimize the catalyst preparation and degradation of heavy metals using photocatalysis, and many gaps have yet to be filled before optimum degradation of heavy metals in industrial wastewater treatment can be ensured. Hence, in the present study, WO_3/TiO_2 was prepared using a sol–gel method, characterized and used for the reduction of lead ions present in an aqueous solution. The obtained experimental data were fitted using Langmuir adsorption isotherm and a relevant kinetic model at different uptakes and rate conditions. A novel and strong correlation between experimental results, kinetics models and mass transfer parameters were established.

2. Materials and methods

2.1. Materials

A precursor of 99.99% Titanium tetraisopropoxide, tungsten chloride, methyl alcohol, Lead(II) nitrate and hydrochloric acid were purchased from Sigma–Aldrich. They were used without any further treatment.

2.2. Synthesis of W–TiO_2 nanocatalyst

Tungsten-doped TiO_2 was synthesized via modified sol–gel process. Samples of 0.5 ml of different concentration of tungsten (1–6 g/L) were vigorously mixed each with 25 ml of methanol and 0.5 ml of 1.3 M HCl at isothermal condition of at 5 °C. Sulfuric acid (5 drops of 5 M) was added gradually to prevent tungsten sedimentation. Other mixtures contain 5 ml of titanium isopropoxide and 25 ml methanol were added drop wise to the first solutions to prevent the sudden formation of gel. The formed milky sol was further stirred for 1 h and then dried in an oven for 12 h at 75 °C. The dried crystalline sample was calcinated at 450 °C for 4 h under inert environment of argon.

2.3. Characterization of W–TiO_2 nanoparticles

Scanning electron microscope (SEM) analysis for the W–TiO_2 samples was conducted using JOEL JSM-6460 LU. The samples were subjected to gold coating for 20 s using sputtering machine. Then field emission-SEM (FE-SEM) analysis was done at different resolutions ranging from 500 to 40,000 cm^{-1}. The XRD patterns of the samples were measured using a Shimadzu XRD-6000 spectrometer. Aluminum sample holder was filled by dried sample and the target element used in the instrument was copper. The samples were tested at 40 kV and 30 mA and the spectra for all samples are obtained at 0.154 nm. The BET surface area and pore volumes for the produced samples were determined using Micrometrics ASAP 2020 using nitrogen adsorption at 77.35 K. A sample of 0.3210 g was degassed and dried at 150 °C under vacuum for 6 h. The specific surface area was measured and calculated by a BET equation and a cross-section area of nitrogen molecule of 0.162 nm^2.

2.4. Kinetics experiments

Kinetics experiments were conducted in a 2-L Pyrex beaker with a glass jacket to control the temperature. A mechanical stirrer with a controllable speed was mounted on the top. The setup was exposed to UV light (254 nm, average intensity of 1000 mW m^{-2}) in dark environment for 20 h to ensure the equilibrium condition. In a typical run, 1.7 L of Pb^{2+} solution with different concentrations (10–25 mg/L) was prepared by dissolving the appropriate amount of lead nitrate in deionized water; the solution temperature was adjusted by controlling the temperature of circulating water in the jacket. The pH of solution was buffered at a value of 6 throughout the experiment. The change in lead concentration was monitored by taking 1-ml sample at different time intervals using syringes with double layered filters to ensure the cut of the reaction immediately after taking the sample. Subsequently, the concentration of the lead was measured using atomic absorption spectrometer (AAS). The kinetics experiments were designed based on two-levels and four-parameters of full factorial Analysis of Variance (ANOVA) as shown in Table 1. The kinetic parameters under investigations are: effects of temperature, initial concentration of Pb^{2+} solution, mass of nanocomposite and stirring speed.

2.5. Model development

The rate of migration of Pb^{2+} molecules from the bulk solution to the catalyst surface is described by the mass balance equation:

$$\frac{dC}{dt} = -\frac{A}{V} k_f (C - C_w) \tag{1}$$

where C and C_w are the liquid phase concentrations of Pb^{2+}ions (mg/L) in the bulk solution and at catalyst surface, respectively. k_f is the liquid film convective mass transfer coefficient, V is the liquid volume in the reactor (L) and A is the total external surface area of the liquid films surrounding the nanocatalyst particles (m^2). Assuming thin spherical films, the nanocomposite total external surface area per unit volume of liquid is approximated by the following equation:

$$\frac{A}{V} = \frac{3}{R}\frac{m_s}{\rho_s} \tag{2}$$

where R is nanoparticle radius (m), m_s is concentration of catalyst in the reactor (mg/L) and ρ_s is nanocatalyst density (g/L).

Further to the transport step across the liquid film, the pollutant molecule follows an adsorption step onto the nanocomposite surface that is described by Langmuir isotherm model:

$$q|_{r=R} = \frac{q_{\max} b C_w}{1 + b C_w} \tag{3}$$

where $q|_{r=R}$ is the solid phase concentration of the contaminant (mg/g) at the nanocomposite surface in equilibrium with C_w, $q_{\max}$ is Langmuir constant (mg/g) related to the nanocomposite maximum adsorption capacity and b is Langmuir isotherm coefficient (cm^3/mg). Consequently, pollutants diffuse inside the pores of the nanocomposite and undergo a reaction driven by UV light. The variation of pollutants concentration inside the nanocomposite particles, q (mg/g), is given by the diffusion equation:

$$\frac{\partial q}{\partial t} = D_e\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) - k_{rxn} I q \tag{4}$$

Table 1
ANOVA variable for kinetic experiments.

Factors	Paremeter	Level 1	Level 2
A	Solution temperature (°C)	4	25
B	Initial concentration (mg/L)	10	25
C	Mass of the nanocomposite (g)	0.5	1.0
D	Stirring speed (rpm)	100	600