
Synthesis of Fe Doped Titania Nanoparticles for the Removal of Hexavalent Chromium from Synthetic Cr(VI) Solution

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ABSTRACT

In the present study, Titanium dioxide (TiO₂) nanoparticles doped with iron are prepared by sol-gel technique using titanium isopropoxide as precursor. The amount of dopant used is 0.5g Fe. TiO₂ particles without adding dopant are also prepared. The synthesized nanoparticles are sintered at 200, 400, 600 and 800°C in a muffle furnace. The particles are characterized by using SEM and XRD. Subsequently, studies on application of these nanoparticles for the removal of hexavalent chromium from synthetic chromium solutions are studied. Doped and non doped TiO₂ particles sintered at 200 and 400°C are considered for the study, to know the effect of dopant. The percentage dosage varied from 0.1 to 1. The amount of chromium removal was analyzed by using Atomic absorption spectroscopy (AAS). Experimental results have indicated the suitability of Fe doped TiO₂ nanoparticles for the removal of chromium. Further, the adsorption data was fitted to Freundlich and Langmuir isotherms. It is found that Freundlich isotherm best fits the experimental data. Binding constants and sorbent capacity is evaluated by using Langmuir and Freundlich isotherms. Kinetic and equilibrium studies are also carried out and have concluded that the adsorption of chromium by Fe doped titaniaparticles obeyed second order kinetics.

KEYWORDS

Titanium dioxide, chromium, nanoparticles, dopants, degradation, isotherms

INTRODUCTION

Titanium dioxide (TiO₂), a nontoxic material, has been taken as one of the popular photo catalysts due to its low cost, high photocatalytic activity and excellent chemical stability. The photocatalytic activity of TiO₂ particles is based on the structure and characteristics of the particles, such as crystallinity and porosity. It has been reported that anatase and nano-sized TiO₂ particles with porous structures showed better photocatalytic activity [1]. In recent literature reports, modification of TiO₂ has been extensively studied to overcome the limitation of pure TiO₂ which has wide energy band gap and low quantum yields. Many groups have been involved in depositing transition metal ions, such as Fe, Au, Ag, V, Cr and Ni, onto the surface of TiO₂ to improve the separation of electrons and holes [2–6]. Being high photocatalytic activity and safety to environment, TiO₂ has been extensively investigated for degrading organic pollutants and removing heavy metal ions [7–9]. It has been found that the Fe(III) ions doped in Titania catalyst can serve as the photo-electron traps and assist the photo-hole transfer to the catalyst surface and enhance its oxidative ability [10]. Titania nanoparticles can be prepared by different techniques, one of which is being the sol-gel technique.

The Sol-Gel technique is most attractive technique due to its many advantages such as easy preparation method, less complicating instruments and less time consuming. Here the Sol-Gel technique was successfully used for synthesizing pure Titania nano-particles followed by characterization process. Titania nano-particles are synthesized using sol-gel technique followed by annealing. These synthesized nano-particles are characterized by SEM and XRD. The SEM range reveals the structure of nano-particles

Reports of TiO₂ with different shape such as nanoparticles thin films, nanorods, nanowires and nanotubes have spurred a great interest in studies on TiO₂ nanostructure synthesis and their application. Shape control has been significant concern in nanotechnology. Properties also vary as the shapes of the shrinking nano materials change. TiO₂ has three polymorphic forms of crystal structure namely brookite, anatase and rutile.

Heavy metal pollutants present in water are very dangerous for mankind as they accumulate in living tissues and get concentrated [11]. Among all the heavy metals, Cr(VI) is highly toxic as it is mobile and solubility is high. It is highly carcinogenic unlike Cr(III) which is less dangerous and can be precipitated easily [12-13].

To check the ability of the synthesized nanoparticles, these are employed for the degradation of chromium from the synthetic chromium solutions. Hence, the objectives of the present work include the synthesis of TiO₂ nanoparticles with and without Fe dopant. Characterize the synthesized nanoparticles by using SEM and XRD. Carry out the adsorption studies by using these particles for the degradation of chromium.

MATERIALS AND METHODS

Synthesis of pure and Fe doped TiO₂ nanoparticles

Titania nanoparticles were synthesized using sol-gel method. Here Titanium isopropoxide (C₁₂H₂₈O₄Ti, Avra Labs) was used as precursor and Ferric Chloride (FeCl₃, LobaChemie) was used as dopant for the synthesis of titania nanoparticles. Iso propyl alcohol (C₃H₈O, IPA, SRL India) was used as the solvent and cetyltrimethylammonium bromide (C₁₉H₄₂BrN, CTAB, SRL India) was used as growth inhibitor. Measured quantities of titanium isopropoxide and CTAB were added to IPA in two separate beakers and are subjected to constant stirring until the solution become clear. Then the two solutions were mixed homogeneously using a magnetic stirrer with simultaneous drop wise addition of aqueous ammonia for precipitation. The formed precipitate was filtered using Whatman 40 filter paper. The precipitate was washed with water continuously. The separated precipitate was subjected to drying for 6 h at 80 °C. The powder was collected and subjected to sintering at two different temperatures of 200 °C and 600°C) for 5 h each. The pure TiO₂ nanoparticles were designated as Ti 200 and Ti 600 respectively.

Titania nanoparticles with different weight % of iron doping were synthesized by adding 0.5, 1 and 1.5 wt% of ferric chloride in IPA. The synthesis procedure was similar to that of pure tinania nanoparticles. The iron doped titania nanoparticles were designated as Ti-Fe 200 and Ti-Fe 600 respectively. The synthesized TiO₂ particles were characterized using x-ray diffraction.

Preparation of Cr(VI) stock solution

The standard stock solution of chromium (1000 mg/L) was prepared by dissolving appropriate quantity of 99.9% analytical grade K₂Cr₂O₇ in 1000 mL of distilled water. All the requireSolutions are prepared with analytical reagents and double-distilled water. Synthetic samples of different concentrations of chromium are prepared by successive dilutions.

Adsorption studies for the removal of hexavalent Chromium

Batch adsorption experiments are conducted for the removal of chromium using pure and doped TiO₂ nano particles. To 50 mL of known concentration of chromium solution 0.5 g of pure or doped TiO₂ nano particles are added and subjected to stirring. After stirring the solution is transferred into centrifuge tubes and centrifuged at 1000 rpm for 20 min. The supernatant liquid is separated and the concentration of hexavalent chromium is analyzed using atomic absorption spectrophotometry (AAS). The parameters that are varied are concentration of chromium solution (10 to 50 ppm) and different time intervals (15 min to 150 min) respectively with different TiO₂ nanoparticles (Ti 200, Ti 600, Ti-Fe 200 and Ti-Fe 600).

The concentration of chromium in the filtrate is measured using atomic absorption spectroscopy. The absorbance values of different known concentrations of hexavalent chromium solution are evaluated using AAS. A calibration curve is plotted between the concentration and absorbance. The absorbance values of unknown solution are evaluated using AAS and the concentration are evaluated using the calibration curve.

Sorption Isotherm Modeling

The successful representation of the dynamic sorption separation of the solute from the solution onto the adsorbent depends upon a good description of the equilibrium separation between two phases. To describe the sorption equilibrium for the uptake of hexavalent chromium species on the solid surface of the adsorbent different isotherms are reported in literature. Experimental data has been tested by using Langmuir and Freundlich isotherms. The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sorption without the interaction between sorbed molecules [14]. It has been mathematically described as follows:

Langmuir Isotherm

$$q_e = \frac{K c_e}{1 + b c_e}$$

Linearization: $\frac{c_e}{q_e} = \frac{1}{b K_L} + \frac{c_e}{K_L}$

Freundlich Isotherm:

Reported literature indicates that Freundlich isotherm can be suggested for heterogeneous surfaces [15] and for extremely low concentrations. The Freundlich isotherm is an empirical model relating the adsorption intensity of the sorbent towards adsorbent. The isotherm was adopted to describe the reversible adsorption and not restricted to monolayer formation. Mathematically, Freundlich isotherm can be represented as

$$q_e = K_f c_e^{\frac{1}{n}}$$

Linearizing the same resulted in the following equation

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e$$

Kinetics of the adsorption is studied by using first order and second order kinetic models. The models are mathematically represented as follows:

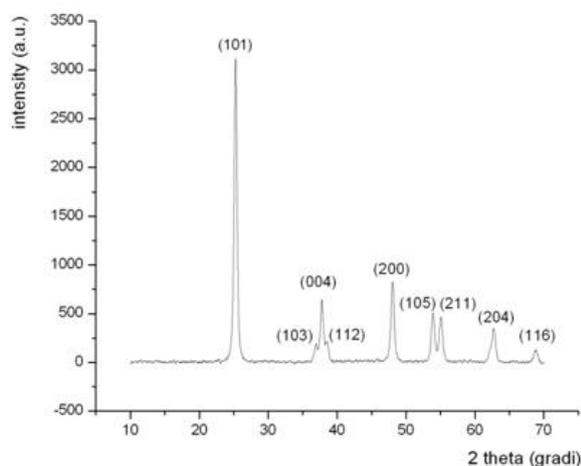
Pseudo first order kinetics

$$\ln (q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t$$

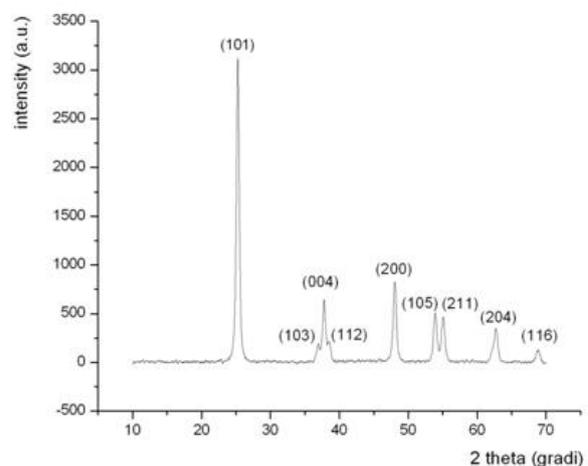
Second order kinetics

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

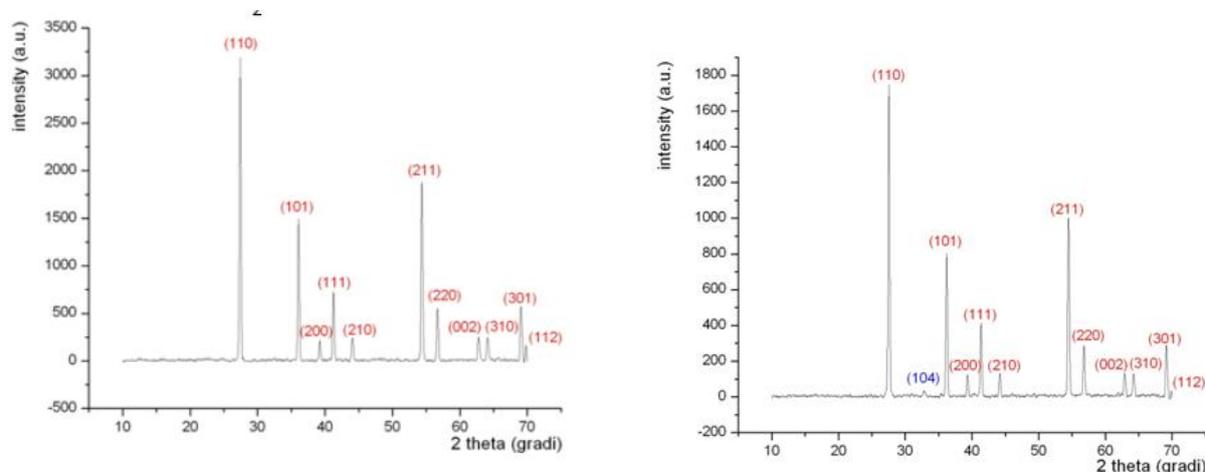
RESULTS AND DISCUSSION



Pure titania calcined at 200 °C



Fe doped titania calcined at 200 °C



Pure titania calcined at 600 °C

Fe doped titania calcined at 600 °C

Figure 1: XRD patterns of pure and Fe doped TiO_2 calcined at 200 °C and 600 °C respectively.

Synthesized titanium dioxide nanoparticles, both by the addition of doped and un doped particles are characterized using XRD. There are three different types of phases for titanium dioxide namely brookite, anatase and rutile. These phases vary during the synthesis for different temperature ranges. Figure 1 shows the XRD pattern of pure and Fe doped titania nanoparticles calcined at 200 °C and 600 °C respectively. The peaks are indexed and analyzed. The analysis showed that pure and doped titania calcined at 200 °C showed complete anatase phase. The phase shifted to rutile phase when the calcination temperature increased from 200 °C to 600 °C.

Solutions of various concentrations of Cr(VI) working solutions are considered and concentration values are calculated using AAS. A calibration curve was drawn between chromium concentration and absorbance. This was taken as reference for further calculation.

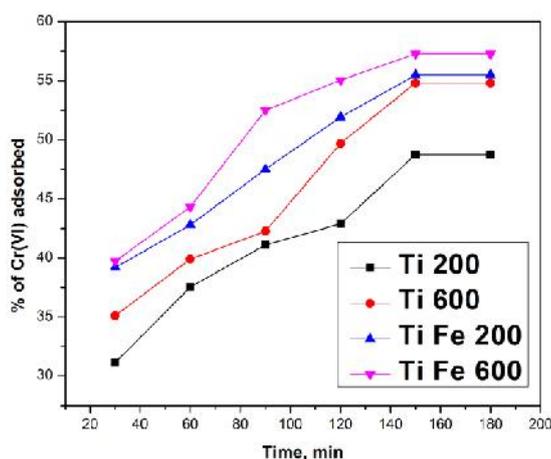


Figure 2. Percentage removal of chromium with respect to time.

The photocatalytic adsorption using pure and doped titania nanoparticles were performed for four different concentrations of Cr(VI). The concentrations are 10 ppm, 20 ppm, 30 ppm and 40 ppm respectively. The time for the studies of adsorption is varied from 30 min to 180 min with an increment of 30 minutes respectively. The graph shows that with increase in time the adsorption of chromium on to the surface of the catalyst also increased. While the percentage removal increased from 35% to 55% for pure titania the value increased to around 60% for Fe doped titania nanoparticles.

Other parameters such as effect of initial concentration of the Cr(VI) solution and catalyst were performed. The effect of initial concentration showed that with increase in initial concentration the percentage adsorption of chromium also increase. The catalyst loading was varied from 0.1 to 1 g. However, the adsorption was not so significant after 0.5 g catalyst dosage. Hence 0.5 g is taken as the catalyst loading. The percentage removal of hexavalent chromium from solution with respect to time with various Titania particles is shown in Figure 2.

Further, the synthesized particles are employed for the degradation of hexavalent chromium from synthetic chromium solutions. The range of initial concentrations of the chromium considered for the studies varies between 10ppm to 40ppm. Samples with different initial concentrations are treated by adding 0.5g of adsorbent and evaluated the performance at different times. Adsorption studies are carried out till the equilibrium. At a given time, the amount adsorbed is relatively more for Fe doped samples than without doped samples. Further, the adsorption for samples sintered at 600 °C is observed to be more than 200 °C at a given time (Figure 3).

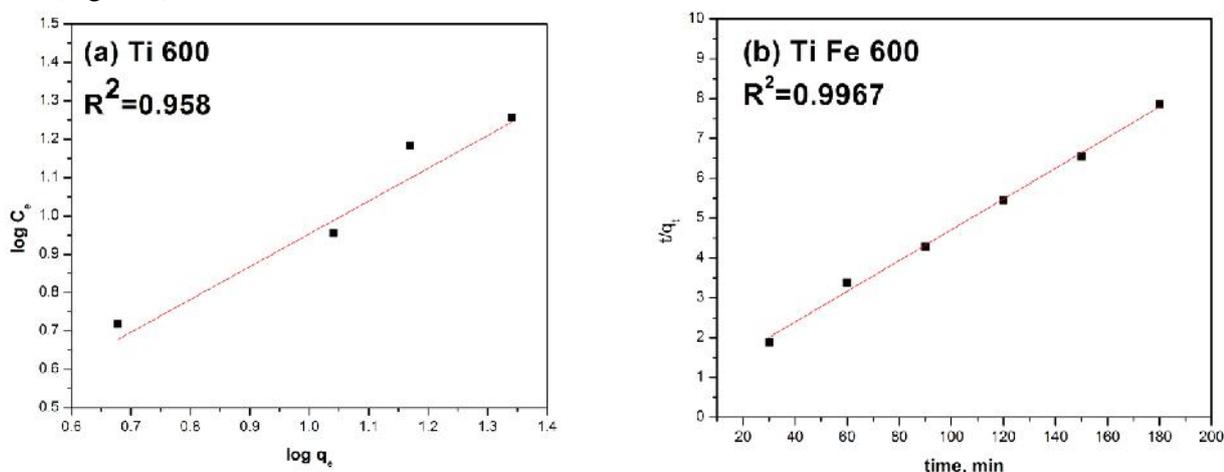


Figure 3: Figures showing the kinetics of pure and Fe doped titania nanoparticles calcined at 600 °C.

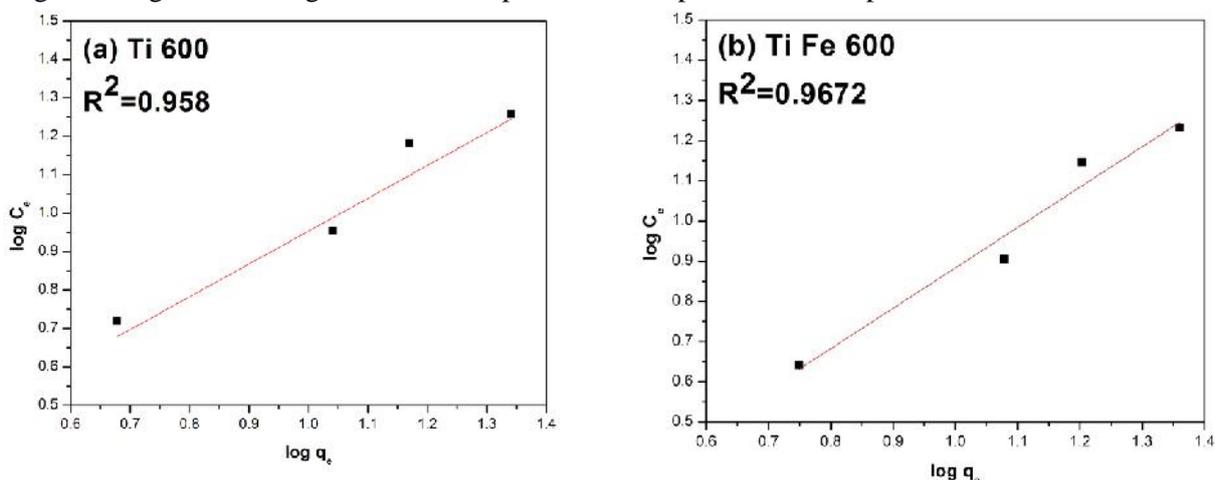


Figure 4 Freundlich Isotherms for pure and Fe doped titania at 600 °C

Kinetic studies by applying first order and the second order kinetic equations indicates that the experimental data follows second order kinetics as compared to first order. The second order data with regression is given in Figure 3.

Equilibrium studies indicate that the Freundlich isotherm describes the data well as compared to the Langmuir isotherm with higher correlation coefficient. The Freundlich isotherms are given in Figure 4 and the Langmuir isotherms are given in Figure 5 respectively.

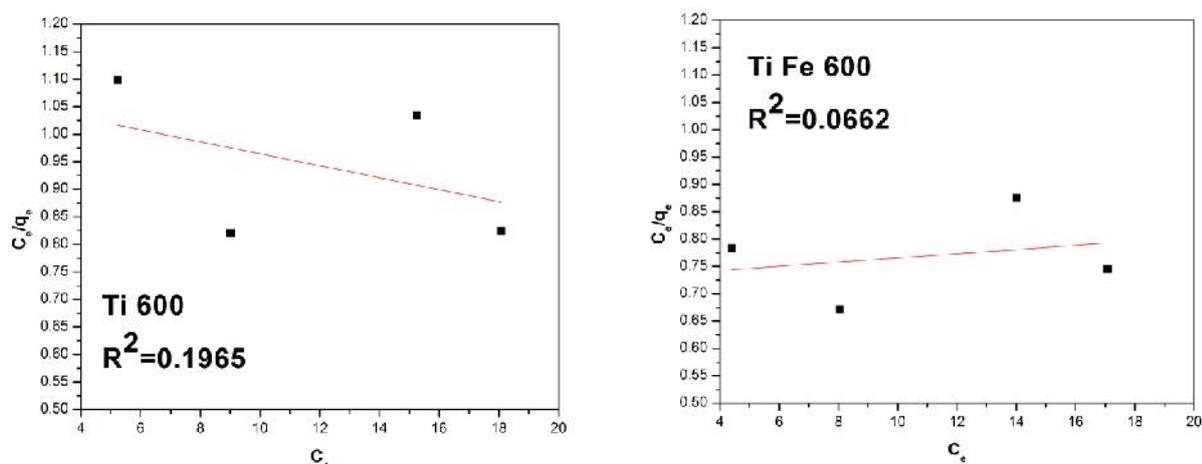


Figure 5. Langmuir isotherms of pure and doped titania nanoparticles calcined at 600 °C.

CONCLUSIONS

Titanium dioxide nanoparticles synthesized by sol-gel method are characterized by SEM and XRD. Sharp peaks are observed in XRD indicating crystalline nature. Fe doped titanium nanoparticles are able to degrade hexavalent chromium to around 60%. The experimental data was fitted to first order and second order kinetic equations. Results indicated that the data follows the second order kinetics. Equilibrium studies are carried out by fitting the data to the Langmuir and Freundlich isotherms. Freundlich isotherms best fits the data.

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