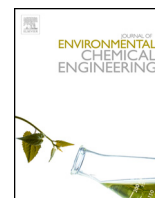




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# Simultaneous photocatalysis and adsorption based removal of inorganic and organic impurities from water by titania/activated carbon/carbonized epoxy nanocomposite

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## ABSTRACT

In the present study, we demonstrate the simultaneous efficient removal of heavy metals such as Pb(II), Cd(II) and Cr(III) ions as well as methylene blue (MB) from water by titania/activated carbon/carbonized epoxy (TiO<sub>2</sub>/AC/CE) nanocomposite with high activity and easy separation. A simple one-step solvothermal process is used for the synthesis of TiO<sub>2</sub> nanosphere for TiO<sub>2</sub>/AC/CE nanocomposite. The as-synthesized TiO<sub>2</sub>/AC/CE nanocomposite is characterized using XRD, SEM, TGA, BET, Raman, FTIR, and UV–vis spectroscopy. The adsorption/degradation characteristic of TiO<sub>2</sub>/AC/CE nanocomposite is evaluated with varying contact time and at a fixed solution pH. The addition of AC on TiO<sub>2</sub> significantly improves the activity of TiO<sub>2</sub>. The TiO<sub>2</sub>/AC/CE nanocomposite is found to be much active than bare TiO<sub>2</sub> nanoparticles and exhibits easy separation. Here, AC significantly enhances the surface area of the TiO<sub>2</sub>/AC/CE nanocomposite and suppresses the phase transition of TiO<sub>2</sub> from photoactive anatase to less active rutile. The performance of the TiO<sub>2</sub>/AC/CE nanocomposite for the decomposition of MB is found to be governed by the crystallinity of anatase phase of TiO<sub>2</sub>. For Pb(II) removal, the as-synthesized TiO<sub>2</sub>/AC/CE nanocomposite shows a high activity, where 97% Pb(II) ions are removed from aqueous solution.

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## Introduction

The frequent use of hazardous contaminants such as heavy metals (As, Cd, Pb, Cr, etc) and aromatic compounds in many textiles, plastic, tannery and paints industries have become a serious threat to the aquatic environment [1]. Owing to the high toxicity and slow biodegradation, these pollutants show a very adverse effect to human health [2–4]. Thus, many efforts have been made in past for the removal of these water pollutants [4,5]. The removal methods of water pollutants depend on their chemical nature and/or structure, according to which water pollutants can be classified into two categories: inorganic and organic. The inorganic impurities can be removed by using the techniques, such as membrane systems, filtration, ion-exchange, adsorption, chemical precipitation, and electro-deposition techniques, in which adsorption is the widely considered method due to its low cost and ease of process [6–11]. Silica gels, oxide and hydroxides of metals, zeolites, polymers and carbonaceous materials such as AC are being used for the adsorption of heavy

metals from water. Among them, AC is the most popular choice due to its high surface area, porous structure and high surface reactivity [12,13]. On the other hand, for elimination of organic pollutants like dyes or phenolic components chemical oxidation, solvent extraction or catalytic degradation methods are being used [14–16]. From the effective and economical perspective, the catalytic degradation is widely accepted process, where organic pollutant is degraded by the photocatalytic chain-reactions [17]. Owing to the excellent photocatalytic properties, TiO<sub>2</sub> is a widely recognized metal oxide, used extensively for the degradation of organic dyes [18]. TiO<sub>2</sub> can exist in three different phases namely rutile, anatase and brookite, where anatase phase shows a very high photocatalytic activity towards the organic pollutants. However, when TiO<sub>2</sub> is used in a suspension, it shows low effective surface area, which prevents its use as an efficient photo catalyzer. Moreover, due to small size the separation of TiO<sub>2</sub> nanoparticles from water is a tedious process [19]. Thus, several attempts have been developed to improve the separation performance of TiO<sub>2</sub>, such as immobilization of TiO<sub>2</sub> nanoparticles in the removable support as porous nickel, glass and AC [20–22]. However, due to the immobilization a decrease in the degradation efficiency is observed as it can reduce the dispersion of TiO<sub>2</sub> and its contact with illumination source. Thus, for the effective separation of TiO<sub>2</sub> nanoparticles from the

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filtered water the dispersion of suspended TiO<sub>2</sub> should be such that it can absorb efficient light as well as organic impurities from water. Recently, the photocatalytic efficiency of TiO<sub>2</sub> is examined by developing the composites of TiO<sub>2</sub> with AC by different methods such as dip coating, impregnation, hydrothermal, sol–gel, metal organic chemical vapor deposition (MOCVD), etc. [23–26]. In presence of visible light irradiation, Kuo et al. have prepared TiO<sub>2</sub>/AC composite by MOCVD method for the oxidation of NO<sub>x</sub> pollutant [27]. Liu et al. have observed the potential of TiO<sub>2</sub>/AC, synthesized by acid-catalyzed hydrolysis, for the degradation of phenol from aqueous media [28]. In these reports, the photocatalyst was separated from water by using tiresome sedimentation processes. Furthermore, for obtaining crystalline TiO<sub>2</sub> generally a high-temperature annealing of >400 °C is needed. However, the use of low temperature is beneficial for the high surface area and to protect the hydroxyl groups, which are present in the surface of photocatalyst.

In the present study, we developed a one-step TiO<sub>2</sub>/AC/CE nanocomposite, as a porous solid, using a simple solvothermal process for the simultaneous removal of inorganic and organic impurities from water. Here, the solvothermal process is adopted for TiO<sub>2</sub>/AC/CE nanocomposite synthesis, as this process is widely acknowledged as a simple and inexpensive way to produce agglomeration free spherical TiO<sub>2</sub> nanoparticles [29]. Owing to high surface area, AC is adopted as it shows high adsorption with favorable surface chemical affinities towards the removal of impurities. Conveniently, as the adsorbents for water purification are used in powdered form, their separation requires special techniques requiring extra cost, time, and complexity. To avoid this problem, here the adsorbent TiO<sub>2</sub>/AC nanocomposite is converted into a porous solid by mixing with epoxy, forming a desired shape (depends on the mold) followed by carbonization at selected temperature. Here, epoxy provides the matrix for TiO<sub>2</sub>/AC nanocomposite. In addition, during carbonization process the epoxy converts to carbon, which can increase the amount of carbon in TiO<sub>2</sub>/AC/CE nanocomposite. Subsequently, the as synthesized nanocomposite is successfully used for the removal of inorganic and organic impurities from water. Here, lead acetate and MB dye, taken as inorganic (Pb ions) and organic impurities sources respectively, are selected as the model pollutants due to their heavy presence in the released water of industries. The structural and photocatalytic properties of TiO<sub>2</sub>/AC/CE nanocomposite are also compared with that of pristine TiO<sub>2</sub> nanosphere. As here AC is employed for the heavy metal adsorption, thus to evaluate the adsorption capabilities of AC, Pb(II) adsorption is also performed with AC/CE composite. Furthermore, to investigate the potential of AC/CE composite for other heavy metals exclusion, the adsorption experiments are also carried out for Cr(III) and Cd(II) ions impurities.

## Experimental

### Preparation of TiO<sub>2</sub>/AC nanocomposite

Here, TiO<sub>2</sub> was prepared by simple one-step solvothermal process, where titanium tetraisobutoxide (TTIB) was used as titanium precursor [30]. The information regarding materials and reagents, used in the study is provided in the Supplementary information (S1). Briefly, TTIB (14 mM) stabilized in 20 ml ethanol was added to the stirred solution of ethanol (120 ml) and acetonitrile (99 ml) with amine (2.4 mM) and water (1 mM). For TiO<sub>2</sub>/AC nanocomposite preparation, a measured amount of AC (37.8 g) was added to the stirred solution of TTIB followed by stirring for 1 h. The obtained composite was dried in the oven at 50 °C for 8 h. To fabricate nanocomposite in the desired shape, the nanocomposite was prepared by mixing the solvothermal

synthesized TiO<sub>2</sub>/AC in a mixture of epoxy (PG-100) and hardener (PH-861) having a ratio of 10:1 (wt/wt), with a TiO<sub>2</sub>/AC to epoxy weight ratio of 40:60. The obtained viscous solution was filled in a die. The die was then aged at room temperature for 48 h and dried at 60 °C for 4 h. For the carbonization of the dried TiO<sub>2</sub>/AC/epoxy nanocomposite, the product, which was obtained from mold, was kept in a quartz tube reactor in the presence of N<sub>2</sub> atmosphere and heated to 400 °C at 5 °C/min for 1 h. Subsequently, the temperature was increased to 800 °C and the nanocomposite was hold in it for 15 min. After the completion of the carbonization process, the nanocomposite was cooled to room temperature in N<sub>2</sub> atmosphere. The final nanocomposite was, thus designated as TiO<sub>2</sub>/AC/CE nanocomposite. To compare the degradation characteristics of TiO<sub>2</sub>/AC/CE nanocomposite with pristine TiO<sub>2</sub>, the TiO<sub>2</sub> nanospheres were also prepared by using the similar procedure as discussed earlier. For this, TTIB (3 mM) was added to the stirred solution of 25 ml ethanol, 20 ml acetonitrile, 1 mM amine and 0.1 ml water. The solution was stirred to 30 min followed by drying at 60 °C. The synthesis method of AC/CE preparation is discussed in the Supplementary information (S2), where the constituents (AC, epoxy, hardener) are added in the same ratio, as used for the preparation of TiO<sub>2</sub>/AC/CE.

### Characterization

To confirm the crystalline size of TiO<sub>2</sub>/AC/CE nanocomposite and pristine TiO<sub>2</sub>, the X-ray diffraction (XRD) measurements were conducted (X'pert Pro, PANalytical) with a Cu K $\alpha$  radiation of wavelength 0.15418 nm in the range of 2 $\theta$ –80° with a scanning rate of 1°/min. The size and surface morphology were examined by scanning electronic microscope (SEM, Zeiss EVO MA-15) as well as transmission electron microscopy (TEM, TECNAI T12, operating voltage 120 V). The elemental composition of TiO<sub>2</sub>/AC/CE nanocomposite was analyzed by energy dispersive X-ray spectroscopy (EDS–Quanta 3D). To study the thermal stability and degradation behavior of nanocomposite and bare TiO<sub>2</sub>, thermogravimetric (TGA) analysis (PerkinElmer Diamond-TG/DTA) has been performed under N<sub>2</sub> flow with a heating rate of 10 °C/min. The total surface area was obtained using Brunauer–Emmett–Teller (BET) method with Autosorb software (Quanta chrome Instruments). Raman spectroscopy was recorded by LabRam Micro-Raman spectrometer (Jobin-Yuon HR 800 UV) using a He–Ne (632.8 nm) laser excitation source. Fourier transform infrared spectroscopy (Bruker-FTIR) was analyzed using KBr pallet in the range of 4000–400 cm<sup>-1</sup>. The absorbance properties of the synthesized samples were acquired by the UV–vis diffuse reflectance spectra (UV–vis DRS) with a UV–vis–NIR spectrophotometer (Varian Cary 500) having an integrating diffuse reflectance fixture in the range of 200–800 nm.

### Photocatalytic degradation study

To evaluate the performance of as-synthesized TiO<sub>2</sub>/AC/CE nanocomposite and pristine TiO<sub>2</sub>, the adsorption and degradation of Pb(II) ions and MB were simultaneously carried out under visible light irradiation (2W, DPLED). The wavelength of the used light source was measured by high-resolution spectrometer (HR 4000; Ocean optics) with a wavelength range of 200–1100 nm, where it was observed that that light source is having the wavelength between 300 and 750 nm. For simultaneous photocatalytic reactions, prior to illumination, known amounts of Pb(CH<sub>3</sub>COOH)<sub>2</sub>, where the concentration of the Pb(II) ions were kept (200 mg/l), and MB (0.62 mM) were mixed into the 200 ml of distilled water. The pH of the solutions was adjusted to 6.5, by using 1 M HCl/NaOH solution. To attain the adsorption/desorption equilibrium, prior to illumination, the as synthesized TiO<sub>2</sub>/AC/CE nanocomposite or pristine TiO<sub>2</sub> was immersed in the solution and then solution was

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