Journal of [Environmental](http://dx.doi.org/10.1016/j.jece.2015.07.009) Chemical Engineering xxx (2015) xxx–xxx

Journal of Environmental Chemical Engineering

journal homepage: <www.elsevier.com/locate/jece>

Simultaneous photocatalysis and adsorption based removal of ² inorganic and organic impurities from water by titania/activated ³ carbon/carbonized epoxy nanocomposite

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A R T I C L E I N F O

Article history: Received 28 April 2015 Accepted 9 July 2015

Keywords: Nanocomposite TiO₂ Photocatalysis Water purification Adsorption

A B S T R A C T

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 $(TIO₂/AC/CE)$ nanocomposite with high activity and easy separation. A simple one-step solvothermal process is used for the synthesis of $TiO₂$ nanosphere for $TiO₂/AC/CE$ nanocomposite. The as-synthesized TiO₂/AC/CE nanocomposite is characterized using XRD, SEM, TGA, BET, Raman, FTIR, and UV–vis spectroscopy. The adsorption/degradation characteristic of $TiO₂/AC/CE$ nanocomposite is evaluated with varying contact time and at a fixed solution pH. The addition of AC on TiO₂ significantly improves the activity of TiO₂. The TiO₂/AC/CE nanocomposite is found to be much active than bare TiO₂ nanoparticles and exhibits easy separation. Here, AC significantly enhances the surface area of the TiO $_2$ / AC/CE nanocomposite and suppresses the phase transition of $TiO₂$ from photoactive anatase to less active rutile. The performance of the TiO2/AC/CE nanocomposite for the decomposition of MB is found to be governed by the crystallinity of anatase phase of TiO₂. For Pb(II) removal, the as-synthesized TiO₂/AC/CE nanocomposite shows a high activity, where 97% Pb(II) ions are removed from aqueous solution.

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⁷ Introduction

 8 The frequent use of hazardous contaminates such as heavy
 9 metals (As Cd, Pb, Cr, etc) and aromatic compounds in many $\frac{9}{10}$ metals (As, Cd, Pb, Cr, etc) and aromatic compounds in many
 $\frac{10}{10}$ to the plastic tannery and paints industries have become a 10 textiles, plastic, tannery and paints industries have become a
 11 corious throat to the aquatic opyronment [1]. Quing to the high ¹¹ serious threat to the aquatic environment $[1]$. Owing to the high $\frac{12}{12}$ to the state of clous higher these pollutants show a very 12 toxicity and slow biodegradation, these pollutants show a very
 13 educate offect to burner boath [2, 4]. Thus magnes forts have been 13 adverse effect to human health $[2-4]$. Thus, many efforts have been
14 made in past for the removal of these water pollutants $[4,5]$. The 14 made in past for the removal of these water pollutants [\[4,5\].](#page--1-0) The removal methods of unter pollutants denoted an their chamical 15 removal methods of water pollutants depend on their chemical 16 16 nature and/or structure, according to which water pollutants can
 17 he classified into two estaggings inerganic and erganic. The ¹⁷ be classified into two categories: inorganic and organic. The
¹⁸ inorganic impurities can be removed by using the techniques, such 18 inorganic impurities can be removed by using the techniques, such 19 are membrane, such as a such an approximate the such as $\frac{19}{2}$ and $\frac{19}{2}$ are membrane. 19 as membrane systems, filtration, ion-exchange, adsorption,
20 abomical precipitation and electro-deposition techniques in 20 chemical precipitation, and electro-deposition techniques, in 21 which adoption is the widely considered method due to its 21 which adsorption is the widely considered method due to its 22 low cost and aggs of process [6, 11]. Silice sple avide and 22 low cost and ease of process $[6-11]$ $[6-11]$. Silica gels, oxide and 23 by by by problem and subpresses and subpresses 23 hydroxides of metals, zeolites, polymers and carbonaceous $\frac{24}{100}$ materials such as AG are being used for the adserption of beauty materials such as AC are being used for the adsorption of heavy

<http://dx.doi.org/10.1016/j.jece.2015.07.009> 2213-3437/ \circ 2015 Published by Elsevier Ltd. metals from water. Among them, AC is the most popular choice due
to its high surface area, porous structure and high surface reactivity 26 to its high surface area, porous structure and high surface reactivity $\frac{26}{112,131}$ On the other hand, for elimination of organic pollutants $\frac{27}{11}$ [\[12,13\]](#page--1-0). On the other hand, for elimination of organic pollutants 27
like dues or phanolic companents shomical ovidation solvent 28 like dyes or phenolic components chemical oxidation, solvent 28
oxitaction or catalytic dogradation mathods are being used 14 29 extraction or catalytic degradation methods are being used $\begin{bmatrix} 14 & 29 \\ 16 & 18 \end{bmatrix}$ [16\].](#page--1-0) From the effective and economical perspective, the catalytic $\frac{30}{2}$ degradation is widely accepted process, where organic pollutant is 31
degraded by the photocatalytic chain reactions [17]. Quing to the 32 degraded by the photocatalytic chain-reactions [\[17\]](#page--1-0). Owing to the $\frac{32}{2}$ excellent photocatalytic properties, $TiO₂$ is a widely recognized 33
metal oxide used extensively for the degradation of organic dyes 34 metal oxide, used extensively for the degradation of organic dyes 34
[12] TiO, can exist in three different phases namely rutile anatase 35 [\[18\]](#page--1-0). TiO₂ can exist in three different phases namely rutile, anatase 35
and brookite, where anatase phase shows a very high photo 36 and brookite, where anatase phase shows a very high photo- 36
extallitie activity towards the organic pollutants However when 37 catalytic activity towards the organic pollutants. However, when 37
TiO, is used in a suspension it shows low effective surface area 38 $\overline{10}_2$ is used in a suspension, it shows low effective surface area, $\frac{38}{12}$ which prevents its use as an efficient photo catalyzer. Moreover, 39
due to small size the conception of \overline{G} approparticles from unterior and the small size of the conception of \overline{G} due to small size the separation of TiO₂ nanoparticles from water is $\frac{40}{2}$
a todious process [10] Thus several attempts have been daughand a tedious process [\[19\]](#page--1-0). Thus, several attempts have been developed $\frac{41}{4}$
to improve the concretion performance of TiO, such as immobili to improve the separation performance of TiO₂, such as immobili-
zation of TiO₂, paperatricles in the removable support as persus $\frac{43}{2}$ zation of TiO₂ nanoparticles in the removable support as porous 43
pickel glass and $0.6120, 221$ However due to the immedilization and 44 nickel, glass and AC $[20-22]$. However, due to the immobilization a 44
decrease in the degradation officiency is observed as it can reduce decrease in the degradation efficiency is observed as it can reduce 45
the dispersion of T_1^1 and its contact with illumination source 46 the dispersion of TiO₂ and its contact with illumination source. 46
Thus for the effective contaction of TiO₂ paperwrickes from the 47 Thus, for the effective separation of $TiO₂$ nanoparticles from the

Please cite this article in press as: P. Benjwal, K.K. Kar, Simultaneous photocatalysis and adsorption based removal of inorganic and organic impurities from water by titania/activated carbon/carbonized epoxy nanocomposite, J. Environ. Chem. Eng. (2015), [http://dx.doi.org/10.1016/j.](http://dx.doi.org/10.1016/j.jece.2015.07.009) [jece.2015.07.009](http://dx.doi.org/10.1016/j.jece.2015.07.009)

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⁴⁸ filtered water the dispersion of suspended $TiO₂$ should be such that
⁴⁹ it are absorb officient light as well as organic impurities from 49 it can absorb efficient light as well as organic impurities from 50 contained 50 ⁵⁰ water. Recently, the photocatalytic efficiency of $TiO₂$ is examined
 $\frac{51}{2}$ by developing the correspondence fill with AG by different with a developing ⁵¹ by developing the composites of TiO₂ with AC by different methods
⁵² cuch as dip coating improgration, hydrothermal, col. gol. metal 52 such as dip coating, impregnation, hydrothermal, sol–gel, metal
 $\frac{53}{2}$ strange chamical upper deposition (MOCVD) etc. [32, 36]. In 53 organic chemical vapor deposition (MOCVD), etc. $[23-26]$ $[23-26]$. In precedence of visible light irradiation Kuo et al. have prepared TiO ⁵⁴ presence of visible light irradiation, Kuo et al. have prepared TiO₂/
⁵⁵ AC composite by MOCVD method for the evidation of NO 55 AC composite by MOCVD method for the oxidation of NO_x
56 anolytiant [27] Liu ot all have observed the potential of TiO *LAC* 56 pollutant [\[27\]](#page--1-0). Liu et al. have observed the potential of TiO₂/AC,
 57 synthesized by acid-catalyzed bydrolysis, for the degradation of 57 synthesized by acid-catalyzed hydrolysis, for the degradation of 58 shopped from aqueous media 581 In these reports, the photo- 58 phenol from aqueous media [\[28\]](#page--1-0). In these reports, the photo-
 59 59 catalyst was separated from water by using tiresome sedimenta-
 60 tion processes. Eurthermore, for obtaining crystalline, TiO ⁶⁰ tion processes. Furthermore, for obtaining crystalline $TiO₂$
⁶¹ generally a bigh temperature appealing of $>400\degree$ C is peeded. 61 generally a high-temperature annealing of $>400^{\circ}$ C is needed.
62 However the use of low temperature is beneficial for the high 62 However, the use of low temperature is beneficial for the high 63 surface area and to protect the hydroxyl groups which are present 63 surface area and to protect the hydroxyl groups, which are present 64 in the surface of photocatalust 64 in the surface of photocatalyst.

⁶⁵ In the present study, we developed a one-step $\text{TiO}_2/\text{AC}/\text{CE}$ 66 nanocomposite, as a porous solid, using a simple solvothermal 67 67 process for the simultaneous removal of inorganic and organic 68 impurities from unter Hara the selucthermal process is adopted ⁶⁸ impurities from water. Here, the solvothermal process is adopted
 $\frac{69}{25}$ for TiO *JACICE* papersemposite synthesis as this process is widely 69 for TiO₂/AC/CE nanocomposite synthesis, as this process is widely 70 acknowledged as a simple and inexpensive way to produce 71 agglomeration free spherical TiO₂ nanoparticles [\[29\]](#page--1-0). Owing to 72 high surface area AC is adopted as it above high adopted with $\frac{72}{73}$ high surface area, AC is adopted as it shows high adsorption with $\frac{73}{73}$ fourshle surface chamical affinitios towards the removal of 73 favorable surface chemical affinities towards the removal of 74 impurities Conveniently as the adsorbents for water purification 74 impurities. Conveniently, as the adsorbents for water purification 75 are used in pourdand form their separation requires special 75 are used in powdered form, their separation requires special to techniques requiring outpack time and comploying To avoid this ⁷⁶ techniques requiring extra cost, time, and complexity. To avoid this reproduced the adsorbent T_0 . $/4C$ papecomposite is converted 77 problem, here the adsorbent TiO_2/AC nanocomposite is converted
78 into a porous solid by mixing with enoxy forming a desired shape ⁷⁸ into a porous solid by mixing with epoxy, forming a desired shape
⁷⁹ (depends on the mold) followed by carbonization at selected ⁷⁹ (depends on the mold) followed by carbonization at selected $\frac{80}{2}$ terms at the second provides the matrix for TiO (AC name) ⁸⁰ temperature. Here, epoxy provides the matrix for TiO₂/AC nano-
⁸¹ composite. In addition, during carbonization process the epoxy
⁸² counts to explore which can increase the amount of explore in ⁸² coverts to carbon, which can increase the amount of carbon in $\frac{83}{100}$ TiO (AC/CE, papecomposite, Subsequently, the as synthesized 83 TiO₂/AC/CE nanocomposite. Subsequently, the as synthesized
 84 nanocomposite is successfully used for the removal of inorganic 84 nanocomposite is successfully used for the removal of inorganic
 85 and organic impurities from water Here lead acetate and MB dye ⁸⁵ and organic impurities from water. Here, lead acetate and MB dye,
⁸⁶ taken as inorganic (Pb ions) and organic impurities sources 86 taken as inorganic (Pb ions) and organic impurities sources
 87 ergnectively are selected as the model pollutants due to their $\frac{87}{100}$ respectively, are selected as the model pollutants due to their
 $\frac{88}{100}$ heavy presence in the released water of industries. The structural ⁸⁸ heavy presence in the released water of industries. The structural 89 and photogatalytic proportion of TiO *IACIC* papercomposite are 89 and photocatalytic properties of $TiO₂/AC/CE$ nanocomposite are
90 also compared with that of pristine $TiO₂$ nanosphere. As here AC is
91 approximately described that the synthetic that ⁹¹ employed for the heavy metal adsorption, thus to evaluate the $\frac{92}{100}$ adsorption can bilities of AC Bb(II) absorption is also performed. ⁹² adsorption capabilities of AC, Pb(II) absorption is also performed
⁹³ unit AC/CE composite Furthermore to investigate the petertial of 93 with AC/CE composite. Furthermore, to investigate the potential of 94 94 AC/CE composite for other heavy metals exclusion, the adsorption
95 Acypariments are also carried out for $Cr(U)$ and $Cd(U)$ ions 95 experiments are also carried out for $Cr(III)$ and $Cd(II)$ ions
96 impurities impurities.

⁹⁷ Experimental

98 Preparation of TiO₂/AC nanocomposite

⁹⁹ Here, TiO_2 was prepared by simple one-step solvothermal
¹⁰⁰ process where titanium tetraisobutoxide (TTIR) was used as 100 process, where titanium tetraisobutoxide (TTIB) was used as 101 titanium precursor [30] The information regarding materials and 101 titanium precursor [\[30\]](#page--1-0). The information regarding materials and 102 reagents used in the study is provided in the Supplementary ¹⁰² reagents, used in the study is provided in the Supplementary
¹⁰³ information (S1) Briefly TTIB (14 mM) stabilized in 20 ml ethanol ¹⁰³ information (S1). Briefly, TTIB (14 mM) stabilized in 20 ml ethanol
¹⁰⁴ was added to the stirred solution of ethanol (120 ml) and ¹⁰⁴ was added to the stirred solution of ethanol (120 ml) and 105 acetonitrile (90 ml) with amine (2.4 mM) and water (1 mM) For ¹⁰⁵ acetonitrile (99 ml) with amine (2.4 mM) and water (1 mM). For 106 TiO- $/4C$ paper position a mass used amount of $4C$ 106 TiO₂/AC nanocomposite preparation, a measured amount of AC
 107 (37.8 g) was added to the stirred solution of TTIB followed by 107 (37.8 g) was added to the stirred solution of TTIB followed by
 108 etiming for 1 b. The obtained composite was dried in the sugn at ¹⁰⁸ stirring for 1 h. The obtained composite was dried in the oven at $109 = 50 \degree$ for 8 h. To fabricate paper supposes the decised change the 109 50 °C for 8 h. To fabricate nanocomposite in the desired shape, the nanocomposite was approximately mixing the solver harmonic nanocomposite was prepared by mixing the solvothermal synthesized TiO₂/AC in a mixture of epoxy (PG-100) and hardener 111
(PH 861) baying a ratio of 10:1 (wt/wt) with a TiO₁/AC to epoxy 112 (PH-861) having a ratio of 10:1 (wt/wt), with a TiO₂/AC to epoxy 112
weight ratio of 40:60. The obtained viscous solution was filled in a weight ratio of 40:60. The obtained viscous solution was filled in a 113
dis. The discuss then and at name temperature for 40 h and drived die. The die was then aged at room temperature for 48 h and dried 114
at 60 °C for 4 h. For the carbonization of the dried TiO (AC/onexy 115) at 60 °C for 4 h. For the carbonization of the dried TiO₂/AC/epoxy 115
nanocomposite the product which was obtained from mold was nanocomposite, the product, which was obtained from mold, was 116
kent in a quartz tube reactor in the presence of N- atmosphere and kept in a quartz tube reactor in the presence of N_2 atmosphere and 117
boated to 400 °C at 5 °C/min for 1 b. Subsequently, the temperature heated to 400 °C at 5 °C/min for 1 h. Subsequently, the temperature 118
was increased to 800 °C and the nanocomposite was hold in it for was increased to 800 °C and the nanocomposite was hold in it for 119
15 min After the completion of the carbonization process the 15 min. After the completion of the carbonization process, the 120
nanocomposite was cooled to room temperature in N₂ atmos nanocomposite was cooled to room temperature in N_2 atmo-
subset The first person posite was thus designated as TiO (AC) sphere. The final nanocomposite was, thus designated as $TiO_2/AC/$ 123
CE papecemposite. To compare the degradation characteristics of CE nanocomposite. To compare the degradation characteristics of 123
TiO, $1AC/CE$ panocomposite with pristing TiO, the TiO, pano. 124 TiO₂/AC/CE nanocomposite with pristine TiO₂, the TiO₂ nano-
spheres were also prepared by using the similar procedure as
discussed earlier For this TTIB (3 mM) was added to the stirred 126 discussed earlier. For this, TTIB (3 mM) was added to the stirred 126
colution of 25 mJ othanol, 20 mJ actority le 1 mM amine and solution of 25 ml ethanol, 20 ml acetonitrile, 1 mM amine and 127
0.1 ml unter The solution was stimed to 20 min followed by druing 0.1 ml water. The solution was stirred to 30 min followed by drying 128
at 60 °C. The synthesis mathed of AC/CE preparation is discussed in at 60 °C. The synthesis method of AC/CE preparation is discussed in 129
the Synplomentary information (S2), where the constituents (AC the Supplementary information (S2), where the constituents (AC, 130
apoyu, bardonar) are added in the came ratio, as used for the 131 epoxy, hardener) are added in the same ratio, as used for the 131
neparation of TiO *IACICE* preparation of $TiO₂/AC/CE$.

¹³³ Characterization

To confirm the crystalline size of TiO₂/AC/CE nanocomposite and

stine TiO₄ the Y ray diffraction (YPD) moscurements were pristine TiO₂, the X-ray diffraction (XRD) measurements were conducted (X'pert Pro, PANalytical) with a Cu K α radiation of 136 unucleograph 0.15418 pm in the range of 20, 80° with a coapping rate of 137 wavelength 0.15418 nm in the range of 20–80° with a scanning rate of 1^{37}
 $1^{\circ}/$ min. The size and surface morphology were examined by 1^{38} $1^{\circ}/$ min. The size and surface morphology were examined by 1^{38}
scanning electronic microscope (SEM, Zeiss EVO MA-15) as well 1^{39} scanning electronic microscope (SEM, Zeiss EVO MA-15) as well ¹³⁹
as transmission electron microscopy (TEM, TECNAL T12, operating 140 as transmission electron microscopy (TEM, TECNAI T12, operating 140
unltage 1201). The elemental composition of TiO (AC/CE name 141 voltage 120V). The elemental composition of TiO₂/AC/CE nano-
composite was analyzed by energy dispersive X-ray spectroscopy 142
(EDS Quanta 2D). To study the thermal stability and degradation 143 (EDS-Quanta 3D). To study the thermal stability and degradation 143
behavior of papocomposite and bare TiO, thermogravimetric (TCA) 144 behavior of nanocomposite and bare T_iO_2 , thermogravimetric (TGA) 144
2 palysis (PerkinElmer Diamond TC (DTA) has been performed under 145 analysis (PerkinElmer Diamond-TG/DTA) has been performed under 145
N. flow with a beating rate of 10 °C/min. The total surface area was 146 N_2 flow with a heating rate of 10 °C/min. The total surface area was 147 obtained using Brunauer–Emmett–Teller (BET) method with Auto- 147 sorb software (Quanta chrome Instruments). Paman spectroscopy. 148 148 sorb software (Quanta chrome Instruments). Raman spectroscopy and the spectroscopy state of the spectrum of the spectrometer (Johin Yuon and the spectrum of the spectrum of the spectrum of the spectrum of the spectrum was recorded by LabRam Micro-Raman spectrometer (Jobin-Yuon 149
HP 800 JM) using a He Me(632.8 nm) laser excitation source Fourier 150 HR 800 UV) using a He–Ne (632.8 nm) laser excitation source. Fourier 150
transform infrared spectroscopy (Bruker-FIIR) was analyzed using 151 transform infrared spectroscopy (Bruker-FTIR) was analyzed using 151
KBr pallet in the range of 4000, 400 cm⁻¹. The absorbance proportion 152 KBr pallet in the range of 4000-400 $\rm cm^{-1}$. The absorbance properties $\rm ^{152}$ of the synthesized samples were acquired by the UV–vis diffuse 153 reflectance spectra (UV–vis DRS) with a UV–vis–NIR spectropho-
tomotor (Varian Cary 500) baying an integrating diffuse reflectance 155 tometer (Varian Cary 500) having an integrating diffuse reflectance 155
fixture in the range of 200, 800 pm fixture in the range of 200-800 nm.

Photocatalytic degradation study and the study of the 157

To evaluate the performance of as-synthesized $TiO_2/AC/CE$ 158
ascennesite and pristine TiO₂ the adsorption and degradation 159 nanocomposite and pristine TiO₂, the adsorption and degradation 159
of Pb(II) ions and MB were simultaneously carried out under visible 160 of Pb(II) ions and MB were simultaneously carried out under visible 160
light, irradiation (2W, DBLED). The wavelength of the used light 161 light irradiation (2W, DPLED). The wavelength of the used light 161
source was measured by high resolution spectrometer (HP 4000: 162 source was measured by high-resolution spectrometer (HR 4000; 162
Ocean optics) with a wavelength range of 200, 1100 nm, where it Ocean optics) with a wavelength range of 200–1100 nm, where it 163
was observed that that light source is having the wavelength 164 was observed that that light source is having the wavelength 164
between 300 and 750 nm For simultaneous photocatalytic 165 between 300 and 750 nm. For simultaneous photocatalytic 165
reactions prior to illumination known amounts of Pb(CH_COOH) 166 reactions, prior to illumination, known amounts of Pb(CH₃COOH)₂, ¹⁶⁶
where the concentration of the Pb(II) jons were kent (200 mg/l) where the concentration of the Pb(II) ions were kept (200 mg/l), 167
and MB (0.62 mM) were mixed into the 200 ml of distilled water. 168 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 169
colution. To attain the adserntion decoration coullibrium, prior to 170 solution. To attain the adsorption/desorption equilibrium, prior to 170
illumination, the assumenceiped TiO (AC/CE paperson posite or 171) illumination, the as synthesized TiO₂/AC/CE nanocomposite or 171 pristine TiO₂ was immersed in the solution and then solution was 172

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