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Solar-catalytic carbon beads immobilized with titanium for mineralization of 4-hydroxynitrobenzene contaminated aquatic environment

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Abstract:

In this work, we have synthesized titanium (Ti)immobilized carbon solar-catalytic beads are good photo-catalyst for 4-hydroxynitrobenzene removal from wastewater. We utilize the monomer based on phenolic resins and these phenols based round materials in the range of size between0.3 to 0.9millimeter (mm)was first synthesized by the suspension polymerization. Nanoparticles of TiO_2 *were combinedwith round carbon material during the middle stage of chemical process of polymerization. Moreover, porosity structure in round materials of doped carbon were created with the help of temperature treatment under* N_2 *atmosphere at 800* ^oC*. Titanium-doped carbon bead was characterized by Fourier transforms infrared (FT-IR) spectroscopy and SEM/EDX analysis. The removal of 4-hydroxynitrobenzene was explored with various parameters such as kinetics, pH and primary concentration (5-500 mg/L) under solar radiation shadowyconditionand also visible light phase.4-hydroxynitrobenzenedecontamination with complete mineralization were completedwithset batch process. The removal of this was increased at 4pH. The more amount of 4-hydroxynitrobenzene removed by titanium doped carbon beads) under solar radiation was 4-fold greater than that of the parent sample material. The process adopted in the study can be an important step towards developing multi-functional solar-catalytic sorbent in other environmental remediation applications.*

Keywords:*4-hydroxynitrobenzene; sorption; visible phase; polymerization; beads;*

1. INTRODUCTION

Pollution in air and aquatic atmosphere has become a major issue in ourliving life world. In aquatic contamination, different type of method such as biological process,chemical-physical sorption process and filtration based on membrane methods have been investigated to decontaminate of aquatic environments [1-2]. Solar-catalytic based heterogeneous semiconductor for solar-catalysis is a modern process of oxidation, which has been completely recognized for modern technology with complete mineralization of contaminated industrial aqueous waste under solar radiation system. One of these organic pollutants is 4-hydroxynitrobenzeneis utilized inoil refineries, petrochemical units, coal gasification sites, etc, industrial source of contaminants produce huge amounts phenolic contamination in aquatic waste. In addition, 4-hydroxynitrobenzene compounds are utilizing extensively in a many sector such as chemical processes, agricultural chemical industry and manufacture of plastic materials etc [3]. The contamination and non-mineralization of 4-hydroxynitrobenzene contaminated aquatic waste affect the aquatic environmental atmosphere. Exposure to para nitro phenol may cause carcinogenic properties in all living environment [2-3].

In occasion of solar-catalytic process, TiO_2 has been chosen as environment friendly catalyst for the heterogeneous kind of solar-catalysis.Additionally,TiO_2 also utilized as a good semiconductor for decontamination and complete mineralization to make safe and green environment, it is because ofinexpensive, good stability and very less harmfuleffect on humans and the environment [4]. Various research reports already reported that improvements in solar-catalysis of titanium dioxide under ultraviolet radiation. Thus, many problems still pending for industrialization process, during solar-catalysisprocess, TiO_2 and similar solar-catalytic metal oxides provide limited range of light photocatalysis, also, provide less mineralization efficiency for decontamination.In the process of solar-catalysis, it is very hard to identified all and every factor’s role and solar catalysis reaction. However, the physio-chemical sorption is one of the important stages during solar-catalytic procedure. Consequently, severalscientists and researcher areinvolvedin the research of metal oxide doping in inert matrix of $TiO_2$for a purpose of increasing the active area as a good way to promote the solar-catalytic action in aquatic and gaseous stages. In persistence of current scenario, various porous mediumisutilizing for immobilization of nanoparticles of TiO_2 on the surface of porous structure of graphene, activated carbon and zeolite with any disturbance of porous activity [5-6].

Numerousresearches have publicized with high efficiency at formation with carbon-based materials. TiO_2 with activated carbon as machine-drivencombinations are continuouslycapable for the solar-catalytic decontamination at aquatic phase as compared with parent oxide of

Ti.Though, many scientific reportsevaderesearchwith non-loosing solar-catalytic activitytitanium dioxide at different metals ions doping and temperature treatment process [7].

At current research study,the phenol based round materials with immobilization of nanoparticles of TiO_2were formed via thechemical process polymerizationof suspension method. Next, various structured activated carbon immobilized with nanoparticles of TiO_2 formed with simple routes. In this method, beads which are large in size were prepared and carbonized to makeporous round carbon materials and then used as a sorbent/photocatalyst for removal of 4-hydroxynitrobenzene (4-NP).

2. MATERIALS AND PROCESS

2.1.Materials

Titanium dioxide, phenol, aqueous formaldehyde solution, poly(vinyl alcohol), trimethylamine, hexamine and acetone were used. All reagents are pure and good quality.

2.2.Preparation method

The carbon beads doped with TiO_2 were formed via chemical processwithformaldehyde and carbon source of phenolic compound with theexistence of TEA (triethylamine) catalyst. A tri-naked glass reactor furnished with water condenser was utilized for suspension polymerization, where, phenol as source of carbon with the amount of 50 g were transferred at initial stage. Afterwards, another chemical formaldehyde at concentration of 30% and a catalyst TEA with the amount of 1.5 mL were mixed into above phenolic compound. Later, above mixture mixed properly upto 40 min and a crosslinking agent hexamine with the amount of 3.5g were added for complete polymerization chemical process. After approximately 40 min, the suspension stabilizing agent, polyvinyl alcohol (PVA, 3g) was added. After approximately 45 min, titanium dioxide (0.5g) was added with heating. After 4h we stopped heating and reaction assembly was permitted to cool down at room temperature.After completion of chemical polymerization, product were cool down at room temperature and filtered to separate solid round materials from solution. The separated round polymeric materials were obtained in the average size range of 0.8 mm which were washed with H_2O, and ethanolic solvents.

TiO_2-incorporated round polymeric materials (TiO_2-CB) withthe average size range of 0.4 to 0.8 mm were convert into carbon via process of carbonization under nitrogen atmosphere with the heating rate of 5^{o}C/min in a tubular reactor up to 750 for 6 hr. Carbon beads (CB) were prepared by above identical method except no addition of TiO_2.

2.3.Material characteristics analysis

The Nicolet Nexus 470 Fourier transform infrared (FTIR) spectroscopic techniques were utilize to determine active functional groups in materials. Another characteristic source for morphological study, a microscopic SEM connected with spectrometric EDX were utilized to check the surface determination and composition of elemental, respectively,inmaterials.

2.4. Physio-chemical sorption and solar-catalytic process

The 4-NP removal process was completed with heightened pH and dosage of materials of TiO_2-CB nanocomposites as aphysio-chemical sorbent with water bath shaking system controlled with temperature in a particular shaking speed underneath room temperature under solar radiation and dark condition. In the study of pH, 100 mL of 100 mg/L 4-NP reaction mixture was maintained to different pH values from 2 to 7. The pH for optimum sorption of 4-NP was decided using 0.1 g of TiO_2-CB nanocomposite. The pH of the reaction solution was initially maintained by 01 N H_2SO_4 and/or ammonia solution. Later on, a conical flask was used for shaking the reaction solution under solar radiation and dark condition, at end mixture solutions were filter with filter paper. 4-NP concentrations of solution, nextappropriate dilution, wasdetermine by UV spectrophotometric analysis.An estimatethe concentration of removed 4-NP forphysio-chemical sorptionunder dark condition,one analytical parameter was altered at a time keeping the various parameter should fix. The consequencefor para nitro phenol concentration on efficient mineralization wereexaminedat

$$q_e = (C_{final} – C_{initial}) \times \text{volume/weight of nanocomposite} \qquad (1)$$

wherever$q_e$can denoted by mineralized 4-NP from aqueous waste using TiO_2-CB nanocomposite, $C_o$isconsider for concentration of initial of 4-NP (mg/L), $C_e$can denoted isconcentration of equilibrium for 4-NP (mg/L), volume of 4-NP sample are denoted by “V” in litre(L), and weight of used TiO_2-CB nanocomposite utilized can denoted by “W”.

3. Results and Disscussions

3.1.SEM/EDX analysis

The morphological study using microscopic SEM analysis and elemental scanning spectra with the help of EDX analysis are shown in Fig.1, which reflected that TiO_2 immobilized carbon solar-catalytic beads prepared and surface covered with titanium nanoparticles (Fig 1a and b). In addition, the surface of Ti NPs uniformly distributed on the round material of carbon (TiO_2-CB) surface which can utilize for bi-process of sorption and solar-catalysis. However, elemental scanning spectra (EDX)provide the information of presence of Ti NPs on the surface of round material of carbon (TiO_2-CB) as shown in Fig 1c.

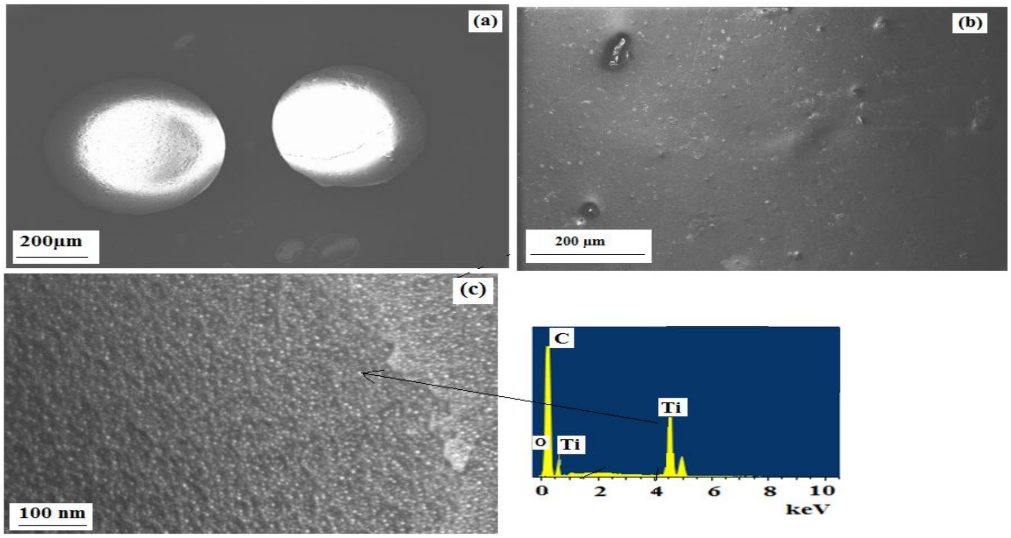

Fig.1. (a) TiO_2 doped carbon beads (0.7 mm), surface of (b) carbon beads and (c) TiO_2 doped carbon beads, (d) EDX of TiO_2-CB

Fig. 1a indicates that carbon beads (CB) can be identified in round shape with the size average value of 0.8 mm and have smootheroutward. Animagery of SEM(Fig.1b) show the absence of TiO_2 particles and smooth surface. As compared with the Fig.1b, the SEM images of TiO_2-CB (Fig1b) were rough surface deposition of small TiO_2 particles on the surface of carbon beads. Figure1c is the representative EDX spectra. Concentration of the titanium gained from the spectrumwhich range are consider with the 0.2 to 0.8% (w/w).

3.2.Spectral analysis by FTIR

Fig. 2represented the FTIR spectra for titanium dioxide and TiO_2-CB. The peaks absorption in the range of 3,344 to 3,550 cm^{-1} corresponded by hydroxyl group, also, band at closely 1,627 cm^{-1}revealH$_2$O molecules absorbed surface [8].

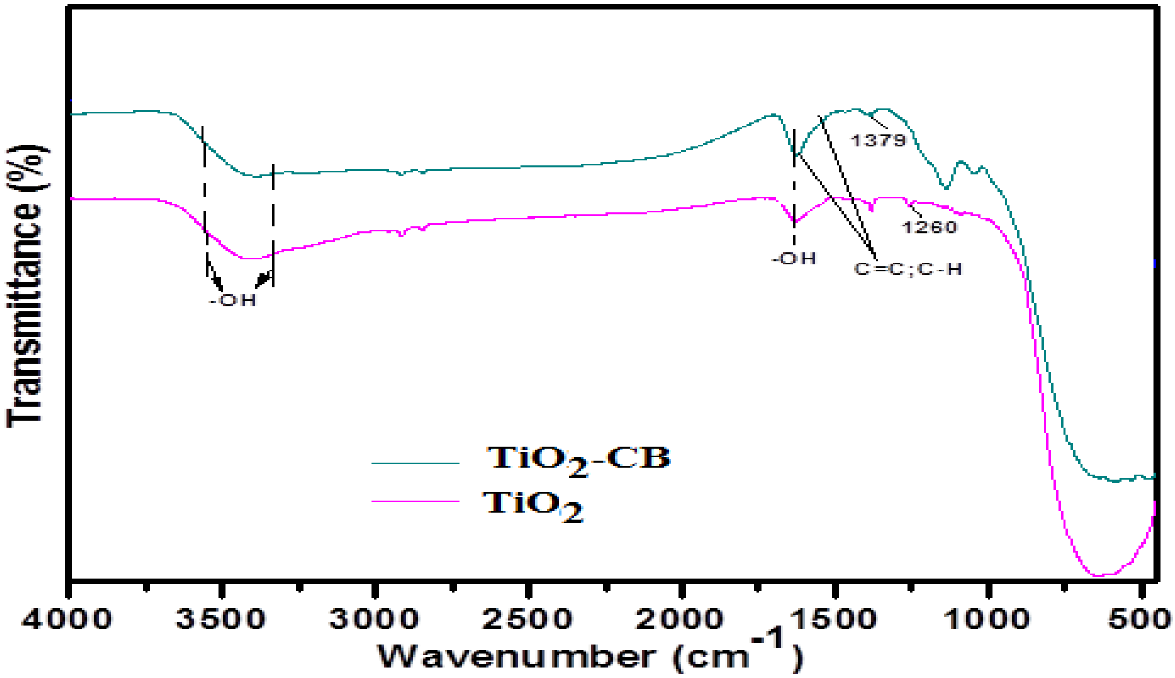

Fig.2. FTIR spectra

In the FTIR spectra of TiO_2-CB, a vibrational ring peak can observeat 1,379 cm^{-1}, which can be accreditedfor stretching of Ti-O-C bond formation [7-8].The peak at 1,616 cm^{-1} corresponds for C=C broadeningof band, which can be specifiesfor non-oxidized vibrational skeletal of carbon. The prepared TiO_2-CB provide the intense peak at 3,420 and 1,627 cm^{-1}, which can be allocatedbond formation in between C=Oand O-H as compared with plane TiO_2 and plane carbon.

3.3.Decontamination of 4-NP under solar radiation and dark condition

The initial pH effect on removal of 4-NP by TiO_2, CB, TiO_2-CB were identified by different solution pH value of 2 to 7**(Fig. 3a).**The efficiency of 4-NP decontamination using all materials can be observed in increasing order at acidic region in pH value from 2.0 to 3.0, however, efficiency of 4-NP decontamination showed decreasing order at the pH value 5.0 to 7.0. Though, at pH value 4.0 [3], shows the highest efficiency of 4-NP decontamination with the efficiencies of 35.7, 48.9, and 98.2 mg/g fortitanium dioxide, CB and TiO_2-CB, respectively. The change in surface charge of materialsare mostlyaccountable for 4-NP decontamination. The pH in the region of acidic (pH < 6), materialssurface formed a positive charge which provide the electrostatic repulsion towardsthe cationic moiety. The pH in the alkaline region pH > 7.5, the materialssurface designed negative charge which afford and dominates the electrostatic repulsion towardscompounds of anionic [9].

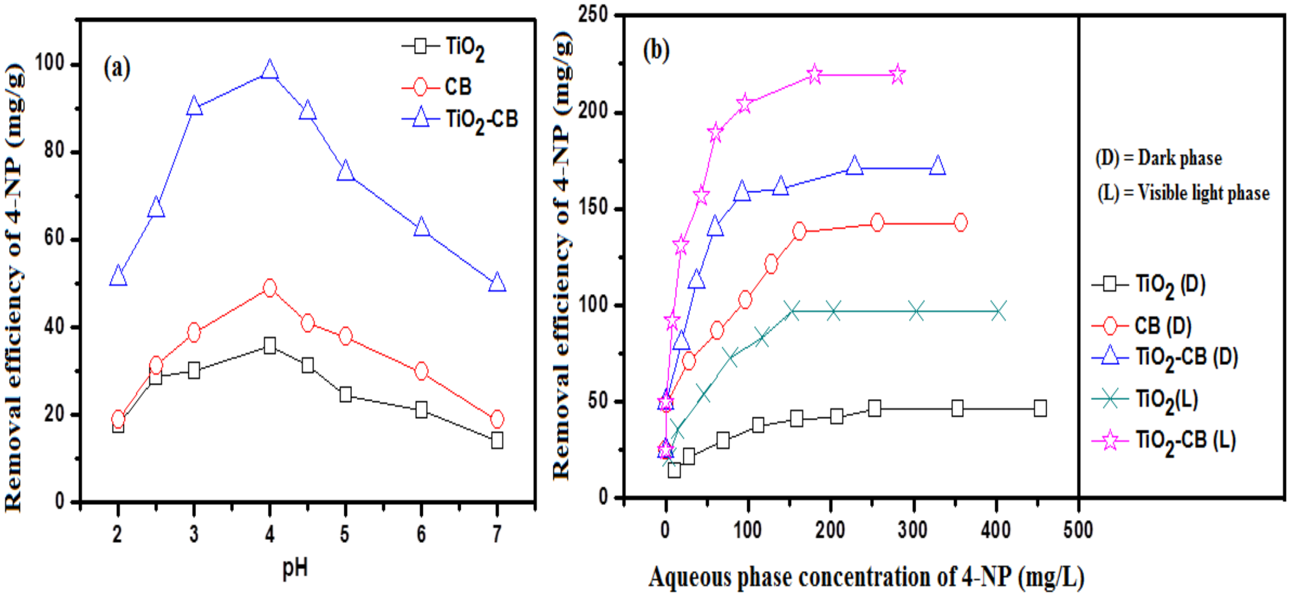

Fig. 3. (a) pH effect for 4-NP and (b) Isotherm for equbilirium under visible radition and dark condition

The equilibration isotherm graph represented in **Fig. 3b,** which indicate that the equilibrationof 4-NP decontamination from aqueous industrial waste under dark condition and visible radiation over the CB, TiO_2 and the TiO_2-CB. To explore the isotherm of 4-NP removal, the 4-NP solution concentrations werediffered from 5 to 500 ppmat the solution volume of 100 milliliter utilizing with 0.1 gmaterials dosein the value of pH 4.0. The efficiency of 4-NP decontamination was greatlyimproved under solar light as a visible radiation as compared to dark phase. The removal efficiency of 4-NP was 46.3, 142.7 and 171.2 mg/g in dark phase for TiO_2, CB and TiO_2-CB, respectively. The removal efficiency of 4-NP in visible phase was 97.1 and 219 mg/g for titanium dioxide and Ti immobilized carbon round materials, correspondingly. Furthermore, improved decontamination efficiency with Ti immobilized carbon round materials can be accreditedbased on acid-base exchangesamidwith 4-NP and activated OH group of Ti immobilized carbon round materials surface.

4. CONCLUSIONS

TiO_2 incorporated phenolic base carbon beads prepared in current research were effectivelyutilized as a solar-catalystfor mineralization of 4-notrophenolfrom from aquatic environmental waste. The removal efficiency greatly increased in visible phase as compared to dark phase. The removal efficiency of 4-NP was 46.3, 142.7 and 171.2 mg/g in dark phase for TiO_2, CB and TiO_2-CB, respectively. The removal efficiency of 4-NP in visible phase was 97.1 and 219 mg/g for TiO_2 and TiO2 incorporated carbon beads, respectively. The methodology adopted in this study can be an important for larger area of solar based catalysis process and dark based sorption methodof environmental remediation applications.

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