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Zero-valent Iron Loaded Activated Carbon Nanocomposites for Photocatalytic Degradation of Potassium Dichromate

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Abstract: Fe-NPs and Fe-AC nanocomposite were synthesised using tulsi leaf extract. The phytochemicals present in the leaf extract help in the formation of nanoparticles and nanocomposites. The present method is simple and free from the use of any organic reagents. The synthesised nanoparticles were well characterised using TEM, HR-TEM, SAED pattern, UV-Vis spectroscopy, FT-IR and EDX analysis. The XRD and EDX analyses confirmed the formation of nanocomposites. The synthesised Fe-NPs and Fe-AC composites have been used for the degradation of potassium dichromate under solar irradiation. A total of ~95% and ~70% of potassium dichromate was completely degraded using Fe-AC and Fe-NPs as a photo catalyst. Fe-AC nanocomposites were found to show better catalytic activity than Fe-NPs.

Keywords: Fe-NPs, Fe-AC nanocomposite, photodegradation, potassium dichromate.

Introduction

Water contamination due to the presence of chromium has become a major problem. The contaminants originating from industries have significantly increased (Luo et al., 2013). Heavy metals are the main pollutants among which chromium is the most dangerous that has many applications in the metal cleaning and plating baths, painting, tannery and fertiliser industries. Chromium is usually present in the aquatic environment in two oxidation states (VI) and (III) (Baral et al., 2006; Katsumata et al., 2013; Lv et al., 2012). Chromium (VI) is more toxic than chromium (III) due to its carcinogenicity, toxicity and high aqueous solubility. Various methods such as ion exchange, membrane filtration, reverse osmosis, etc. were employed for the removal of chromium (VI) from water and waste water (Devi et al., 2016a; 2016b; Machado et al., 2013) but these methods have drawbacks such as low efficiency, high energy demand, high cost and problems of sludge disposal (Jung et al., 2013; Liu et al., 2010; Vaiopoulou and Gikas, 2012). In this regard, nanocomposites have aroused interest among the researchers for the degradative removal of organic pollutants from water. Various nanocomposites have been reported in the literature for the remediation of water and wastewater pollutants; among which magnetic nanocomposites have attracted attention for their easy separation process and higher degradation ability. In this context, facile, green synthesis of iron nanoparticles and iron-loaded activated carbon nanoparticles using *Ocmiumtenuiflorum* leaves extract were developed. The developed nanocomposites have been utilised for the photoreduction of hexavalent chromium (VI) from water by loaded iron nanocomposite, which is used as a catalyst.

Materials and Methods

Reagents and Materials

The following reagents were used without further purification throughout the work: ferrous sulphate ($FeSO_4$), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), potassium dichromate ($K_2Cr_2O_7$), phosphoric acid (H_3PO_3). Ultrapure water was used to prepare the aqueous solutions and extracts.

Preparation of Tulsi Leaves Extract

A total of fresh 10 g of *Tulsi leaves* was refluxed for 30 min with 250 ml of distilled water in a round-bottom flask. The extract was filtered using Whatman No. 41 filter paper to obtain the pure extract.

Preparation of Activated Carbon

The precursor, tea waste (TW), was collected from a local market. The dried samples were impregnated with ortho-phosphoric acid on a hot plate at 105°C. The duration and heating rate were adequate for intercalation and complete distribution of the chemical in the sample matrix. The samples were then washed with water to remove excess chemicals and dried in an oven at 60-70°C to evaporate the water molecules. The sample was kept for 6 hours in order to remove the adsorbed water and volatile matter completely. The dried material was then carbonised under a nitrogen atmosphere at a temperature of 550°C. The resulting activated carbon was thoroughly washed with distilled water to remove unreacted acid from the surface and dried in an oven for 6 hour. The final product was pulverised in a mortar and kept in a desiccator until use.

Synthesis of Zero Valent Iron Nanoparticles

The biosynthesis of Fe (0) nanoparticles was carried out by using 150 ml of tulsi leaves extract with 50 ml of $FeCl_3.6H_2O$ (0.025 mol) and 50 ml of Fe_2SO_4 (0.05 mol) and stirred for 5 hours at room temperature. After 5 hours, the green colour of the solution turned into black colour, which clearly indicates the formation of Fe (0) NPs.

Synthesis of Iron Loaded Activated Carbon Nanocomposite

A total of 50 mg of activated carbon was transferred to 50 ml of Fe NPs colloidal solution and stirred for 5 hours. The mixture was centrifuged and washed five times and then the settled portion was dried for 12 hour at 50°C. Thereafter, the iron nanoparticles loaded with activated carbon were obtained.

Characterisation of Fe NPs and Fe Loaded Activated Carbon Nanocomposite

Absorption spectra were recorded on Cary 100 BIO UV-visible spectrophotometer. The prepared Fe nanoparticles loaded with activated carbon were characterised using the P-XRD method with Phillips X'Pert PRO diffractometer with CuK radiation of wavelength 1.5418. For the morphological study, FT-IR spectroscopy and elemental study, JEM-2100 Transmission Electron Microscope, Bruker Hyperion 3000, FEG-SEM, Model: JSM-7600F, magnification: ×25 to 1,000,000a have been used.

Photodegradation Study of Iron Nanoparticles and Iron Loaded Activated Carbon Nanocomposite

The photodegradation activity of the synthesised iron loaded activated carbon nanocomposite was evaluated by degradation of potassium dichromate. A total of 30 mg of the catalyst was dispersed in 150 ml (10ppm) of potassium dichromate aqueous solution. The experiment was carried out on a sunny day at Silchar City Assam, between 10 a.m. to 2 p.m. (outside temperature 35-40°C). At a regular interval of time, 4ml of suspension was withdrawn, centrifuge immediately and absorbance were recorded using UV-visible spectroscopy.

It was observed that the absorbance band at 340 nm (due to potassium dichromate) decrease gradually with an increase in the irradiation time. After 3 hours of irradiation time, it was observed that approximately 95% and 70% of potassium dichromate were degraded using Fe-AC-NC and Fe-NPs. From the photodegradation study, it was observed that Fe-AC-NC shows better catalytic activity than Fe-NPs.

Results and Discussion

The UV-Visible spectra of as-synthesised Fe (0) nanoparticles using tulsi leaf extract showed an absorption band at 270 nm which clearly indicates the formation of iron nanoparticles. As observed in the TEM images, the average particle sizes of iron-loaded activated carbon and Fe (0) NPs were 25-30 and 15-25 nm, respectively. HR-TEM image and SAED pattern revealed that as-synthesised nanocomposites were polycrystalline in nature. From the XRD spectra, we observed peaks at 44.5°, 65.01° and 82.41° correspondingto the lattice plane (110), (200) and (211), respectively, of the bcc structure of iron nanoparticles. The XRD pattern of activated carbon portrays two broad diffraction peaks at 26° and 43°, which can be indexed to (0 0 2) and (1 0 0) graphite-like reflections.

FT-IR spectra of leaf extract showed the presence of bands at 3410, 1618 and 1048 cm^{-1}, which are attributed to O-H stretching and C=O stretching in carboxyl or C=N bending in the amide, C-O stretching indicating the presence and involvement of these functional moieties in the fabrication, respectively. The peaks at 3410 shifted to 3450 cm^{-1} indicating that the O-H groups strongly participate in the formation of nanocomposites. The appearance of peaks at 601 cm^{-1} was due to the presence of N-H functional moieties in the prepared nanocomposites. EDX spectra of the Fe-AC nanocomposites showed the presence ofiron and carbon elements and confirmed the formation of Fe-AC nanocomposite. The appearances of other peaks can be assigned to the presence of tulsi leaf extract.

Evaluation of Photocatalytic Activity of Fe Nanoparticles and Fe-AC Nanocomposite

The photocatalytic properties of as-synthesised Fe NPs and Fe-AC NC were investigated for the degradation of potassium dichromate in presence of sunlight using UV-Vis spectroscopy at 340 nm.

AC showed higher adsorption efficiency towards organic compounds. Therefore, it is of utmost importance to study the adsorption capacity of Fe-AC nanocomposite and adsorption/desorption equilibrium using potassium dichromate solution in the dark. A total of ~40 and 20% dichromate adsorption were found within 1 hour using Fe-AC and Fe NPs. The photocatalytic activities of potassium dichromate were then investigated, which revealed that the intensity of the peaks at 340 nm decreases with an increase in radiation time and completely disappeared within 180 min. The photo reduction of dichromate followed the pseudo-first order kinetics and is indicated as follows:

$$\ln (C_0/C_t) = kt \qquad (1)$$

where k is the rate constant, C_0 and C_t are the absorbance or concentration before and after photoreduction, respectively. The rate constant (k) for the photoreduction of dichromate was 3.6×10^{-2} min^{-1}. The percentage efficiency of photoreduction of dichromate is calculated as shown in the following equation:

$$X = [(C_0–C)/C] \times 100 \qquad (2)$$

where C_0 and C are the absorbance or concentration before and after photoreduction, respectively. The percentage of photoreduction efficiency of dichromate was 95 and 70% using Fe-AC composite and Fe-NPs, respectively. Therefore, it is concluded that Fe-AC nanocomposite exhibited improved photocatalytic activities than Fe-NPs.

Table 1 represents the comparison of catalytic activities of Fe-NPs and Fe-AC nanocomposite. It was observed that Fe-AC nanocomposite showed better catalytic property than that of Fe-NPs. Figure 1(a-b) represents the photo degradation spectra of dichromate using Fe NPs and Fe-AC NC under solar irradiation. Figure 1(c-d) represents the plot of ln (C_0/C_t) versus time and percentage of efficiency for the degradation of dichromate using Fe-AC nanocomposite.

Mechanism of Photo Catalytic Reduction of Dichromate Using Fe-AC as a Photo Catalyst

During photo catalytic reduction process using Fe-AC nanocomposite, AC plays a double role. In the first step, AC adsorbed organic pollutants due to its high surface area and high adsorption performance. The adsorbed pollutant located on the surface of the activated carbon can migrate continuously to support the photocatalytic activity. In the second step, several functional groups on the AC surface are able to excite the electrons from the valence band to the conduction band of Fe NPs and createa hole (h^+) in the valence band. These holes were trapped on the surface of the hydroxyl group to furnish OH ions radicals. Then superoxide radical anions O_2^- were generated due to the reaction of dissolved oxygen molecules with conduction band electrons. In the last step, hydroxyl radicals HOO were generated on protonation of superoxide radical anions O_2. Finally, the dichromate reduction took place due to the activity of the superoxide anions. The probable mechanism for the photo reduction of dichromate is shown in Scheme 1.

Table 1: Comparison study of catalytic activities of Fe-NPs and Fe-AC-NC

Nanoparticles	*Compound*	*Time (min)*	*Amount of catalyst used (mg)*	*Percentage degradation*
Fe Nanoparticles	$K_2Cr_2O_7$	180	30	70
Fe loaded activated carbon nanocomposite	$K_2Cr_2O_7$	180	30	95

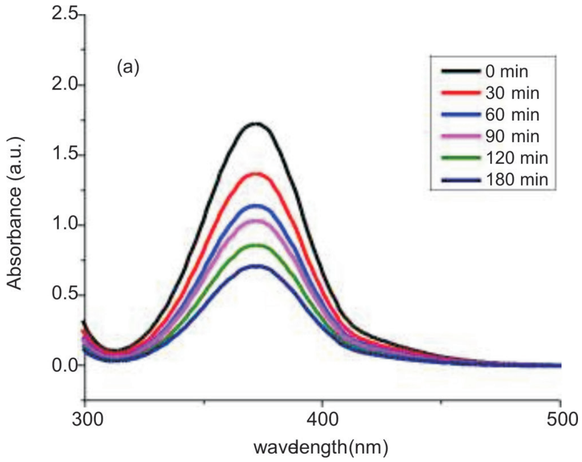

Figure 1 a: Photodegradation of dichromate using Fe NPs under solar irradiation.

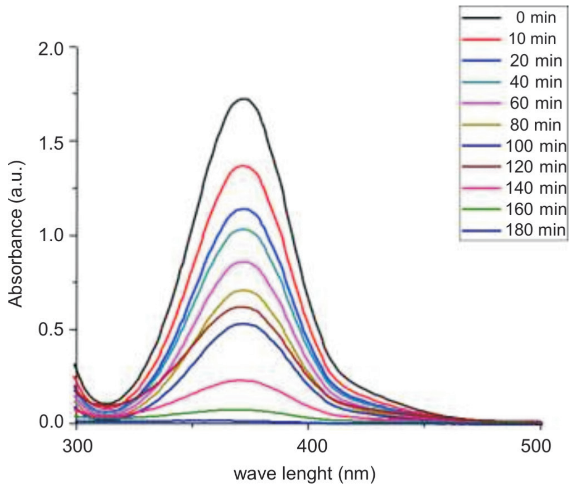

Figure 1 b: Represents the photodegradation of Fe-AC NC under solar irradiation.

$$Fe + h \longrightarrow e^- + h^+$$
$$H_2O + h^+ \longrightarrow OH^- + H^+$$
$$OH^- + h^+ \longrightarrow {}^{\cdot}OH$$
$$e^- + O_2 \longrightarrow {}^{\cdot}O_2^-$$
$${}^{\cdot}O_2 + H^+ \longrightarrow {}^{\cdot}OOH$$
$$PDC + h \longrightarrow PDC$$
$$PDC* + Fe\ Fe(e^-) \longrightarrow PDC + Fe(e^-)$$
$$+ O_2\ Fe(e^-) + {}^{\cdot}O^-_2 \longrightarrow Fe + O_2^-$$
$$2 + H^+ \longrightarrow Fe + H_2O_2$$
$$Fe(e^-) + H_2O_2 \longrightarrow Fe + {}^{\cdot}OH + OH^-$$
$$h^+ + PDC \longrightarrow \text{degradation products}$$
$$PDC^* + O_2\text{or } {}^{\cdot}OH \text{ or } O_2^- \longrightarrow \text{degradation products}$$

Scheme 1: Probable mechanism for the photoreduction of dichromate.

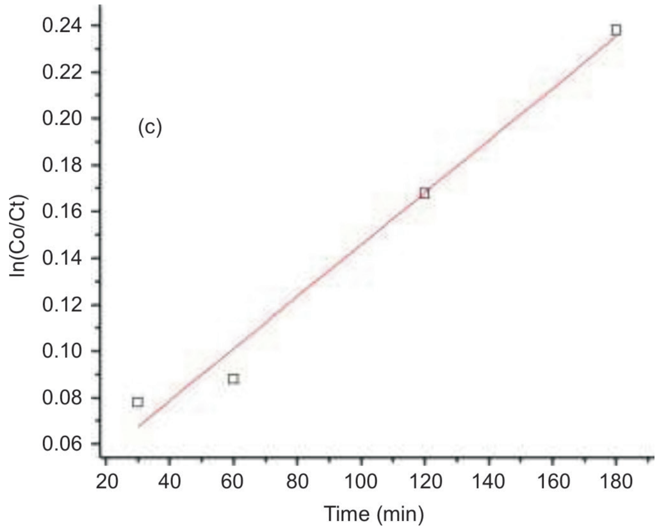

Figure 1 c: Plot of ln (C_0/C_t) versus time for photocatalytic degradation of $K_2Cr_2O_7$.

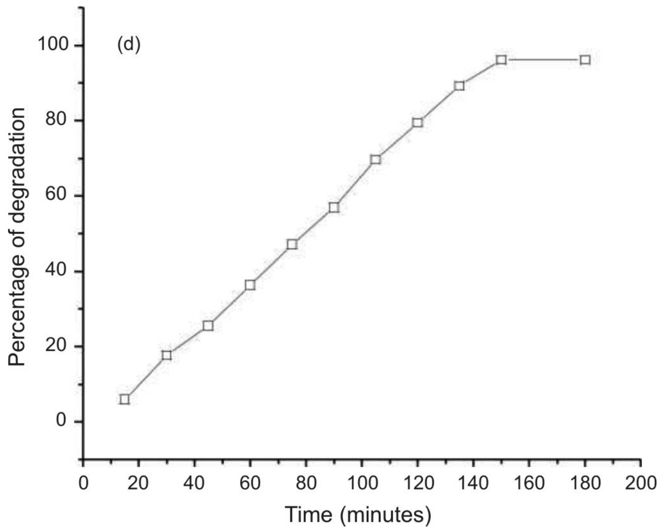

Figure 1 d: Percentage of efficiency for the degradation of dichromate using Fe-AC nanocomposite.

Conclusions

We successfully synthesised Fe-NPs and Fe-AC nanocomposites using tulsi leaf extract. The phytochemicals present in the leaf extract help in the formation of nanoparticles. The present method is simple and free from the use of any organic solvents. The XRD and EDX analyses confirmed the formation of nanoparticles. The synthesised nanoparticles were well characterised using TEM, HR-TEM, SAED pattern, UV-Vis spectroscopy, FT-IR and EDX analysis. The synthesised Fe-NPs and Fe-AC composite have successfully degraded the toxic potassium dichromate under solar irradiation. About 95% and 70% of potassium dichromate was completely degraded using Fe-AC and Fe-NPs as a photo catalyst. It was found that Fe-AC NC shows better catalytic activity than Fe-NPs.

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