SnO_2 embedded activated carbon nanocomposites: Anchoring adsorption behavior for removal of iron from water

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Abstract
Detection and removal of iron are of great interest to environmental chemists. Herein, activated carbon has been synthesized from saw dust. Tin oxide nanoparticles were loaded on activated carbon to prepare efficient nanoadsorbent for the removal of iron from water. The prepared adsorbent was investigated and characterized by various techniques, such as FTIR, SEM, XRD, EDX analysis.

The removal of iron was monitored by considering various parameters like amount of adsorbent, contact time and concentration of iron. Kinetic studies showed best fitting of pseudo first order kinetics with rate constant 0.012 min^{-1}. The adsorption process was analyzed by using Freundlich isotherm and Langmuir isotherm models.

Keywords: Activated carbon, adsorption, desorption, regeneration.

Introduction

The occurrence of iron in ground is a great concern for clean, potable drinking water. Along with iron, various other toxic compounds / heavy metals and other water contaminants are major threats to the biosphere. Hence, development of low-cost methods for efficient water decontamination is of great scientific interest[19]. High doses of Fe are found to cause sloughing of mucosa areas in the stomach, hemorrhagic necrosis and tissue damage to a variety of organs.[4] The oxidative stress caused by large amount of iron can cause brain damage.[7] Iron in water supplies gives bad odour, colour and taste, staining and deposition in the water distribution system, thereby, leading to high turbidity. The maximum permitted limit of iron concentration in drinking water is 0.2 mg/L.[17]

Various technologies such as chemical precipitation, ion-exchange, adsorption[4] ultra-filtration, oxidation/ reduction[19] are applied to remove iron from water. But these processes add to cost. Earth abundant natural precursors such as agricultural wastes are of great use in order to develop economical solution to water purification.[8]

Large surface area and porous nature facilitate the use of powdered and granular activated carbon (GAC) for drinking water treatment for the removal of pollutants[13]. The processes such as (GAC) for drinking water treatment are used for the removal of pollutants[13]. The processes such as electrodialysis and chemical precipitation are generally costly and a long-term maintenance is always required[7]. Thus, there is an urgent need of cost effective and safe method for removal of water contaminants. Among the various techniques, adsorption has been the most attractive method for efficient water decontamination and activated carbon has been used as an effective adsorbent[5].

Various researchers have employed activated carbon made from rice husk,[2,10,12,15,16] oil palm shell,[11] coconut husk,[1,9,14,18] fly ash[5], neem bark[3] etc. for removal of contaminants. Due to their size, nanomaterials exhibit a large number of novel properties which can be used to develop new technologies. The properties of nanoparticles such as large surface area to volume ratio, high specificity, potential for self-assembly and catalytic potential are used for water treatment applications[6].

Herein, SnO_2 nanoparticles were embedded in activated carbon made from saw dust. The synthesized SnO_2-NP-AC nanocomposite is used as adsorbent for removal of iron from water.

Material and Methods

All the reagents used were of analytical grade and purchased from Sigma Aldrich and Merck. The carbon source was saw dust obtained from local saw mill. XRD patterns were obtained using Philips X'PERT powder X-ray diffractometer with Cu-Kα radiation (λ=1.54056 Å). TEM images were obtained on a JEOL, JSM-6360 equipment, LEO, 1430vp equipment and on Quanta 150 equipment with an accelerating voltage of 1KV-30KV. EDS was taken with the same instrument. FTIR was taken in a 3000 Hyperion microscope with Vertex 80 FTIR system. Nitrogen adsorption-desorption measurements were performed using a Quanta Chrome Nova 1000 gas adsorption analyzer. The adsorption studies were performed by thiocyanate method using GENESYS 10S UV–visible spectrophotometer.

Synthesis: Activated carbon was prepared by adding phosphoric acid (10 ml) to about 5 g of saw dust and heated at high temperature. Then one gram of activated carbon was taken in a conical flask and 25 ml of distilled water was added to it. A solution of $SnCl_4.5H_2O$ was prepared by taking 3 g of the salt in 25 ml of distilled water. Then the conical flask containing AC was kept for stirring and the prepared tin chloride solution was added dropwise to it until completion. After that the pH was observed and it was maintained at around 7 by adding NaOH solution dropwise with continuous stirring. The process is sol-gel method of synthesis and the ratio of C and tin is 1:1. Then the contents

were centrifuged, dried and were calcined at 400°C for 2 hours.

Time-Dependent Studies: Adsorption studies were done in batch method. 10 ppm Fe (III) stock solution was prepared and 50 ml of it was used to optimize the amount of adsorbent for maximum removal of iron from water. The optimum amount of adsorbent (0.040g) corresponding to maximum removal was used for further adsorption studies. For kinetics studies, Fe(III) solution (50ml, 10ppm) was mixed with the adsorbent (0.020g) at pH 6 and stirred vigorously at a constant rate of 200 rpm.

The points of collection of samples were done at 15, 30, 45, 60, 75, 90, 120, 150 mins. The samples were collected, diluted and 1µml of 1.5M ammonium thiocyanate solution was added. After colour generation (20 mins), the solutions were analyzed using UV-Vis spectrophotometer.

Concentration-Dependent Studies: The pH of the iron solution (50 mL, 10 ppm) was maintained at 6 by adding the requisite amounts of 0.1 M HCl solution. Samples of concentration 2, 4, 6 and 8 ppm were prepared from the stock solution by dilution method. The prepared nanoadsorbent (0.040 g) was added to the test solutions and put on an orbital shaker.

The samples were collected, diluted and 1µml of 1.5M ammonium thiocyanate solution was added. After colour generation (20 mins), the solutions were analyzed using UV-Vis spectrophotometer. All absorbance values taken for calculations are at a wavelength of 470 nm.

Desorption Studies and Recycling of Adsorbent: The desorption of Iron from the adsorbent surface was done using NaOH (10 mL, 1 M) by shaking the mixture for 12 h using a mechanical shaker at 50 rpm. The samples were collected, diluted and 1µml of 1.5 M ammonium thiocyanate solution was added. After 20 mins, the solutions were analyzed.

Results and Discussion

Characterization of the nanoadsorbent: SEM micrograph indicated granular particles with rough surface morphology and randomly oriented pits (Figure 1a). The average particle size is found to be around ~35.3 nm. TEM micrograph revealed the granular of SnO_2 NPs embedded in the carbon matrix (Figure 1b).

The SAED pattern showed concentric rings indicating polycrystalline nature of the nanoadsorbent (Figure 1c). The EDS spectrum (Figure 1d) validated the elemental composition revealing the presence of P and Ca along with C, Sn and O as major constituents which may be because of utilization of bio-precursor.

Figure 2 (a) showed the XRD patterns of the synthesized nanocomposite. Bragg reflections were found to be consistent with (110), (101), (200), (211), (002) and (112) reflections of tetragonal rutile SnO_2 (JCPDS Card No 21-1250). The (110) plane of rutile SnO_2 is found to be overlapping with the (002) plane of hexagonal graphitized carbon. IR spectra (Figure 2 b) of pure SnO_2 and SnO_2-C nanocomposite showed a band at 500-575 cm^{-1} attributed to the stretching mode of the Sn-O bond. The peak at 1039 cm^{-1} is assigned to C-O stretching. The broad band at 3416 cm^{-1} and sharp peak at 1617 cm^{-1} can be assigned to O-H stretching and bending vibrations respectively indicating the presence of surface hydroxyl groups on the nanoadsorbent.

Time dependent studies: Pseudo first order and pseudo second order kinetics were employed to study the kinetics of adsorption. The concerned equations are as follows:

$$\mathrm{Log}(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{qe}\right) t \quad (2)$$

where q_t (mg/g) is the amount of adsorbate adsorbed at any time t. k_1 and k_2 are the first order (min^{-1}) and the second-order (g/mg min) rate constants and t is the time (min).

Figure 3 (a,b) showed the time profile of the Fe(III) adsorption over SnO_2-AC composite and figure 3 (c,d) showed the kinetics model fitting. From the kinetic parameters (Table 1), it is evident that the adsorption data fit better to the pseudo first order kinetic model. The rate constant is found to be 0.012 min^{-1}.

Table 1
Pseudo first order and pseudo second order kinetic parameters for Iron adsorption on tin-oxide activated carbon nanocomposite

Kinetic models	Kinetic parameters	Values
Pseudo-first order	q_e experimental	11.38 mg/g
	q_e calculated	10.21 mg/g
	K_1	0.012 min^{-1}
	R^2	0.9926
Pseudo-second order	q_e calculated	8.49 mg/g
	K_2	0.004 g mg^{-1} min^{-1}
	R^2	0.9172

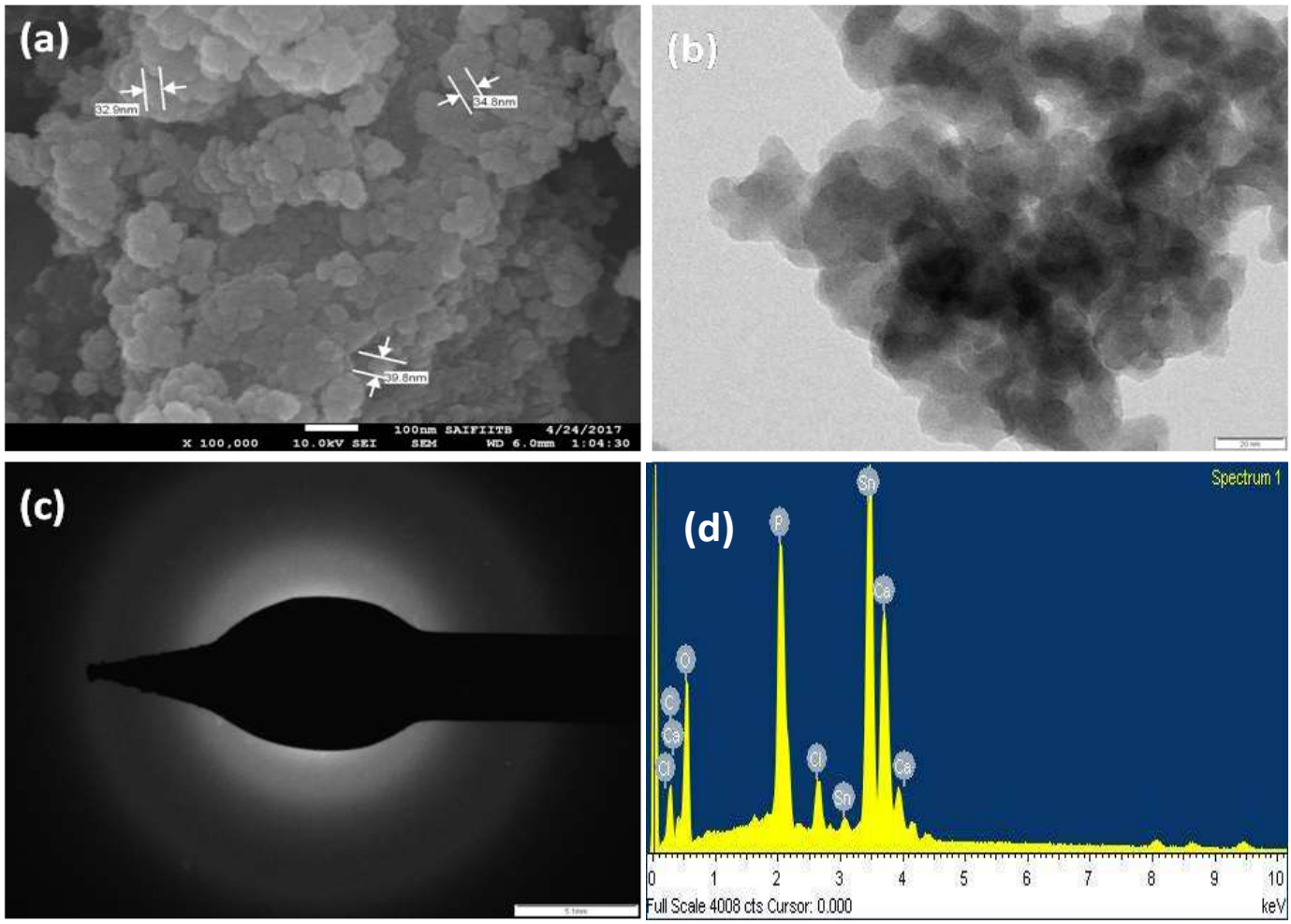


Figure 1: (a) SEM micrograph (b) TEM micrograph (c) SAED pattern and (d) EDS spectrum of SnO_2-AC nanocomposites

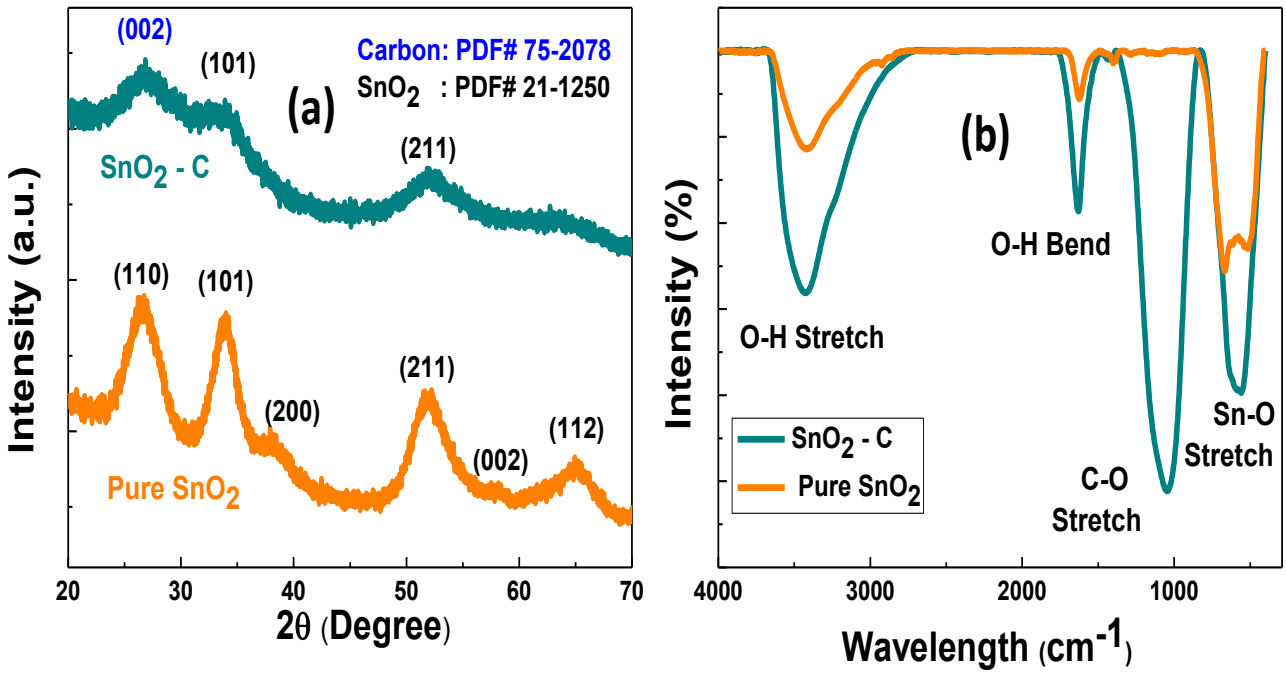
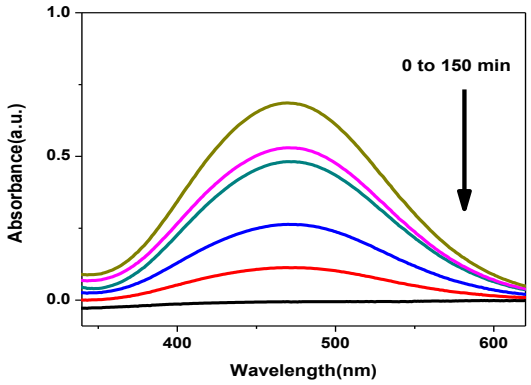
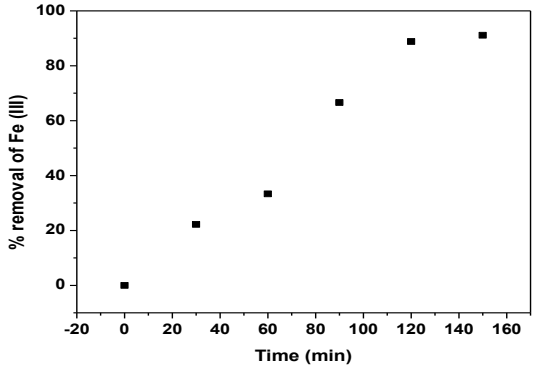


Figure 2: (a) XRD analysis (b) FTIR spectra of SnO_2 and SnO_2–AC nanocomposite



(a)



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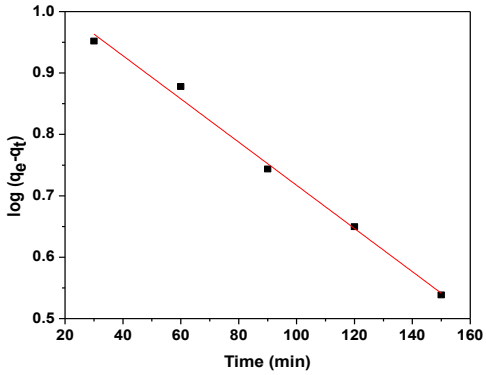
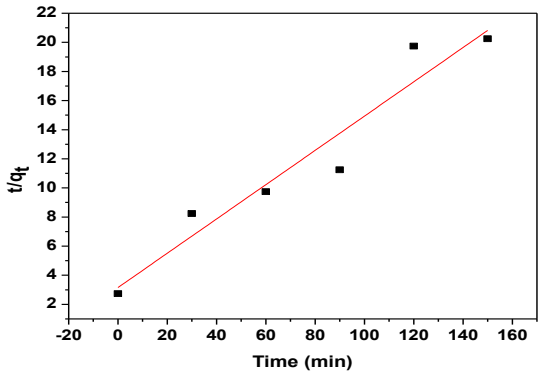
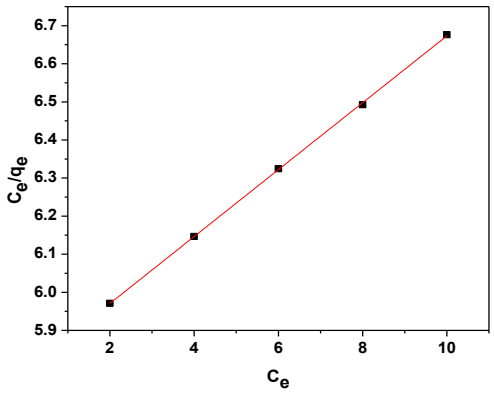


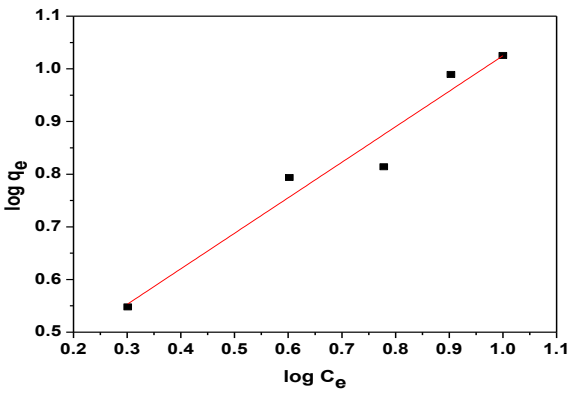
(c)



(d)



(e)



(f)

Figure 3: (a, b) Time profile of Iron adsorption at pH 6 (c) Pseudo first order and (d) Pseudo second order kinetic plots for Iron adsorption (e) Langmuir and (f) Freundlich isotherm plots for Iron adsorption

Table 2
Langmuir and Freundlich parameters for Iron adsorption

Isotherm models	Parameters	Values
Langmuir model	q_m (mg/g)	11.95
	K_L	0.015
	R_L	0.868
	R^2	0.998
Freundlich model	K_F (mg/g)	2.23
	1/n	0.674
	R^2	0.944

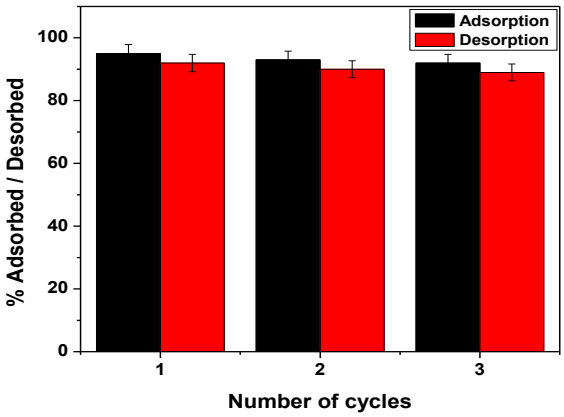


Figure 4: Percentage adsorption/desorption efficiency during three consecutive cycles

Concentration dependent studies: Langmuir and Freundlich isotherms were employed to monitor the adsorption process [Figure 3 (e and f)]. Equations (3) and (4) showed the linear form of Langmuir and Freundlich isotherms.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$$log\ q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

where K_L and q_m are the Langmuir constant (L/mg) and maximum adsorption capacity (mg/g) respectively. K_F and n are Freundlich capacity and adsorption intensity respectively. The R^2 value reflected that the Langmuir Model fitted better suggesting monolayer adsorption of iron over tin-oxide activated carbon nanoadsorbent (Table 2). The Freundlich constant (1/n) and separation factor (R_L) indicated the favorability of the adsorption process. The Langmuir adsorption capacity is calculated to be 11.95 mg/g which is in close agreement with the experimental q_e values of 11.38 mg/g.

Hence from the isotherm studies, it is evident that the nanocomposite could be an efficient adsorbent for Fe(III) adsorption due to good affinity towards iron and excellent adsorption capacity. As per pseudo first order mechanism, the adsorption process is physical and Langmuir fitting indicated monolayer adsorption of Fe(III) over SnO_2-AC nanocomposite surface.

Regeneration and reusability: Desorption of Fe from adsorbent surfaces was done using 1M NaOH. The reusability of the regenerated adsorbent was studied by observing three consecutive cycles of adsorption-desorption (Figure 4). The capacity retention was found to be ~85-90 % even after third cycle, indicating great reusability of the nanoadsorbent.

Conclusion

The present work demonstrates an approach towards utilization of low-cost precursors towards addressing burning issues like water decontamination. Saw dust was found to be a low-cost precursor for nanoporous activated carbon synthesis. SnO_2 nanoparticles were successfully incorporated into the nanoporous ACs using sol-gel technique. The synthesized adsorbent was characterized by FTIR, XRD, SEM, TEM and EDX techniques.

The adsorption of iron over SnO_2-AC was found to follow pseudo first order kinetics with rate constant 0.012 min^{-1}. ~ 92% of removal efficiency was achieved within 150 min time. Anion exchange reaction is most likely to be dictating the mechanism of adsorption. Efficient adsorption, good capacity and fast removal implied the potentiality of the synthesized nanocomposite as an efficient adsorbent for removal of iron.

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