Chemical Engineering Journal 163 (2010) 344–354

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Intensification of textile effluent chemical oxygen demand reduction by innovative hybrid methods

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ARTICLE INFO

Article history:
Received 22 March 2010
Received in revised form 31 July 2010
Accepted 3 August 2010

Keywords:
Sono-sorption
Sono-Fenton-sorption
Activated tea waste
COD reduction
Textile effluent

ABSTRACT

This study presents the reduction of textile effluent chemical oxygen demand (COD) by sonolysis, sorption, sono-sorption and sono-Fenton-sorption methods. Eco-friendly, cost effective, easily available tea waste activated using sodium hydroxide, formaldehyde, ultrasound irradiation (US), formaldehyde followed by US, and sodium hydroxide followed by US was used as an adsorbent. Better activation was obtained with formaldehyde followed by US treatment and this was confirmed from scanning electron microscopy (SEM) images obtained and Boehm titration. The effect of sorbent dosage, particle size and initial pH of the effluent on COD reduction was studied. The sono-Fenton-sorption with 50 mg/L of Fe(II) and 400 mg/L of H_2O_2 offered a maximum COD reduction of 95.5%. Langmuir–Hinshelwood kinetics was used to fit the data obtained with sono-sorption and sono-Fenton-sorption. The analysis of adsorption mechanism revealed that the intra-particle diffusion coefficient was enhanced by several folds by the incorporation of ultrasound. The changes in morphology of the sorbent before and after sono-Fenton-sorption were analyzed using SEM images. The changes in surface functional groups of the sorbent before and after sono-Fenton-sorption were analyzed using Fourier transform infrared (FT-IR) spectroscopy and Boehm titration. This novel hybrid treatment enhanced the biodegradability (BOD/COD) of the waste water from 0.31 to 0.71. The ecotoxicity test using disk diffusion method showed that the treated effluent was less toxic than untreated one. It was found that, the tea waste can be reused up to three cycles effectively.

1. Introduction

The textile industry wastewater contains various kinds of synthetic dyestuffs and other chemicals and the main processes generate wastewater in textile unit include washing, bleaching, dyeing and finishing [1]. There are about more than 100,000 different commercial dyes existing and over 7×10^5 tons of dyestuffs are produced annually [2,3]. It is estimated that 10–15% of the overall production of dyes is released into the environment mainly through wastewaters let out by the industry [4]. Many techniques have been developed for the removal of dyes from wastewaters but currently much attention has been focused on advanced oxidation processes (AOPs) [5]. Among the AOPs, sonolysis has received considerable attention due to its particular efficacy in degrading complex organic compounds [6,7]. On the other hand, sorption technique is proved to be an effective and attractive technique for the treatment of dye containing wastewater [8,9]. The inclusion of ultrasound having frequency above 20 kHz with sorption has found to significantly improve the efficiency of the process [10]. The incorporation of cavitation with sorption provides unusual conditions, which offer improved degradation of effluents [11,12].

Entezari and Sharif Al-Hoseini [13] reported higher removal of methylene blue from aqueous solution by sono-sorption compared to sorption using waste newspaper as an adsorbent and also reported that the enhancement is due to the activation of pores present in the waste newspaper by ultrasound. In an another study, Entezari and Soltani [11] investigated the simultaneous removal of cadmium and lead ions from binary aqueous solution using sono-sorption method in which biomass was used as an adsorbent (willow family (*Salicaceae*)) and reported that the presence of ultrasound reduced the adsorbent dosage compared to control. The simultaneous removal of copper and lead ions from binary aqueous solution has also been reported and more than 90% of lead and 60% of copper ions were removed within 2 min from the solution in the presence of sonication [12]. Sonawane et al. [14] studied the effect of ultrasound on the adsorption of phenol using nano clay and observed decrease in intra-particle diffusion resistance while sonication was used. Recently, Uddin et al. [15] investigated the removal of methylene blue by using tea waste as an adsorbent and

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doi:10.1016/j.cej.2010.08.013

reported that the adsorption equilibrium was achieved in 5 h for the concentration ranging from 20 to 50 mg/L whereas the extent of dye removal increased with an increase in initial dye concentration. Zhihui et al. [16] used Fe@Fe_2O_3 core–shell nanowires as Fenton iron reagent to degrade Rhodamine B and reported complete decolorization (at pH 2) within 60 min through sono-Fenton system. They compared the performance of Fe@Fe_2O_3 core–shell nanowires with other commercial zerovalent iron powders and reported that these nanowires showed much higher activity compared to other commercial materials. These researchers extended their studies at neutral pH [17] and indicated that novel Fenton iron reagent could be recycled in sono-Fenton system working at neutral pH and the efficiency of this system even reached 92% when 0.001 mol/L of Fe^{2+} was added.

In most of the studies reported in the literature, the simulated wastewater prepared with single dye was used to study the decolorization efficiency of sono-sorption method. In the present study, hybrid methods such as sono-sorption and sono-Fenton-sorption using activated tea waste as an adsorbent were investigated for the treatment of real textile effluent besides sonolysis and sorption. Since India is the largest producer and consumer of tea in the world, tea waste has been chosen as an adsorbent. The results obtained were analyzed with Langmuir–Hinshelwood kinetics and the relevant adsorption mechanism was also explored.

2. Materials and methods

2.1. Materials

The textile dyeing unit effluent was collected from a dyeing unit located at the southern part of Tamil Nadu, India and its physicochemical characteristics are given in Table 1. The tea waste was collected from the canteen located inside the campus and its characteristics are presented in Table 2. All the chemicals and reagents used for the experiments and analyses were of analytical grade and purchased from Chemspure, Chennai, India.

Table 1
Physicochemical characteristics of real textile effluent.

Parameter	Values
Color	Greenish Blue
pH	5.0–5.2
COD (mg/L)	29,333–30,667
BOD_5 (mg/L)	9,260
TDS (mg/L)	8,800
Density (kg/m^3)	973.8

2.2. Sonicator

The ultrasonic irradiation was carried out with sonicator of 3.5 L volume operating at a frequency of 30 kHz (Oscar Ultrasonics, OU-Mini type) and the transducer is located at the bottom of the bath. The temperature of the sonicator was controlled using cooling coil.

Table 2
Chemical and physical properties of tea waste used in the experiment.

Parameter	Value (%)
Chemical characteristics	
Water soluble components	5.2
Insoluble components	83.8
Moisture	8.0
Ash	3.0
Physical characteristics	
Bulk density	0.279 g/cm^3
Particle size	80–354 μm

2.3. Activation of tea waste

The discarded tea dust was collected and washed with water to remove the dirt particles [15]. It was then boiled in distilled water to remove methylxanthine, caffeine, tannin, lipids, amino acids, mineral substances and volatile compounds, and washed with distilled water till the wash liquor is free from color. The washed tea waste was then dried in an oven at 105 °C for 16 h. The size of the prepared tea waste was reduced using laboratory grinder. In order to improve the surface activity, tea waste was activated using sodium hydroxide, formaldehyde, ultrasound and two different sequential treatments such as formaldehyde followed by ultrasound and NaOH followed by ultrasound.

A known amount of tea waste was mixed with 10% NaOH solution and the mixture was stirred at atmospheric condition for 24 h. Then, it was filtered and the sorbent was washed with excess amount of distilled water till the pH of the wash liquor reaches the neutral conditions. The washed materials were dried in an oven in order to remove all the surface and entrapped moisture. Similarly, a known amount of sorbent was added into formaldehyde solution (36%) and 0.1 mol/dm^3 HCl and the mixture was gently stirred for 1 h at 50 °C. The treated waste was filtered and then dried. About 10 g of tea waste was added into 500 mL of distilled water and the contents were exposed to ultrasound irradiation for 30 min, to study the influence of ultrasound on the activation of tea waste. Two different sequential pretreatments such as formaldehyde followed by US (by treating the tea waste first with formaldehyde and then with ultrasound for 30 min) and NaOH followed by US were carried out. To find the best activation method, SEM analysis and Boehm titration were used.

2.4. Experimental

2.4.1. Sorption

The sorption experiments were carried out in 250 mL conical flask containing 100 mL of effluent and 6 g/L of activated tea waste. The entire contents were stirred at 700 rpm and the experiments were carried out at ambient conditions Sorption experiment was mainly carried out to identify the better activation method.

2.4.2. Sonolysis and sono-sorption

Sonolysis was carried out using 500 mL of effluent in sonicator and the sonolysis time was 180 min. To carry out sono-sorption, sorbent dosage of 6 g/L was added into 500 mL of effluent and the entire contents were sonicated for 180 min. The samples were collected from reactor at uniform time intervals (every 30 min) and were subjected to COD determination. The influencing parameters such as initial pH (1–10), sorbent size (80–354 μm) and dosage (2-6 g/L) were studied and the optimum values were arrived based on the maximum % COD reduction. In addition, in order to evaluate the reduction in sorbent size during sono-sorption, the sorbent was collected after use and dried. Then, the sorbent was screened and the undersize particles (that is the particles which are smaller than the studied size range) were weighed and was expressed in % w/w.

2.4.3. Sono-Fenton-sorption

In this process, the initial pH of the effluent was adjusted to 3.0 by adding concentrated HCl and 3 g of sorbent, 50 mg/L of Fe (II) and 500 mg/L of H_2O_2 were added into the effluent before sonication. Then, the mixture was sonicated for 180 min. The influencing parameters such as Fe(II) dosage, H_2O_2 dosage were studied and the optimum values were arrived based on the maximum % COD reduction. The blank experiments were conducted in the absence of tea waste and US (Fenton's process) and in the absence of tea waste (sono-Fenton process) to enumerate the contribution of individual process.

2.5. Characterization of sorbent

The changes in morphology of the sorbent before and after the desired process were observed using scanning electron microscopy (Hitachi S-4800, 15 kV). The qualitative analysis of surface functional groups on sorbent before and after use was studied by Fourier transformed infrared (FT-IR) spectroscopic analysis. In this analysis, aliquots of the sample were diluted and mixed with KBr and then the produced KBr pellets were then vacuum pressed. Absorbance spectra were recorded from 4000 to 400 cm^{-1} using FT-IR spectroscope (FT-IR-2000, PerkinElmer one). By comparison with standard frequency patterns, various characteristic chemical bondings (or stretching) were determined, from which functional groups present were arrived. The specific surface area of the activated tea waste before and after sono-sorption was studied by N_2 adsorption at 77 K using Micromeritics ASAP 2020, in which the sample was out gassed at 200 °C for 12 h.

2.6. Boehm titration

The Boehm titration was used to determine the number of surface functional groups. Weighed samples of tea waste were added into aqueous solutions (0.1 mol/L) of hydrochloric acid, sodium hydroxide, sodium carbonate and sodium bicarbonate separately. These vials were sealed and stirred for 48 h at 25 °C and then filtered. Then, 5 mL of each filtrate was pipetted out and the excess base or acid present therein was titrated with HCl or NaOH, respectively [18]. The amount of acidic groups was calculated by assuming: NaOH neutralizes carboxylic, hydroxylic (phenolic) and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; $NaHCO_3$ neutralizes only carboxylic groups [19]. The amount of basic groups was calculated from the amount of HCl that reacted with the basic groups of the carbon surfaces.

2.7. Point of zero charge measurements

To determine the pH at which the point of zero charge (PZC) occurs, 0.1 g of activated tea waste was added with 20 mL of 0.1 mol/L NaCl solution after adjusting the initial pH with NaOH or HCl solution. The containers were flushed with N_2, sealed and placed in a shaker for about 24 h, after which the pH of the solution was measured. The PZC occurs when there is no change in the solution pH after contact with activated tea waste [20].

2.8. Ecotoxicity test

The ecotoxicity of the effluent before and after treatment was studied using disc diffusion method. Disc diffusion method is one of the oldest and most widely used antimicrobial susceptibility testing methods in laboratories. The test was performed as outlined by the NCCLS [21]. Briefly, a suspension of *Escherichia coli* (MTCC 443) was spread on the agar media plates. Filter paper discs (6 mm in diameter) were impregnated with 15 μL of the effluent and placed on the inoculated plates. These plates were kept at 4 °C for 2 h and then incubated at 35 °C for 24 h. The diameters of the inhibition zones were measured with a ruler in millimetres. It should be noted that the values reported in the present study includes the disc diameter (6 mm).

2.9. Analytical methods

The COD was estimated using open reflux method and the BOD_5 was estimated by following standard methods [22]. A digital calibrated pH meter (Elico, Li 127 type) was used to measure the pH of the effluent.

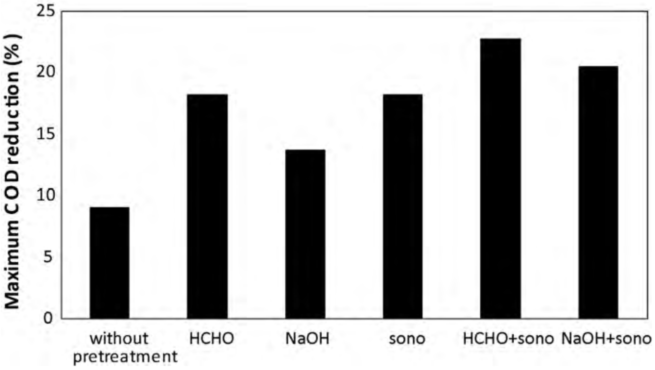

Fig. 1. Effect of different pretreatment of tea waste on maximum COD reduction (%) [conditions: effluent volume: 100 mL; sorbent dosage: 6 g/L; temperature: 30 °C; pH: natural (5.0)].

3. Results and discussion

3.1. Activation of tea waste

The influence of activation of tea waste on the reduction of COD was studied and the results are shown in Fig. 1. Without pretreatment, the maximum COD reduction observed was just 9.09%. Little higher maximum COD reduction (13.6%) was obtained when tea waste activated using NaOH. The reduction was little more (18.18%) for the HCHO pretreated and ultrasonically activated tea waste. Generally it is known that, ultrasound will produce higher activation compared to chemical pretreatment. In the present study, similar trend was observed in case of ultrasound and NaOH pretreated tea waste. Whereas the reduction observed for HCHO pretreated activated tea waste was similar to that of ultrasonically pretreated.

Highest COD reduction (22.73%) was achieved when the tea waste was activated using sequential pretreatment, i.e., HCHO followed by US. This may be due to the synergic effect of HCHO and US and moreover, the surface was activated chemically and mechanically through HCHO and US, respectively. This kind of treatment produces numerous micropores on the surface of the sorbent, which was confirmed from SEM images obtained (discussed later). The COD reduction of 20.45% was obtained when another sequential pretreatment, NaOH followed by US, was employed. The surface characterization of tea waste obtained using different pretreatments was done with Boehm titration and the results obtained are presented in Table 3. The application of ultrasound did not produce significant effect and the increment in COD reduction after US treatment was due to the cavitational effect. When the tea waste was pretreated with HCHO, better increment in surface acidity groups was observed whereas when tea waste was pretreated with NaOH, better increment in surface basicity groups was observed. The sequential treatment of HCHO followed by US and NaOH followed by US also produced enhancement in surface groups compared to that of other pretreatments. This is due to the fact that the inclusion of US did not affect the surface groups significantly. So, it can be concluded that, when tea waste pretreated by HCHO followed by US, the enhancement of COD reduction was due to increase in surface groups produced by HCHO and the effect caused by US on the surface of the tea waste. Hence, further experiments were performed using the tea waste activated using HCHO followed by US.

3.2. Sonolytic degradation

The effect of sonication time on % COD reduction was studied and the results obtained are shown in Fig. 2. The % COD reduction

Table 3
Boehm titration of surface groups on tea waste before and after different pretreatment methods.

Tea waste pretreatment method	Basic groups (mmol/g)	Acidic groups (mmol/g)	Carboxylic (mmol/g)	Phenolic (mmol/g)	Lactonic (mmol/g)
Before pretreatment	0.179	0.251	0.123	0.119	0.009
US	0.186	0.259	0.127	0.121	0.011
HCHO	0.209	0.344	0.156	0.147	0.041
NaOH	0.311	0.21	0.089	0.111	0.01
HCHO + US	0.215	0.349	0.113	0.191	0.045
NaOH + US	0.318	0.214	0.087	0.114	0.013

obtained after 180 min of sonication was 39%. In sonolysis, the COD reduction was due to acoustic cavitation, which involves a process of formation, subsequent growth and implosion of bubbles filled with vapor and/or gas. When these bubbles collapse explosively, the temperature and pressure in the bubbles can reach up to several thousand Kelvin and several hundred atmospheres, respectively [23,24]. Under these extreme conditions, the organic pollutants were decomposed by pyrolysis and hydroxyl radicals were produced due to the decomposition of water molecules. These highly reactive radicals are transferred to the bubble interface and then to the bulk solution, which promote the degradation of organic compounds. It has been proved that hydrophilic compounds with low vapor pressures were effectively destroyed in bulk solution by an oxidative degradation using hydroxyl radicals produced during bubble collapse. The hydrophobic compounds with high vapor pressures undergo thermal decomposition inside the bubbles [25]. In the present study, as real textile effluent was employed, the effluent might contain different organic pollutants that are hydrophilic or hydrophobic in nature. Thus in sonolysis, the COD reduction might be due to both the degradation mechanisms.

3.3. Sono-sorption using activated tea waste

The sono-sorption was carried out using activated tea waste as sorbent under the influence of US. The effect of time on % COD reduction for sono-sorption is shown in Fig. 2. It can be seen that the COD reduction observed with sorption was 22.73% and with sonication was 39.13%. When the sorption was performed in the presence of US, the COD reduction was 77.27%. The drastic increase in COD reduction with sono-sorption may be due to the synergistic effect of US and sorption. In the presence of ultrasonic irradiation, the large molecules of organic pollutants were converted into smaller molecules by pyrolytic decomposition and by oxidation [25]. Furthermore, the application of ultrasound increases the mass transfer and makes the pores present in the sorbent available for sorption. The results are in accordance with previous studies [11–14].

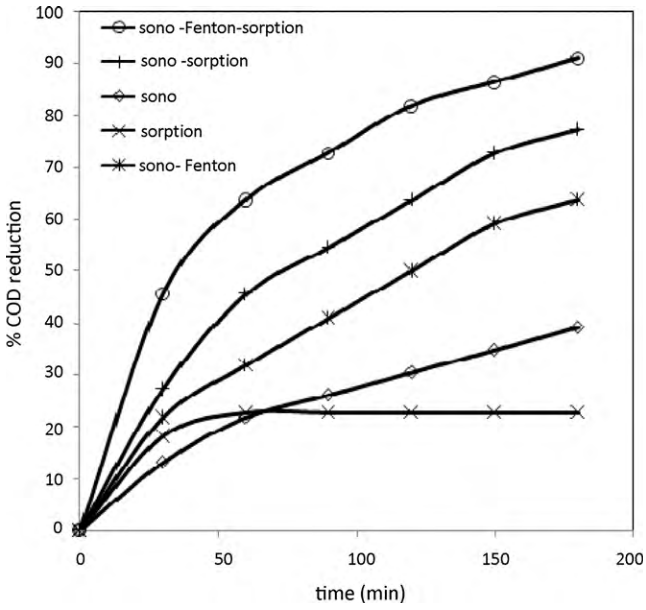

Fig. 2. Effect of time on % COD reduction in sorption, sonolysis,sono-sorption, sono-Fenton and sono-Fenton-sorption [conditions: effluent volume: 500 mL; initial pH = 5.0, sorbent dosage: 6 g/L (for sorption, sono-sorption and sono-Fenton-sorption)].

3.3.1. Effect of adsorbent dosage

The effect of adsorbent dosage on COD reduction in sono-sorption (SS) was studied and the results are shown in Fig. 3. The COD reduction observed for 2, 4, and 6 g/L of adsorbent dosage after 180 min was 54.5, 68 and 77.3%, respectively. The results showed that the COD reduction was increased with an increase in sorbent dosage and this may be attributed to the fact that the increase in dosage increased the availability of more adsorption sites. Similar results were reported by Entezari and Soltani [13] and Uddin et al. [15]. The other important effect due to the presence of sorbent is the increase in cavitation bubbles due to the supply of crevices and the wall of solid particle plays a vital role in producing tiny bubbles with a promotion of jet towards the wall. The wall of the particle may easily break the spherical symmetry of the large sized cavitation bubbles, which produces large amount of tiny cavitation bubbles. The increase in cavitation bubbles accelerates the production of oxidant radicals during their collapse, which in turn offer more degradation. Keck et al. [26] reported that the addition of inert particles double the reaction rate compared with the absence of particles. On the other hand, Nakui et al. [27] investigated the role of coal ash on the intensification of phenol degradation in the presence of US and concluded that the presence of inert particles led to increase in nucleation site for cavitation bubble due to its surface roughness. Similar conclusions were reported by Tuziuti et al. [28].

3.3.2. Effect of particle size

The effect of activated tea particle size on COD reduction was studied keeping other parameters as constant and its effect on the

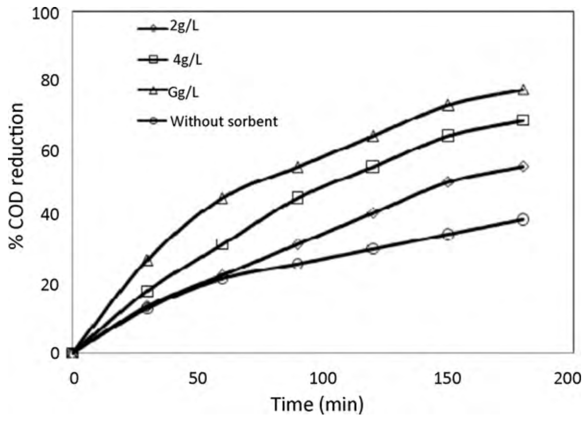

Fig. 3. Effect of sorbent dosage on % COD reduction in sono-sorption [conditions: effluent volume: 500 mL; pH: natural (5.0); frequency: 30 kHz].

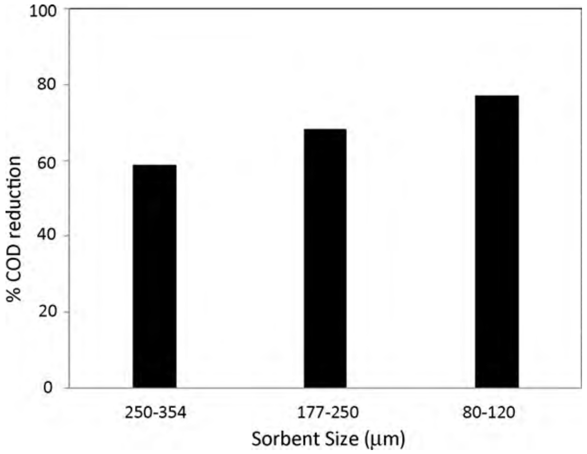

Fig. 4. Effect of sorbent size on % COD reduction in sono-sorption [conditions: effluent volume: 500 mL; natural pH (5.0); sonication time: 180 min, frequency: 30 kHz; sorbent dosage: 6 g/L].

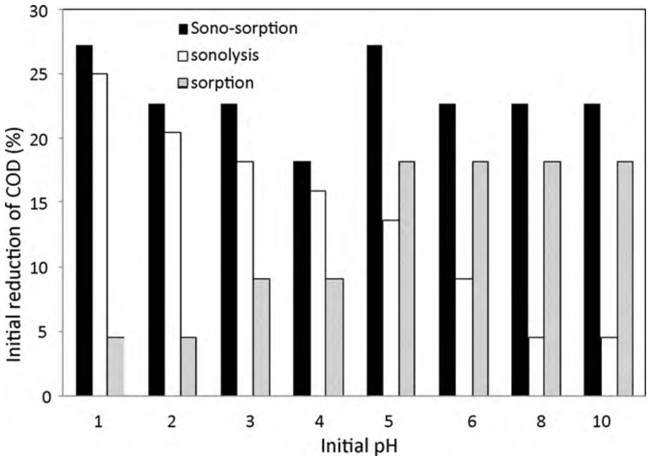

Fig. 5. Effect of initial pH of the effluent on % initial COD reduction during sorption, sonolysis and sono-sorption [conditions: effluent volume: 500 mL; sonication time: 30 min; frequency: 30 kHz; sorbent dosage (for sorption and sono-sorption): 6 g/L].

degradation is shown in Fig. 4. It was observed that the decrease in particle size increased the COD reduction. The sorbent size has two major effects; the decrease in particle size increases the surface area, which increases the adsorption rate and increase in number of particles will create more nucleation sites. For larger particles, the diffusion resistance to mass transport is higher [29] and most of the internal surface of the particle may not be utilized for sono-sorption, which reduces the efficiency.

The size of the sorbent before and after the sono-sorption was analyzed to find out the changes occurred on its size due to ultrasound irradiation. It was found that the amount of tea waste, which has lost its original size was about 8% for the size 80–120 µm. Whereas, very little (<3%) amount of tea waste was found to be affected for the larger particles (177–250 and 250–354 µm). The results showed that the ultrasound irradiation produced more breakage on smaller size particles compared to larger size particles. It should be noted that these particles were already exposed to ultrasound (with same frequency) during pretreatment. The breakage of sorbent particles leads to enhancement in surface area thereby increases the adsorption rate. In addition, increase in number of particles enhances the number of nucleation sites that accelerates sono-degradation. The specific surface area of activated tea waste before and after sono-sorption was found to be 21.02 and 11.13 m^2/g, respectively. The decrease in surface area clearly indicates the occurrence of sorption on tea waste.

3.3.3. Effect of initial pH

The influence of initial pH of the effluent on COD reduction by sonolysis and sono-sorption was studied. In order to investigate the initial pH, it is apt to analyze the initial degradation rate than the final one, since the pH changes as the reaction proceeds. The COD reduction profiles obtained as a function of initial pH of the effluent for sonolysis, sorption and sono-sorption are compared in Fig. 5. The results showed that the initial COD reduction was higher (25%) for sonolysis at pH 1. The initial COD reduction observed at pH 2, 3, 4, 5, 6 and pH 8–10 was 20.5, 18.2, 16, 13.6, 9, and 4.5%, respectively. Higher rate of degradation was occurred at acidic conditions in sonolysis and this may be due to the occurrence of more protonation and pyrolysis at acidic conditions [30,31]. The enhancement in degradation rate under acidic conditions can also be attributed to the higher rate of formation/accumulation of hydroxyl radicals, which enhanced the degradation of organic pollutants [32,33]. At pH 5–10, the initial COD reduction was found to be very less compared to acidic conditions. This is due to the lower concentration of hydroxyl radicals at these conditions because only about 10% of the hydroxyl radicals that are generated in the bubble can diffuse into the bulk liquid [1,34,35]. In addition, at pH 5–8, a higher number of hydroxyl radicals recombine to form H_2O_2 that leads to decrease in hydroxyl species concentration [1]. Similar trends were observed for the ultrasonic degradation of many organic pollutants, such as methyl orange, azo dyes, and nitro phenol [30,31,36].

In sorption, the initial COD reduction was found to be 4.55% at extreme acidic conditions (pH 1–2) whereas at pH 3–4, the initial COD reduction was 9.09%. Higher initial COD reduction (18.18%) was observed at pH 5 and similar reduction was observed at neutral and basic conditions.

In sono-sorption, the initial COD reduction observed for pH 1 was 27% and it was decreased gradually to 18% when the pH was increased to 4. Thereafter, the reduction was increased to 27.3% when the pH was increased to 5. The initial COD reduction was nearly almost same (22.73%) in the pH range 6–10. The initial reduction of COD was higher at acidic condition (pH 1) and decreased when the pH was increased from pH 2 to 4. When the pH was increased beyond 4, significant increase in reduction was observed. The results observed showed that the contribution due to sonolysis was very less when the pH was above 6. Therefore the COD reduction was found to remain constant in the pH range 6–10.

The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of the different pollutants present in the effluent [15,37]. The change in pH affects the adsorptive process through dissociation of several functional groups on the adsorbent surface active sites.

In the present study, the PZC of the activated tea waste was found to be 4.6. When the actual pH was greater than PZC, the surface of the tea waste may get negatively charged due to the adsorption of hydroxyl radicals and also the carboxyl group present on the surface of the tea waste may get deprotonated thereby producing negatively charged adsorption sites. Therefore, when the pH was greater than 4.6, the negatively charged radicals especially hydroxyl radicals were repelled by the active sites (negatively charged) and thus, all the hydroxyl radicals are available for the degradation. In addition, the positively charged pollutants present in the effluent were get adsorbed easily on the negatively charged active sites. Thus, at initial pH 5, higher COD reduction was observed. At neutral and basic pH, it was found that the initial COD reduction was almost constant (22.73%). In sono-sorption, after 180 min, the COD reduction was found to be 90.91% at an initial pH 5 whereas at neutral conditions (pH 6–8), the COD reduction was 86.36%. The COD reduction obtained at basic conditions after 180 min was 81.82%. The effect of initial pH on COD reduction was

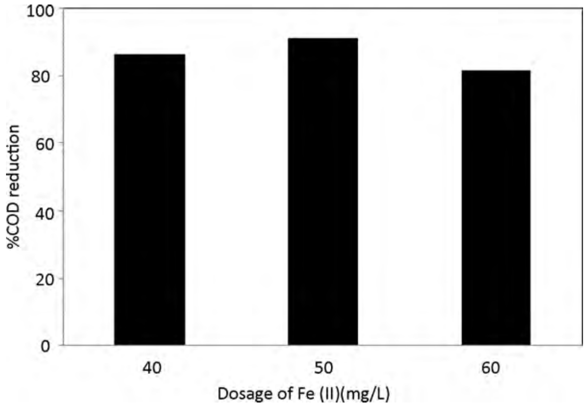

Fig. 6. Effect of Fe(II) dosage on % COD reduction during sono-Fenton-sorption [conditions: effluent volume: 500 mL; sorbent dosage: 6 g/L; H_2O_2 dosage: 500 mg/L; temperature: 30 °C; frequency: 30 kHz; sonication time: 180 min].

not investigated for sono-Fenton-sorption process because in all the sono-Fenton-sorption processes, the pH of the solution was adjusted to pH 3 to avoid iron precipitation as iron hydroxide [35].

3.4. Sono-Fenton-sorption

In sono-Fenton-sorption technique, sorption was performed in the presence of Fenton reagent under ultrasonic irradiation. The Fenton system uses ferrous ions and hydrogen peroxide and reaction between them produces hydroxyl radicals, which are strong oxidizing agents. Ferrous sulfate will produce Fe^{3+} in acidic medium and Fe^{3+} will in turn react with H_2O_2 to produce an intermediate $Fe\text{–}OOH^{2+}$ that can be decomposed into Fe^{2+} and $^{\bullet}OOH$ spontaneously. The Fe^{2+} produced reacts with H_2O_2 and produced hydroxyl radicals again and a cycle mechanism was established [38]. For this set of experiments, the pH was adjusted to 3 using sulfuric acid, in order to prevent the precipitation of iron as iron hydroxide [35]. In the present study, 50 mg/L of Fe(II) and 500 mg/L of H_2O_2 were used as Fenton reagent. It can be observed from Fig. 2 that the COD reduction was higher (90.91%) after 180 min for sono-Fenton-sorption compared to sono-sorption (77.27%) and sono-Fenton (63.64%). Blank experiment was conducted to analyze the effect of Fenton process alone and the COD reduction observed was 27.27%. The enhancement in sono-Fenton-sorption may be attributed to the factors such as enhanced production of hydroxyl radicals, decomposition of organic pollutants by pyrolysis due to US and combined effect of sonolysis, sorption and Fenton reaction. The effect of Fe(II) and H_2O_2 dosage on % COD reduction in sono-Fenton-sorption was studied and the results obtained are discussed below.

3.4.1. Effect of Fe(II) dosage

In order to investigate the influence of Fe(II) dosage, sono-Fenton-sorption was performed by varying the Fe(II) dosage from 40 to 60 mg/L, keeping H_2O_2 concentration (500 mg/L) as constant and at initial pH 3. The effect of Fe(II) dosage on % COD reduction is shown in Fig. 6 and the COD reduction observed for 40 and 50 mg/L of Fe(II) was 86.4 and 90.9%, respectively, but for 60 mg/L Fe(II), the COD reduction observed was 81.82%. The increase in % COD reduction when the concentration was increased from 40 to 50 mg/L may be due to the enhanced production of hydroxyl radicals that are responsible for oxidizing the organic pollutants. Further increase in Fe(II) concentration reduced the COD reduction, which is due to self quenching of hydroxyl radicals (Eq. (1)) that leads to decrease in concentration of both Fe(II) and hydroxyl radicals:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \qquad (1)$$

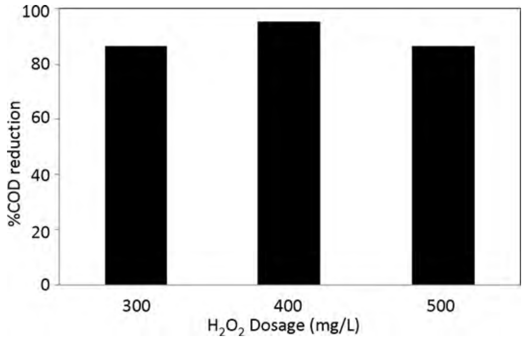

Fig. 7. Effect of H_2O_2 dosage of on % COD reduction during sono-Fenton-sorption [conditions: effluent volume: 500 mL; sorbent dosage: 6 g/L; Fe(II) dosage: 50 mg/L; temperature: 30 °C; frequency: 30 kHz; sonication time: 180 min].

Ghodbane et al. [35] analyzed the effect of addition of Fe(II) on degradation of Acid Blue 25 and reported the similar trend.

3.4.2. Effect H_2O_2 dosage

The influence of H_2O_2 dosage on COD reduction was studied by varying the dosage from 300 to 500 mg/L and the Fe(II) concentration was maintained constant as 50 mg/L. The results obtained are shown in Fig. 7. The higher COD reduction was observed with 400 mg/L and the increase or decrease in concentration than the optimum value decreased the COD reduction. The increase in % COD reduction may be attributed to the increase in H_2O_2 concentration and the decomposition of H_2O_2 into hydroxyl radicals at high temperatures and pressures formed during the collapse of cavitation bubbles [39]. The decrease in COD reduction when the dosage was increased beyond a certain value may be due to the detrimental effect which was occurred at higher concentration. At higher concentrations, the recombination reaction of hydroxyl radicals is more predominant and also H_2O_2 itself acts as the hydroxyl scavenger (Eq. (2)), which lowers the availability of the hydroxyl radicals for degradation process [35]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \qquad (2)$$

Teo et al. [40] reported that the increase in concentration of H_2O_2 increased the initial rate of degradation of 0.4 mM of p-chlorophenol with an increase in H_2O_2 concentration from 0 to 20 mM but further increase in H_2O_2 concentration to 40 mM showed a marginal effect on degradation. Furthermore, the increase in concentration beyond 40 mM decreased the rate of degradation.

3.5. Biodegradability analysis

The biodegradability of the waste water was analyzed to study the performance of different methods investigated. The biodegradability was quantified in terms of BOD_5 to COD ratio. The BOD_5/COD ratio of untreated effluent was 0.31. After sonication for 180 min, the ratio was found to be 0.45. The biodegradability after sorption, Fenton process, sono-Fenton and sono-sorption treatment were found to be 0.37, 0.42, 0.55 and 0.60, respectively. The biodegradability was enhanced to 0.71 using sono-Fenton-sorption process. This shows that the hybrid methods made waste water more biodegradable and the enhancement was highest in sono-Fenton-sorption due to the combined effect of sonolysis, Fenton reaction and sorption process. It shows that, after sono-Fenton-sorption process, the effluent can be easily treated using biological treatment methods.

3.6. Reusability of adsorbent

Repeated adsorption/desorption cycles were performed to examine the reusability of adsorbent and % COD reduction in sono-Fenton-sorption process. After 180 min, the COD reduction observed in first, second and third cycles are 95.5, 86.36 and 72.73%, respectively. The % COD reduction was found to decrease as the number cycles increases. This may be due to the damages occurred on the binding sites by pollutants and morphological changes on the surface due to the use of ultrasound. The continuous pitting on surface of the adsorbent contributes for the morphological changes. Under ultrasonic irradiation, the violent explosion of bubbles near the surface caused microjets which produced non-symmetrical shock waves that caused pitting on surface.

3.7. Adsorption mechanism

In liquid–solid adsorption, three major consecutive steps involved are transport of adsorbate molecules from the bulk liquid to the external surface of the adsorbent by diffusion through liquid boundary layer, diffusion from the external surface into the pores of the adsorbent (intra-particle diffusion), and adsorption of diffused pollutants on the active sites present internal surface of the pores. The last step is usually very rapid compared to that of first two steps. Hence, the determination of rate controlling step is restricted to only two steps (steps 1 and 2). Therefore, the overall rate of adsorption is controlled by either liquid film or intra-particle diffusion or by both.

The intra-particle diffusion coefficient (K_w) can be determined using the following equations [41]:

$$C = C_0 - K_w t^{1/2} \tag{3}$$

$$C_0 - C = K_w t^{1/2} \tag{4}$$

$$q = \frac{K_w t^{1/2}}{w} \tag{5}$$

$$w = \frac{C_0 - C}{q} \tag{6}$$

where C_0 is the initial COD of the effluent (mg/L), C is the COD of the effluent at any time t (mg/L), t is the time (min), q is the amount of pollutant adsorbed at any time t (mg/g), and W is the weight of adsorbent per volume of the solution (g/L).

From the plot between $(C_0 - C)$ and $t^{1/2}$, K_w was determined and the values obtained in the present study were 142.8, 1696.0 and 2304.0 mg/(L min) for sorption, sono-sorption and sono-Fenton-sorption, respectively. It can be observed that the intra-particle diffusion coefficient obtained in sono-sorption is much greater than the values obtained in the absence of US (sorption process). The results show that the incorporation of US enhanced the intra-particle diffusion by nearly 12 times. This may be attributed to the induced turbulence and additional convective mass transfer inside the pores caused by the micro jets with high velocity produced by US [41]. In addition, the cavitation also produced acoustic microstreaming or formation of tiny eddies that enhance the mass transfer at the liquid–solid interface nearby the sorbent surface and also within the pores. The intra-particle diffusion coefficient was still higher for sono-Fenton-sorption process. This is due to the fact that, highly reactive hydroxyl radicals were produced simultaneously through ultrasound and Fenton reagent. The complex pollutant molecules were oxidized by the hydroxyl radicals produced to simpler molecules. In addition, under the influence of ultrasound irradiation, pyrolysis also made the larger pollutant molecules to smaller molecules. Moreover sonolysis also increases the turbulence and in turn mass transfer. This enables the pollutants to diffuse easily through the pores and hence the intra-particle diffusion coefficient was enhanced considerably compared to other methods.

The mass transfer coefficient through liquid film can be determined using the following equation [42]:

$$V\left(\frac{dc}{dt}\right) = -k_s A(C - C_s) \tag{7}$$

where C_s is the COD of the pollutant at the surface (mg/L), C is the COD of the pollutant at the bulk liquid (mg/L), A is surface area for the external mass transfer (m^2), k_s is the liquid film mass transfer coefficient (m/min), t is the time (min), V is the volume of the solution taken for analysis (L).

The integration Eq. (7) with the boundary conditions, $C = C_0$, $t = 0$ and $C = C$, $t = t$, gives the following expression:

$$-\ln\left(\frac{c}{c_0}\right) V = k_s A t \tag{8}$$

To determine the liquid film mass transfer coefficient, $(-\ln C/C_0)V$ is fitted against time t. It is better to standardize the external mass transfer coefficient by total surface area of the adsorbent as k_sA, rather than k$_s$ alone. The values obtained for k_sA were 3.0×10^{-6}, 6.0×10^{-6} and 10.0×10^{-6} m^3/min for sorption, sono-sorption and sono-Fenton-sorption, respectively. It can be observed that, the k_sA was enhanced by 100% due to the addition of US than those obtained in the absence of US. This enhancement may be attributed to the extreme conditions generated during the violent collapse of bubbles in the bulk liquid. The symmetric collapse was hindered when the bubble was collapsed near the solid surface and thus the bubbles will collapse asymmetrically. These asymmetrical collapses in a heterogeneous system produced the micro jets with higher velocity. In addition, these symmetric and asymmetric collapses generate high pressure shock waves, which cause turbulence at the interface of liquid–solid; thereby the rate of mass transfer increased near the solid surface. In addition with high speed micro jets and shockwaves, the sonication also produced acoustic vortex micro streaming [6,43,44], which enhanced the mass transfer into the bulk solution as well as in the boundary layer [43]. Higher k_sA values were observed for sono-Fenton-sorption compared to sono-sorption. This is due to the fact that, as explained earlier, the combination of sonication and Fenton process produced numerous highly reactive hydroxyl radicals and also increased the turbulence, which offered higher values. Moreover, in sono-Fenton-sorption process, the observed k_sA values are highly influenced by the degradation of organic matter.

3.8. Adsorption kinetics

3.8.1. Langmuir–Hinshelwood kinetics

Langmuir–Hinshelwood kinetics is the most commonly used kinetic model to analyze heterogeneous reactions and is given as [43]:

$$r = \frac{k_r KC}{1 + KC} \tag{9}$$

where r is the rate of reaction (mg/(L min)), C is the COD of the solution at any time t (mg/L), K is the equilibrium constant for the adsorption of the substrate on sorbent, k_r is the limiting rate constant of reaction at maximum coverage under the given experimental conditions.

Eq. (9) can be rewritten as:

$$\frac{1}{r} = \frac{1 + KC}{k_r KC} \tag{10}$$

At initial conditions, $r = r_0$ and $C = C_0$, it can be written as:

$$\frac{1}{r_0} = \frac{1 + KC_0}{k_r KC_0} = \frac{1}{k_r KC_0} + \frac{1}{k_r} \tag{11}$$

The initial concentration of the organic pollutant is an important parameter in wastewater treatment processes. The initial rates were determined form the plot between C/C_0 versus t (plot not shown) [33]. It was observed that the initial rates were increased with an increase in initial concentration. The inverse of initial rate was fitted against inverse of initial concentration as shown in Fig. 8. The linear fit of obtained explains that the initial rates were well followed the L–H kinetics. The values of L–H parameters such as k_r and K are as determined. The k_r value was 1.77×10^{-2} and $2.56 \times 10^{-2}\,\text{min}^{-1}$ and the K value was 3.02×10^{-5} and 3.38×10^{-5} L/mg for sono-sorption and sono-Fenton-sorption, respectively. It can be observed that the higher values were observed for sono-Fenton-sorption compared to sono-sorption. This is due to the fact that the degradation was significantly enhanced due to the synergic effect of Fenton process and sorption in the presence of ultrasound irradiation.

3.8.2. Adam–Thomson relation

The initial adsorption kinetic coefficient can be determined using Adam–Thomson relation [10] and is given as:

$$\frac{dq}{dt} = K_1 C(q_m - q) - K_2 q \tag{12}$$

where q is the adsorption capacity of the sorbent (mg/g), C is the COD of the solution at any time t (mg/L), K_1 is the adsorption kinetic constant (L/(mg min)), K_2 is the desorption kinetic constant (min^{-1}), q_m is the maximum COD on the surface (mg/L), and t is the time (min).

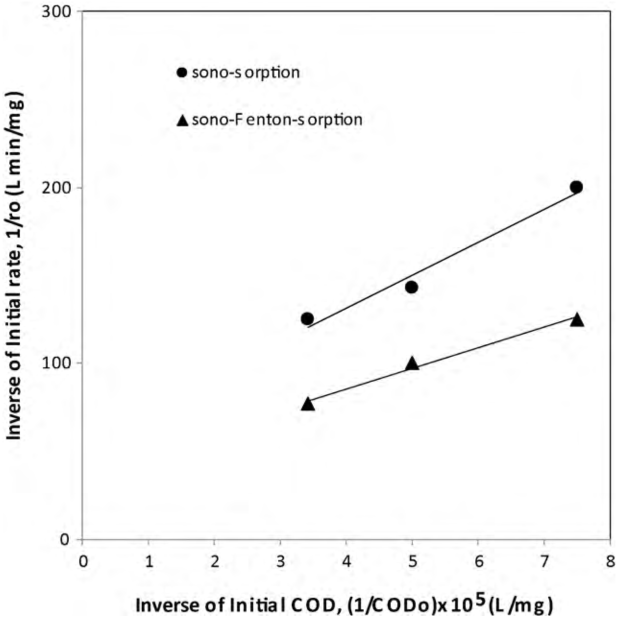

Fig. 8. Variation of the inverse of the initial rate versus the inverse of the initial COD of the effluent.

The incorporation of initial conditions ($t = 0$, $q = q_0$, and $C = C_0$) into Eq. (12) gives:

$$\left(\frac{dq}{dt}\right)_{t\to 0} = \frac{V}{W}\left(\frac{d(C - C_0)}{dt}\right)_{t\to 0} = K_1 C_0 q_m \tag{13}$$

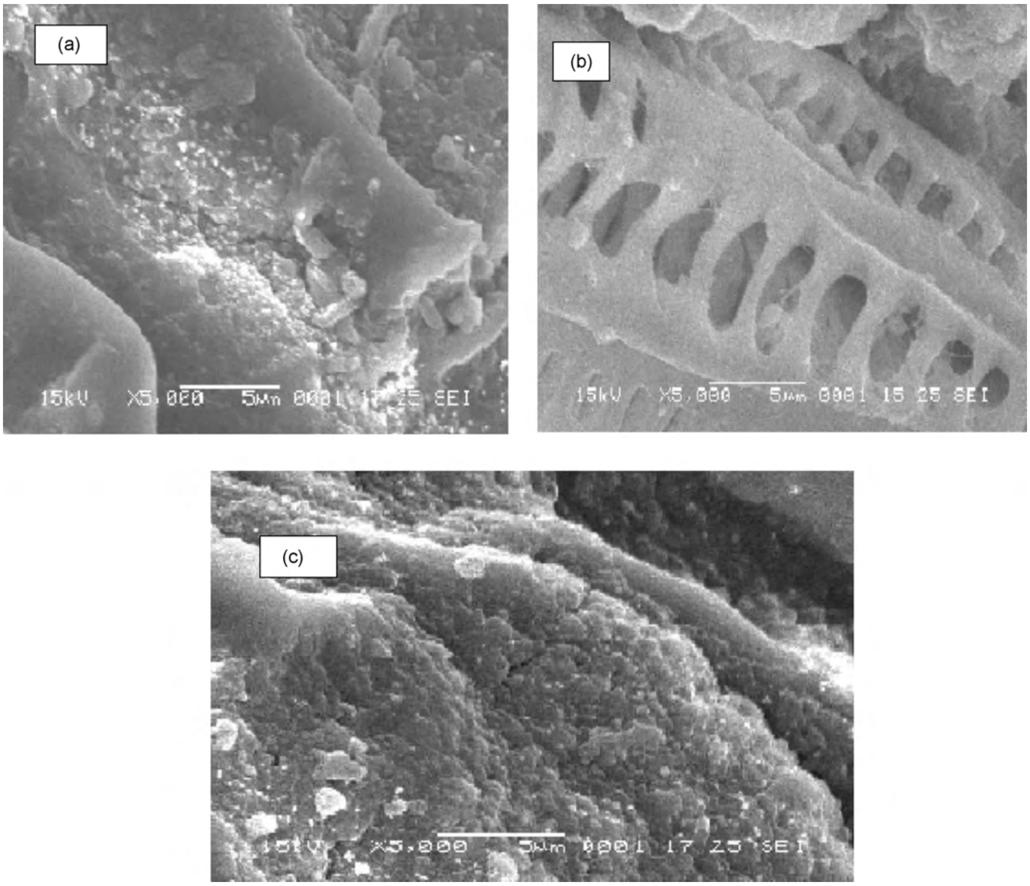

Fig. 9. SEM micrographs of tea waste: (a) untreated tea waste, (b) activated tea waste, and (c) tea waste after sono-Fenton-sorption process.

where V is the volume of the solution (L) and W is weight of the sorbent taken (g). The initial adsorption kinetic coefficient (γ) is given as:

$$\gamma = K_1 q_m = -\frac{V}{C_0 m}\left(\frac{dC)}{dt}\right)_{t\to 0} \tag{14}$$

The initial adsorption kinetic coefficients were determined from the initial slopes and the values obtained for sorption, sono-sorption and sono-Fenton-sorption were 2.27×10^{-8}, 4.54×10^{-8}, and 7.38×10^{-8} L/(g min), respectively. It can be seen that the value was doubled in the presence of US compared to that in the absence of US. Hydrodynamic effects induced by the sonication promote a significant increase in mass transfer across the boundary layer [10]. The enhancement of mass transfer across the liquid film may be due to the reduction in thickness of laminar boundary layer by the micro scale turbulence created by ultrasound. The coefficient was still higher for sono-Fenton-sorption process. This enhancement was due to the synergic effect of these processes such as sonolysis, Fenton process and sorption.

3.9. Surface analysis

The surface morphology of the sorbent was characterized using scanning electron microscopy (SEM) [45] and Fig. 9a shows the surface of the untreated sorbent, which contains rough and irregular layers that will enable sorption. The changes in the morphology of sorbent due to the pretreatment by formaldehyde followed by US is shown in Fig. 9b. It could be seen that the sonicated sample exhibits patterns of uniform micropores on the surface of pretreated sorbent and it might be caused by two modes of caviational bubble collapse. In the first mode, cavitational bubbles collapsed on the surface of the sorbent may cause direct damage by shock waves produced due to implosion. In the second one, the bubbles collapsed near the surface on the liquid bath caused microjets and these hit the surface of the sorbent, which produced non-symmetrical shock waves that caused pitting on sorbent surface. The sorbent with a majority of micropores adsorbs molecules more readily. The sorbent after sono-Fenton-sorption is shown in Fig. 9c. The surface of the sorbent was completely covered by thick layer of adsorbate. The micropores present on the surface (appeared in Fig. 9b) were not seen since the micropores were occupied by sorbate molecules. Similar pitting effect was reported on iron surface due to US by Dai et al. [46]. In order to confirm the adsorption of pollutants on sorbent and investigate the changes in surface functional groups, FT-IR analysis and Boehm titration were carried out and results were discussed later.

3.10. FT-IR analysis and Boehm titration

The FT-IR spectra of activated tea waste before and after sono-Fenton-sorption are shown in Fig. 10. The spectrum (Fig. 10a) shows a number of absorption peaks, indicating the complex nature of tea waste. The broad trough at 3454 cm^{-1} indicates the hydroxyl stretching vibration band. The presence of amide was observed at 1633 cm^{-1}. The band in the region 1300–1000 cm^{-1} may result from tertiary nitrogen species incorporated into the carbon structure [47]. The presence of amide and nitrogen species in the tea waste may be attributed to its plant origin. The spectra of tea waste after sono-Fenton-sorption is shown in Fig. 10b. Several new peaks were observed on this spectrum may be due to the adsorption of pollutants. It can be observed that the peaks in the range of 3900–3400 cm^{-1} may be due to OH stretching of phenolic and hydroxyl group. The peaks in the range 1650–1600 cm^{-1} may be due to stretching vibrations aromatic ring. The band around 1200–1100 cm^{-1} may be CO stretching vibrations of carboxylic and phenolic groups. The peak around 800 cm^{-1} may be due to out of plane bending vibrations of aromatic compounds. A shallow peak was observed in tea waste after sono-Fenton-sorption at 563 cm^{-1}. This low intensity peak may be due to the presence of Fe on the surface of the sorbent. So, it can be concluded that, some amount of Fe either used or unused was adsorbed on the tea waste. The surface acidity and basicity strengths of activated tea waste before and after sono-Fenton-sorption obtained through Boehm titration are presented in Table 4. The data show that the amount of acidic and basic groups on surface of the activated tea waste was increased significantly after use compared to before use. It clearly shows that different pollutants were adsorbed on the surface of the tea waste during sono-Fenton-sorption. In particular, significant increase in surface basicity groups was observed after sono-Fenton-sorption process. This may be due to the fact that, the pH of the solution (effluent) was maintained at 3, as indicated earlier and the pH was well below PZC (pH = 4.6). Therefore, the surface might have more acidic groups which attracted negatively charged pollutants during the process. Thus, at the end of the process, more basic groups were present on the surface. The obtained data is well in accordance with FT-IR spectra.

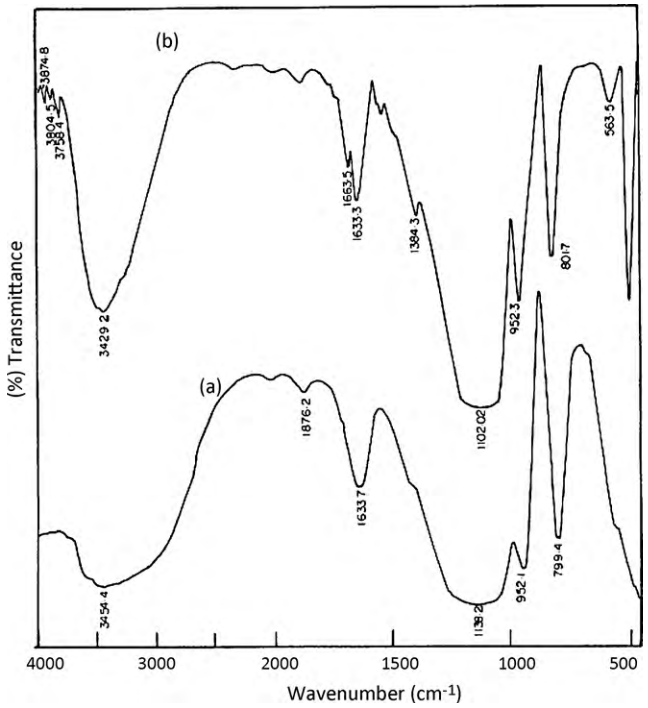

Fig. 10. FT-IR spectra of activated tea waste: (a) before use and (b) after sono-Fenton-sorption.

3.11. Ecotoxicity test

Oxidative degradation of textile effluent may produce organic intermediates/final products, which are sometimes more toxic than

Table 4
Boehm titration of surface groups on activated tea waste before and after sono-Fenton-sorption.

Activated tea waste	Basic groups (mmol/g)	Acidic groups (mmol/g)	Carboxylic (mmol/g)	Phenolic (mmol/g)	Lactonic (mmol/g)
Before use	0.215	0.349	0.113	0.191	0.045
After use	0.796	0.655	0.219	0.331	0.105

the untreated effluent. To analyze the toxicity of effluent after sono-Fenton-sorption, disk diffusion susceptibility test was carried out with *Escherichia coli*. Under similar conditions, the diameter of inhibition zone was found to be 19 mm with respect to untreated effluent whereas it was just 9 mm for effluent after treated with sono-Fenton-sorption process. These values includes disk diameter of 6 mm. So it can be concluded that, the ecotoxicity test clearly indicates that, this hybrid method reduced the toxicity of the effluent.

4. Conclusions

The present study presents the treatment of real undiluted textile effluent using hybrid methods such as sono-sorption, sono-Fenton and sono-Fenton-sorption using activated tea waste as an adsorbent. Five pretreatment methods were employed to activate the surface of tea waste and the results showed that sorbent treated with formaldehyde followed by US produced higher COD reduction than the other methods. SEM image of the sorbent activated by sequential pretreatment (HCHO + US) showed more number of micropores and rough surface than the sorbent treated with other methods. The increase in dosage and decrease in particle size increased the COD reduction due to enhancement in cavitation and increase in number of active sites. Initial pH of the effluent was found to affect the initial rate of sorption and degradation by sonolysis. In sonolysis, higher COD reduction was observed at acidic conditions and increase in pH reduced the initial COD reduction whereas, in sono-sorption, higher initial COD reduction was obtained at around pH 5. For the Sono-Fenton-sorption, the optimum dosage of Fe(II) and H_2O_2 was found to be 50 and 400 mg/L, respectively. The maximum COD reduction obtained in sorption, sonolysis, sono-sorption, sono-Fenton and sono-Fenton-sorption were 22.73, 39.13, 77.27, 63.64 and 95.5%, respectively.

The intra-particle diffusion coefficient and the global external mass transport coefficient values were found to be higher for the sono-Fenton-sorption. The experimental data were fitted with L–H kinetic model and the L–H parameters determined show that, the COD reduction was higher for sono-Fenton-sorption compared to sono-sorption process. The initial adsorption kinetic coefficient determined using Adam–Thomson relation was found to be higher for sono-Fenton-sorption. The adsorption of different organic pollutants on the surface of the tea waste was confirmed by SEM, FT-IR, Boehm titration and surface area analysis. In addition, ecotoxicity test using disk diffusion method was performed and the results showed that the treated effluent was less toxic compared to untreated one. The biodegradability (BOD/COD ratio) of the effluent was increased from 0.31 to 0.71 and this increment made the biodegradation of the treated effluent simple. It was also found that the tea waste can be effectively reused up to three cycles. Moreover, after the exhaustion, it may be incinerated and the ash produced can also be used as an adsorbent [15].

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