



Studies in liquid phase mineralization of cation exchange resin by a hybrid process of Fenton dissolution followed by wet oxidation

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ABSTRACT

The spent ion exchange resin poses a disposal problem. A novel process, dissolution followed by wet oxidation (WO), for mineralization of the cation exchange resin (gel type) was studied by using homogeneous CuSO_4 as the catalyst. The waste obtained after copper catalyzed dissolution of ion exchange resin by H_2O_2 was then further treated by wet oxidation for mineralization. The process parameters for dissolution were studied and optimum parameters were established. The wet oxidation was studied in the temperature range of 453–493 K and the oxygen partial pressure range of 0.34–1.38 MPa at pH 6.5. The kinetic data were modeled using the power law rate expression in terms of chemical oxygen demand (COD).

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1. Introduction

The cation exchange resin in acid form ($\text{R-SO}_3\text{H}$) is replacing sulfuric acid as the catalyst in many reactions of industrial importance such as esterification, etherification, alkylation and so on. The cation exchange resin is also used in the demineralization of boiler feed water in high pressure steam generators. In the nuclear industry the cation exchange resin is used to purify reactor coolant to trap any radioactive cations, for instance cesium in the system. Over the period, the resin gets deactivated due to loss of sulphonic acid groups (high temperature desulphonation of cation exchange resin due to local hot spots or prolonged use at elevated temperatures) and due to heavy metal contamination. The characteristics of spent resin depend on the actual application. For instance, the spent resin in the nuclear industry might have severe polymer matrix degradation due to radioactivity than that used in the chemical process industry (CPI) as the catalyst. The spent resin from nuclear industry needs elaborate treatment processes, which are excluded from the scope of this paper. The disposal of spent resin from chemical process industry poses a challenge to environment management system. The easiest way to dispose the spent resin is to have land filling at the designated site by local or state pol-

lution control authority. Incineration of spent ion exchange resin (polymer beads of styrene divinyl benzene copolymer) in a properly designed coal fired fluid bed boiler could also be a possible alternative. Ion exchange resins can also be treated by direct wet oxidation (WO), but due to involvement of aromatic polymeric matrix there is possibility of undesirable carbon formation, which might prolong wet oxidation. We have, therefore, concentrated on dissolution of polymer matrix by Fenton chemistry (H_2O_2) followed by conventional wet oxidation as an integrated process to mineralize cation exchange resin in order to address the waste disposal problem. There is practically no information available in the published literature on dissolution of resin followed by mineralization of the dissolved mass using wet oxidation process. We, therefore, thought it is desirable to study the possibility of mineralization of the ion exchange resin using liquid phase process to aid strategies for final disposal of spent cation exchange resin.

Kubota [1] has carried out decomposition of cation exchange resin by a century old Fenton chemistry [2] wherein dissolved Fe catalyses oxidation of substrate by H_2O_2 in liquid phase under acidic conditions. The major disadvantage of the Fenton chemistry-based process is that the product exhibits finite chemical oxygen demand (COD). The acetic acid, oxalic acid formed as low molecular weight compounds during Fenton reaction are refractory compounds towards oxidation by H_2O_2 [2]. Recently, Pignatello et al. [3] have presented a comprehensive review on the Fenton process.

The wet air oxidation or wet oxidation provides answers to above challenges. Wet oxidation is a powerful environmental engi-

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Nomenclature

COD	chemical oxygen demand (mg L^{-1})
$[\text{COD}]_i$	initial COD (mg L^{-1})
$[\text{COD}]_t$	COD at time 't' (mg L^{-1})
$[\text{CuSO}_4]$	concentration of copper sulfate (kmol m^{-3})
E	energy of activation (kJ mol^{-1})
H_{O_2}	Henry's constant for O_2 ($\text{kmol m}^{-3} \text{MPa}^{-1}$)
k	rate constant
k_0	pre-exponential factor
m	order with respect to O_2
n	order with respect to COD
$[\text{O}_2]$	oxygen concentration (kmol m^{-3})
p	order with respect to catalyst loading
P_{O_2}	partial pressure of O_2 (MPa)
r	rate of oxidation reaction with respect to COD reduction ($\text{mg L}^{-1} \text{min}^{-1}$)
R	universal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$)
t	time (min)
T	temperature (K)
TOC	total organic carbon (mg L^{-1})

neering process for the mineralization of toxic aqueous effluents, which cannot be either biotreated or too dilute to incinerate [4]. It is a subcritical mineralization of pollutants. The enhanced solubility of oxygen in aqueous solutions at elevated temperatures and pressures provides a strong driving force for oxidation. The free radical reaction proceeds through formation of various intermediates before total mineralization takes place. The low molecular weight acids are the stable intermediates formed. Many times their oxidation to CO_2 and H_2O is the rate-controlling step. Depending upon substrate exhibiting COD, the temperature used during wet oxidation process varies between 420 and 550 K and the partial pressure of oxygen varies between 0.1 and 3 MPa. The system pressure will be higher depending upon the temperature of operation and hence prevailing water vapour pressure. Also the system pressure depends upon purity of O_2 used varying from 90% O_2 to air containing about 21% O_2 . In order to reduce the severity of operating conditions and to achieve highest mineralization homogeneous as well as heterogeneous catalysts have been used [4–6]. Shende and Mahajani [7,8] and Shende and Levec [9] have studied wet oxidation of some acids, which are refractory products of Fenton chemistry.

The characteristics of spent resin would vary depending upon the source. In order to have uniform resin we have used 'virgin' gel type cation exchange resin to demonstrate the process at bench scale.

To mineralize cation exchange resin, it was thought desirable to dissolve the cation exchange resin first by the process demonstrated by Bibler and Orebaugh [10], wherein the dissolution of cation exchange resin was carried out by partial oxidation (Fenton process continued up to certain extent) to make the polymer matrix by degradation, more hydrophilic thereby make it to dissolve in water completely. Further this process requires less amount of H_2O_2 than that of the process demonstrated by Kubota [1]. The dissolution process can be then followed by wet oxidation. In order to keep operating cost lower it is desirable to have consumption of H_2O_2 as minimum as possible.

We, therefore, present here bench scale research investigation of a hybrid process FENTWO, Fenton process (dissolution) followed by wet oxidation to mineralize virgin cation exchange resin in gel form.

Table 1

Characterization of the virgin cation exchange resin.

Type	Strongly acidic gel type
Ionic form	H^+
Functional group	$-\text{SO}_3^-$
Matrix	Crosslinked polystyrene divinyl benzene
Exchange capacity	1.8 mequiv./ml of wet resin
Particle size range	0.3–1.2 (mm)
Moisture content	47–53% (w/w)

2. Experimental

2.1. Chemicals

The cation exchange resin used was of nuclear grade gel type (strongly acidic) resin INDION-223H, of Ion exchange (India) Ltd. The characteristics of the virgin cation exchange resin have been depicted in Table 1. Hydrogen peroxide (30%, w/v), copper sulfate, ferrous sulfate and all other reagents used for chemical oxygen demand analysis were of analytical reagent grade, purchased from s.d. fine Chemicals, Mumbai, India. Oxygen from gas cylinder with a minimum stated purity of 99.5% was obtained from Inox Air Products Ltd., India. The enzyme catalase (crystal suspension in water was obtained from Merck Co., Germany). Peroxide test strips for quick indication of H_2O_2 were also obtained from Merck Co., Germany. All solutions were prepared in distilled water.

2.2. Experimental set-up and procedure

We present experimental set-up and procedure for both processes, namely Fenton process to dissolve the resin and wet oxidation of the dissolved resin, separately.

2.2.1. Dissolution of resin

The dissolution studies were carried out in a 300 cm^3 capacity with i.d. 70 mm mechanically agitated glass reactor, immersed in a constant temperature bath. The details of the reactor are shown in Fig. 1. The reactor had an anchor type impeller of 60 mm diameter made of glass as depicted in Fig. 1. The speed of agitation was maintained at 4.2 rps. In each experiment calculated amount of cation exchange resin and catalyst (FeSO_4 or CuSO_4 , as the case may be)

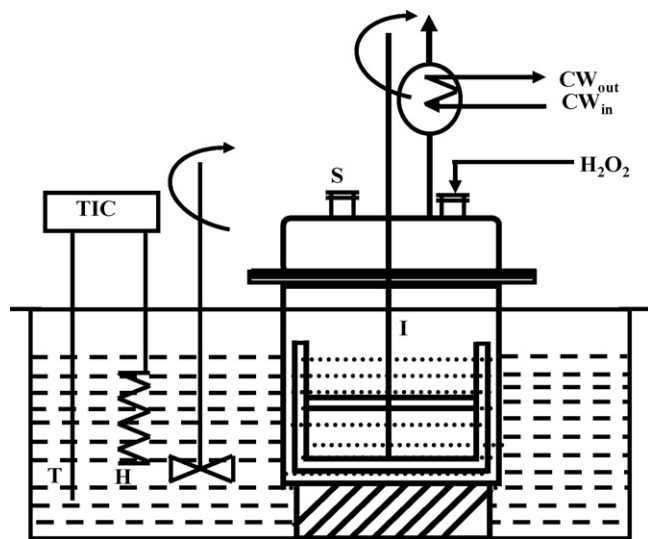


Fig. 1. Schematic diagram of experimental set-up for dissolution process (CW_{in} , cooling water inlet; CW_{out} , cooling water outlet; H, heater; S, sampling port; I, impeller; TIC, temperature indicator and controller; T, temperature sensor).

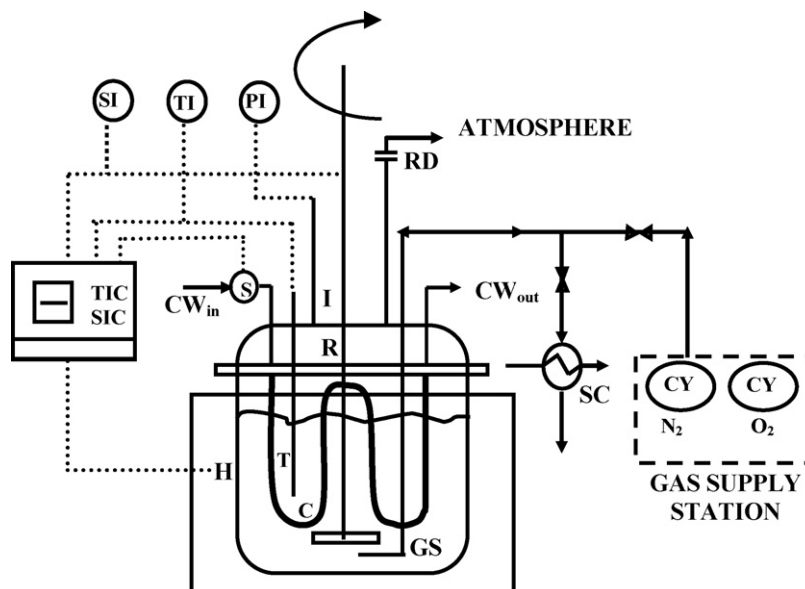


Fig. 2. Schematic diagram of experimental set-up for wet oxidation (PI, pressure indicator; TI, temperature indicator; SI, speed indicator; R, reaction vessel/autoclave; T, thermocouple; H, electric heater; RD, rupture disc; I, impeller; GS, gas sparger; SC, sample condenser; CY, gas cylinder; C, cooling coil; CW_{in}, cooling water inlet; CW_{out}, cooling water outlet; S, solenoid valve).

were added into the solution to be treated. The pH was adjusted to desired value by sulfuric acid. About 150 cm³ of aqueous suspension was used in each experiment. After setting the desired speed of agitation and temperature, hydrogen peroxide (30%, w/v) was then added batchwise at fixed intervals to avoid degradation of H₂O₂ by temperature and to prevent excessive temperature rise during the reaction. Before adding next quantity of H₂O₂ it was ensured that the concentration of free H₂O₂ in the liquid was less than 5 mg L⁻¹ as indicated by peroxide test strips (Merck make). The time required for dissolution was determined visually by taking a sample by wide bored pipette and holding it against the high intensity light. Prior to the analysis of the reaction mixture for COD, the enzyme catalase solution was added to knock off any unreacted hydrogen peroxide (if any, though complete H₂O₂ consumption was ensured by using peroxide strips before stopping the dissolution reaction), remained in the reaction mixture. This is done because free H₂O₂ in the presence of catalyst would degrade the dissolved mass further and thus alter the characterization (COD, total organic carbon (TOC) and intermediates). This ensured that the resin solution of uniform quality. But in commercial operation one can keep H₂O₂ therein to facilitate catalytic wet air peroxidation. Many experiments were duplicated to examine the reproducibility and the error in reproducibility was found to be less than 3%.

2.2.2. Wet oxidation

The wet oxidation studies were carried out in SS-316 Parr High Pressure Reactor of 600 cm³ capacity equipped with a Parr 4842 controller (Parr Instruments Company, USA). The details of the reactor are shown in Fig. 2. The reactor was equipped with a pressure indicator, a gas sparging tube into the liquid phase beneath the impeller. The impeller speed was varied between 0 and 20 rps with a variable speed motor. The reactor was also provided with a rupture disc as well as a non-return valve at the gas inlet as a safety device. The liquid samples were collected through a chilled water condenser-cum-cooler mounted on the reactor. The reactor was first charged with 300 cm³ of an aqueous solution of known COD and a predetermined amount of catalyst (CuSO₄). The reactor was then purged with nitrogen, prior to the start of the experiment to ensure an inert atmosphere inside the reactor and to check the

leaks. All the lines were closed. The speed of agitation was adjusted to a predetermined value. The reaction temperature was set. The reactor contents were heated to the desired temperature. Once the temperature was attained, the sample was withdrawn through a sample condenser. This was deemed to be zero time for the reaction. In the catalytic reaction, a catalyst of known concentration was added while charging the reaction mixture in a reactor. As soon as the zero time sample of the reaction was taken, oxygen was sparged into the reactor to a predetermined pressure level and maintained at that value while collecting samples for COD analysis. In all experiments, it was ensured that oxygen was available in far excess than that of theoretically required. The experiments were carried out at different temperatures, oxygen partial pressures and at various catalyst concentrations for the kinetic study. The variation in COD measurement was less than 3% during wet oxidation.

2.3. Analytical techniques

The standard dichromate reflux method [11] was used for chemical oxygen demand. The total organic carbon was measured with the help of "ANATOC SERIES II, TOC analyzer, SGE Australia". The scanning electron microscopy (SEM) analysis was done by using JEOL-JSM6380LA SEM instrument of JEOL Ltd., Japan. Oxalic acid was analyzed by using high-performance liquid chromatography (Knauer, HPLC model with a pump module no. K-501 and detector module no. K-2501) equipped with RP-18 column (Merck make) of 250 mm length and a UV detector at $\lambda = 210$ nm. A mobile phase used was phosphate buffer of pH 2.5 at flow rate of 0.8 ml min⁻¹. SO₄²⁻ was analyzed by using high-performance ion chromatography (DIONEX, USA, HPIC model with pump module GS50 and electrochemical detector module ED50) equipped with AS 11 column (DIONEX make) and an electrochemical detector in conductivity mode. The eluent used was 10 mM NaOH at 0.1 ml min⁻¹.

3. Results and discussion

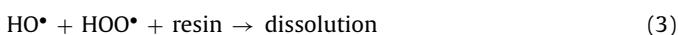
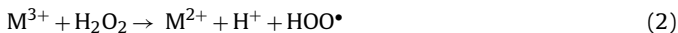
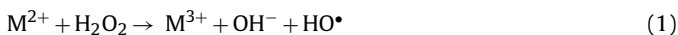
In the present investigation the mineralization of gel type cation exchange resin was studied by dissolution by Fenton process fol-

lowed by subsequent wet oxidation of the resultant dissolved mass.

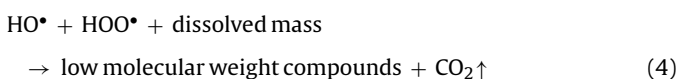
3.1. Fenton process (dissolution)

The metal ion (M^{2+}) catalyzed Fenton process follows following reaction pathways:

Main reactions:



Side reactions:



During the dissolution reaction various short lived species, viz. hydroxyl (HO^\bullet) and perhydroxyl (HOO^\bullet) radicals are formed. HO^\bullet radical is one of the most powerful oxidizers ($E^\circ = 2.73$ V). It is twice as reactive as chlorine, with an oxidation potential between that of atomic oxygen and fluorine. These radicals react with the polymeric matrix and effect dissolution. During dissolution side reactions (Eqs. (4) and (5)) such as further oxidation of the dissolved mass and decomposition of H_2O_2 also take place. H_2O_2 is costly and dangerous for storage, so emphasis was given for dissolution only (partial oxidation up to complete dissolution of resin charged) and not to reduce COD. Further, for dissolution process the primary constraint considered was maximum dissolution with minimum requirement of H_2O_2 (30%, w/v) per gram of resin in considerably less amount of time. So other parameters (catalyst concentration and resin loading) were selected by studying their effect on dissolution in terms of H_2O_2 requirement and safety constraints associated with the Fenton process, i.e. catalyst concentration should be as low as possible to avoid the possible danger of runaway reaction. The % dissolution was defined as percentage of initial resin dissolved (on dry basis). Some preliminary experiments indicated that the good dissolution, in our opinion, was possible only at 368 K. The various parameters for dissolution were studied at 368 K and at initial pH 2 (as cation exchange resin is acidic and Fenton process requires low pH). Further at 368 K the reaction exhibited an induction period of 2.25–2.5 h (no dissolution was occurred in first 2.25–2.5 h). It was observed that all $-SO_3H$ was oxidized to SO_4^{2-} , as expected.

3.1.1. The catalyst for dissolution process

Copper sulfate ($CuSO_4$) has been reported to be very good catalyst for wet oxidation, particularly for low molecular weight acids [7,8]. It was, therefore, thought desirable to use $CuSO_4$ as the catalyst for the dissolution process as well, in place of the conventional catalyst $FeSO_4$ used in the Fenton process. In order to study the effect of catalyst on the performance of dissolution reaction, experiments were conducted at 368 K with resin loading of 150 g kg^{-1} (15%, w/w) using equimolar amount (0.02 kmol m^{-3}) of catalyst. The results are depicted in Table 2. It was observed that complete dissolution was possible within 3 h by using $CuSO_4$ as the catalyst. However, $FeSO_4$ catalyst required prolonged reaction time (6 h) for the same dissolution. Further, the dissolution with $CuSO_4$ catalyst required less amount of H_2O_2 than that with $FeSO_4$. The initial pH for the dissolution process was kept at 2. It was observed by Oliveira et al. [12] that most favorable pH for Fe^{2+} catalyzed Fenton reaction was between 3 and 3.5. It was also observed that at pH less

Table 2

The catalyst for dissolution process.

	Catalyst	
	$CuSO_4$	$FeSO_4$
%Dissolution	100	98–99
Final COD (mg L^{-1})	116,000	103,177
Final TOC (mg L^{-1})	42,500	40,553
H_2O_2 (30%, w/v) required/g resin charged (ml)	0.53	0.71
Time of reaction (h)	3	6

than 3, the process becomes less effective. This is because at very low pH values, the regeneration of the Fe^{2+} (through the reaction between Fe^{3+} and H_2O_2) is inhibited because the formation of Fe^{3+} peroxocomplexes (as intermediates) decreases when pH decreases. It might not be the case with Cu^{2+} at low pH. That is possibly why $CuSO_4$ catalyst outperformed $FeSO_4$ catalyst under the experimental conditions. Thus the choice of $CuSO_4$ as the catalyst was obvious even for the Fenton process.

3.1.2. Catalyst concentration

In order to study the effect of catalyst concentration on the dissolution, experiments were performed at 0.01, 0.02 and 0.04 kmol m^{-3} of catalyst concentration (Table 3). It was observed that at catalyst concentration of 0.01 kmol m^{-3} jelly was formed. The quantity of H_2O_2 required and dissolution time were practically the same at concentrations of 0.02 and 0.04 kmol m^{-3} of $CuSO_4$. The reason behind this was the short span of dissolution reaction as the reaction exhibited an induction period of 2.25–2.5 h at 368 K. So the actual dissolution reaction was getting completed within 0.5–0.75 h after induction period. The higher catalyst concentration may cause vigorous decomposition of H_2O_2 , which can cause dangerous conditions as more peroxide is present with large amount of oxidisable material at higher catalyst concentration. In Fenton process, safety is of prime concern as we handle dangerous H_2O_2 . It should be noted that many people label H_2O_2 as 'green' chemical because one of the products of degradation is H_2O . However, from process engineering point of view it is 'red' chemical due to safety issues associated with its handling and reaction. The studies pertaining to dissolution were restricted at catalyst concentration of 0.02 kmol m^{-3} . From Table 3, it can be seen that by adding more $CuSO_4$ there is marginal increase in COD/TOC.

3.1.3. Resin loading

It was thought desirable to study the effect of resin loading on dissolution using $CuSO_4$ as catalyst. This effect was studied in the loading range of $30\text{--}300 \text{ g kg}^{-1}$ (3–30%, w/w) with 0.02 kmol m^{-3} of catalyst concentration. The experimental results are tabulated in Table 4. The profound effect of resin concentration on the course of dissolution was observed. The results depicted in Table 4 show that the % dissolution improved with increase in the resin loading up to 150 g kg^{-1} (15%, w/w). But at 300 g kg^{-1} (30%, w/w) a jelly type mass was formed which was dissolved in water after dilution to 50%. Further, it was observed that higher resin loading at 15% (w/w)

Table 3

Catalyst concentration.

	Catalyst concentration		
	0.01 kmol m^{-3}	0.02 kmol m^{-3}	0.04 kmol m^{-3}
%Dissolution	Jelly was formed	100	100
Final COD (mg L^{-1})	–	116,000	123,000
Final TOC (mg L^{-1})	–	42,500	45,000
H_2O_2 (30%, w/v) required/g resin charged (ml)	0.53	0.53	0.53
Time of reaction (h)	3	3	3

Table 4
Resin loading.

	Resin loading		
	3% (30 g kg ⁻¹)	15% (150 g kg ⁻¹)	30% (300 g kg ⁻¹)
%Dissolution	100	100	Jelly was formed
Final COD (mg L ⁻¹)	16,700	116,000	–
Final TOC (mg L ⁻¹)	7900	42,500	–
H ₂ O ₂ (30%, w/v) required/g resin charged (ml)	1.55	0.53	0.33
Time of reaction (h)	3	3	6

resulted in less consumption H₂O₂, faster dissolution compared to (3%, w/w).

In order to have a feel of the process of dissolution at microscopic level, scanning electron microscopy analysis of the ion exchange resin during the course of dissolution was done. For this purpose a typical experiment was carried out at 368 K with 150 g kg⁻¹ (15%, w/w) of resin and CuSO₄ concentration of 0.02 kmol m⁻³. The samples of slurry were withdrawn at different time intervals. The samples were then immediately collected over filter paper to soak the surface water content of the sample. After removing the water the samples were dried in a lime filled desiccator at 303 K. These dried samples were then analyzed by SEM. Fig. 3 exhibits the SEM images of fresh ion exchange resin and resin at the time just before the dissolution. It can be seen that ion exchange resin started disintegration during the course of the reaction. We postulate that the disintegration as seen in Fig. 3(b) could be because of two reactions. First the matrix attack by hydroxyl radical resulted in matrix collapse. Secondly, due to further oxidation, CO₂ is formed (Eq. (4)) and the entrapped CO₂ might exert high

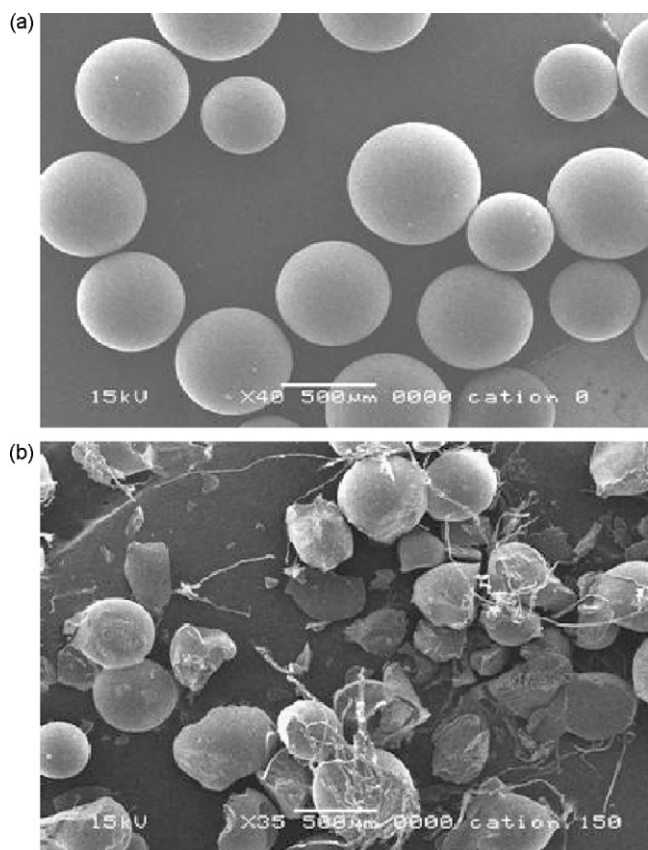


Fig. 3. Scanning electron micrographs (SEM) of cation exchange resin ((a) zero time, (b) after 2.5 h).

Table 5
Characterization of the products of dissolution.

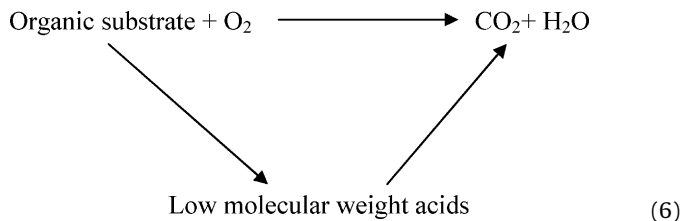
COD	~116,000 mg L ⁻¹
TOC	~42,500 mg L ⁻¹
Oxalic acid	~13,600 mg L ⁻¹

enough pressure to disintegrate the polymer matrix. In our dissolution process the end effect of matrix going into solution is more important than by which single or mixed mechanism it is getting dissolved.

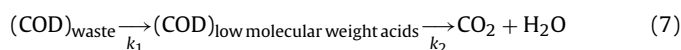
For wet oxidation study, a batch of 150 g kg⁻¹ (15%, w/w) was carried out by maintaining pH at 2 and by keeping reaction temperature at 368 K. At the end of the reaction, the residual H₂O₂ was knocked off by using catalase. The characterization of the waste is given in Table 5. This mass was further used for wet oxidation by keeping CuSO₄ therein and adding make up CuSO₄ as the case may be. It is interesting to note that one of the stable products of the Fenton oxidation process was oxalic acid. No acetic acid was detected. The detailed characterization w.r.t. other products of degradation was excluded from the scope of this investigation as our objective was to mineralize whatever was formed during the Fenton dissolution process.

3.2. Wet oxidation process

For wet oxidation study the waste obtained from dissolution process was diluted to 500 mg L⁻¹ of COD and pH was adjusted to 6.5 (about neutral). The wet oxidation of organic substrate in the aqueous phase involves free radical mechanism. The hydroxyl radicals formed are also once again oxidizing agents. In general wet oxidation can be represented as [4].



The steps involved during the wet oxidation are the destruction of organic molecules (COD reduction) into lower molecular weight acids and subsequent oxidation of these acids into CO₂ and H₂O and the simultaneous oxidation of organic compounds into CO₂ and H₂O. The waste consists of a mixture of various organic compounds contributing to COD. Our preference to characterize the waste in terms of COD over total organic carbon content lies in the fact that TOC analysis does not reflect in the quantification of COD when compounds containing oxygen in the molecule, such as acetic acid, oxalic acid are present in the waste. Also contribution of other atomic species to COD like H, S, etc. is neglected in TOC analysis. The kinetics of destruction of low molecular weight compounds like acetic acid, oxalic acid, etc. is influenced by other free radicals present. In order to avoid complexity and make design approach reliable and simple it was thought that it is better to have results expressed in terms of COD reduction of original substrate represented by following path [7]:



Thus in wet oxidation, the reaction would exhibit two different kinetic paths, viz. the fast oxidation of organic substrate followed by slower oxidation of low molecular weight compounds formed such as acetic acid, oxalic acid. The knowledge of kinetics of both steps is desirable. On the other hand, if complete wet oxidation is desired

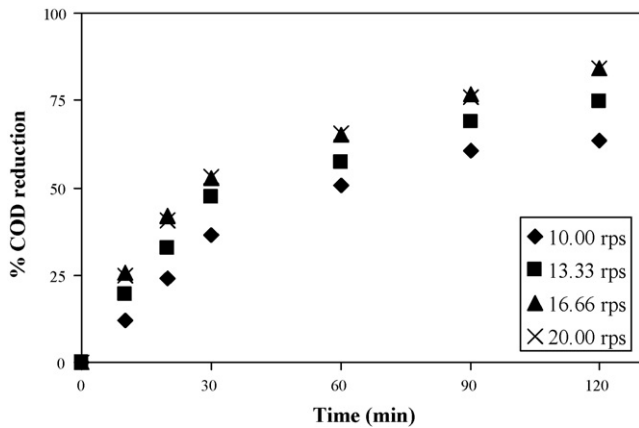


Fig. 4. Effect of intensity of turbulence on COD reduction (initial COD 500 mg L^{-1} , 473 K , O_2 partial pressure 0.69 MPa , $\text{pH } 6.5$, $\text{CuSO}_4 \text{ } 4.70 \times 10^{-4} \text{ kmol m}^{-3}$).

to recycle the water, the knowledge of the second step would be essential to design the wet oxidation system.

3.2.1. Mass transfer considerations

Wet oxidation is heterogeneous gas–liquid reaction. The diffusion of O_2 from the bulk gas phase into a liquid phase and the reaction of dissolved oxygen with organic substrate (COD) in the liquid phase is the series process. The resistance of gas phase for diffusion of O_2 was deemed to be negligible due to high diffusivity of O_2 , high temperature of gas phase and low solubility of oxygen in water at such high temperatures employed in wet oxidation. In order to discern true kinetics, it is necessary to eliminate the diffusional resistances. The mass transfer resistance offered by the liquid phase for diffusing dissolved oxygen from gas–liquid interface to the bulk of liquid phase depends on the intensity of turbulence in the liquid phase. The effect of speed of agitation on the rate of reaction may be deemed as a gauge to measure the intensity of turbulence. Therefore, the effect of speed of agitation was studied in the range of 10–20 rps. The effect is depicted in Fig. 4. It was observed that the liquid side mass transfer resistance was completely eliminated at impeller speed of 20 rps. Thus to get true kinetics all further experiments were carried out in the kinetically controlled regime. As solution is very dilute, $\text{COD} \sim 500 \text{ mg L}^{-1}$, the solubility of oxygen was considered to be same as that of in water and was estimated from the data published by Crammer [13].

3.2.2. Kinetic study

The kinetics of catalytic wet oxidation of the waste obtained after Fenton process was studied in the temperature range of $453\text{--}493 \text{ K}$ and the oxygen partial pressure in the range of $0.345\text{--}1.38 \text{ MPa}$ at a near neutral pH (6.5). The catalyst (CuSO_4) concentration was varied in the range of 1.54×10^{-4} to $6.16 \times 10^{-4} \text{ kmol m}^{-3}$. The effect of temperature on COD reduction is shown in Fig. 5.

As wet oxidation is very complex and it proceeds through formation of various reaction intermediates through numerous pathways modeling of each individual reaction would be impractical. Therefore, a lumped parameter model was used to develop an intrinsic rate equation for COD.

The rate expression by using power-law expression for first and second steps in Eq. (2) can be written as

$$r = -\frac{d[\text{COD}]}{dt} = k[\text{O}_2]^m[\text{COD}]^n[\text{CuSO}_4]^p \quad (8)$$

where $k = k_0 \exp(-E/RT)$

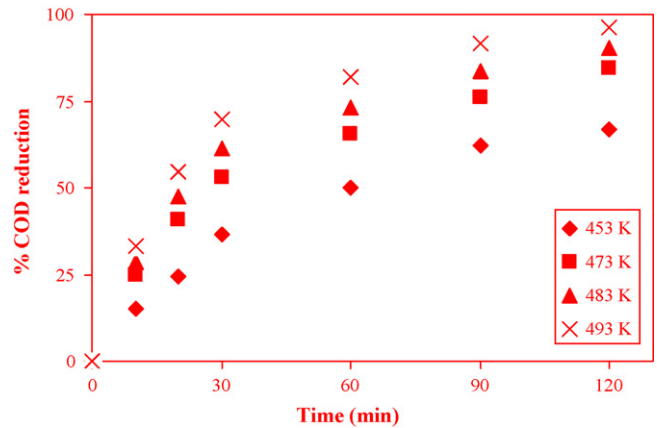


Fig. 5. Effect of temperature on COD reduction (initial COD 500 mg L^{-1} , O_2 partial pressure 0.69 MPa , $\text{pH } 6.5$, $\text{CuSO}_4 \text{ } 4.70 \times 10^{-4} \text{ kmol m}^{-3}$).

The oxygen concentration in the liquid phase is correlated to the partial pressure P_{O_2} and the solubility parameter H_{O_2} . Eq. (6) can be written as

$$r = -\frac{d[\text{COD}]}{dt} = k[\text{H}_{\text{O}_2}P_{\text{O}_2}]^m[\text{COD}]^n[\text{CuSO}_4]^p \quad (9)$$

$$r = -\frac{d[\text{COD}]}{dt} = k'[P_{\text{O}_2}]^m[\text{COD}]^n[\text{CuSO}_4]^p \quad (10)$$

where $k' = k[\text{H}_{\text{O}_2}]^m$

It was presumed that the first order behaviour w.r.t. $[\text{COD}]$ due to low concentration.

For a given partial pressure of oxygen and the catalyst loading, term $k'[P_{\text{O}_2}]^m[\text{cat}]^p$ becomes constant and the rate expression takes form

$$r = -\frac{d[\text{COD}]}{dt} = \bar{k}[\text{COD}]^n \quad (11)$$

where $\bar{k} = k'[P_{\text{O}_2}]^m[\text{CuSO}_4]^p$

From Eq. (6) for $n = 1$, we have

$$\ln \frac{[\text{COD}]_i}{[\text{COD}]_t} = \bar{k}t \quad (12)$$

From Fig. 6 it was concluded that the order with respect to $[\text{COD}]$ is one, since $\ln[\text{COD}]_i/[\text{COD}]_t$ versus time gives a straight line. The first order kinetic plots at different temperatures are also shown in Fig. 6. The reaction follows a two step mechanism viz. the fast

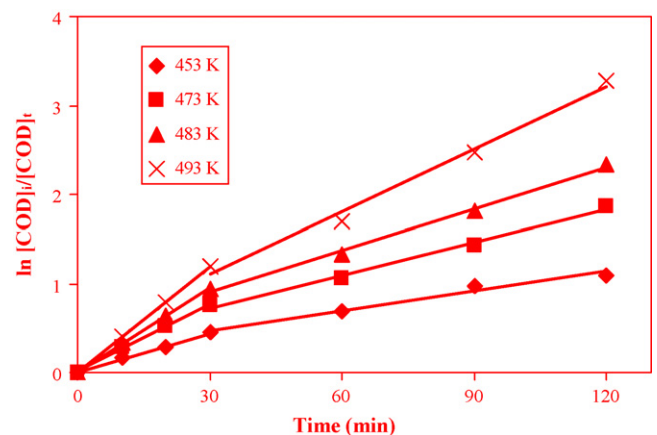


Fig. 6. First order kinetic plot w.r.t. COD (initial COD 500 mg L^{-1} , O_2 partial pressure 0.69 MPa , $\text{pH } 6.5$, $\text{CuSO}_4 \text{ } 4.70 \times 10^{-4} \text{ kmol m}^{-3}$).

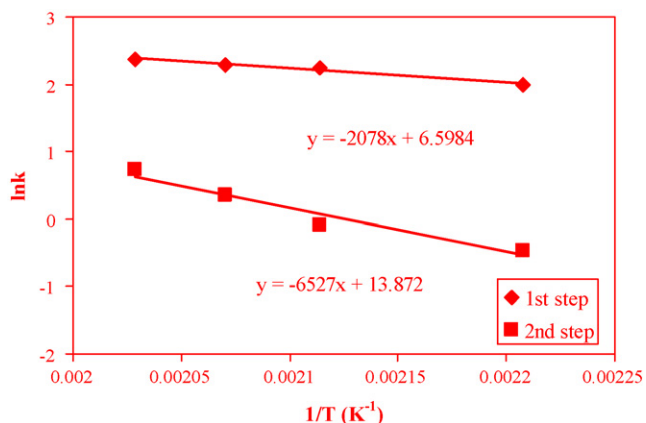


Fig. 7. Arrhenius plot.

oxidation of organic substrate followed by slower oxidation of low molecular weight compounds formed such as acetic acid, oxalic acid.

Arrhenius plot was drawn by plotting log of rate constant values versus inverse of temperature (Fig. 7). The activation energy, pre-exponential factor and variation of H_2O_2 as a function of temperature were then calculated from graph. The activation energy for first and second step was found to be 17.28 and 54.26 kJ mol^{-1} , respectively.

Global rate equations for first and second steps are

First step

$$r = -\frac{d[\text{COD}]}{dt} = 7.34 \times 10^2 \exp(-2078/T)[\text{COD}] \{ (1.34 \exp(-2192/T))^{0.75} [\text{P}_{\text{O}_2}]^{0.75} \} [\text{CuSO}_4]^{0.28} \quad (13a)$$

Second step

$$r = -\frac{d[\text{COD}]}{dt} = 1.06 \times 10^6 \exp(-6527/T)[\text{COD}] \{ (1.34 \exp(-2192/T))^{0.65} [\text{P}_{\text{O}_2}]^{0.65} \} [\text{CuSO}_4]^{0.30} \quad (13b)$$

4. Conclusions

The hybrid process dissolution followed by wet oxidation was found to be suitable technique for the treatment of gel type cation exchange resin. The parameters for complete dissolution were optimized. CuSO_4 was found to be good catalyst for dissolution (up to 15%, w/w of slurry) as well as for wet oxidation. The results presented would aid process development of treatment strategy of waste containing cation exchange resin.

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References

- [1] M. Kubota, J. Radioanal. Chem. 78 (1983) 295–305.
- [2] R.J. Bigda, Chem. Eng. Prog. 91 (1995) 62–66.
- [3] J.J. Pignatello, E. Oliveros, A. MacKay, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.
- [4] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Ind. Eng. Chem. Res. 34 (1995) 2–48.
- [5] S. Imamura, Ind. Eng. Chem. Res. 38 (1999) 1743–1753.
- [6] P.D. Vaidya, V.V. Mahajani, Chem. Eng. J. 87 (2002) 403–416.
- [7] R.V. Shende, V.V. Mahajani, Ind. Eng. Chem. Res. 33 (1994) 3125–3130.
- [8] R.V. Shende, V.V. Mahajani, Ind. Eng. Chem. Res. 36 (1997) 4809–4814.
- [9] R.V. Shende, J. Levec, Ind. Eng. Chem. Res. 38 (1999) 3830–3837.
- [10] N.E. Bibler, E.G. Orebaugh, Ind. Eng. Chem. Res. 15 (1978) 136–138.
- [11] F.D. Snell, L.S. Etre, Encyclopedia of Industrial Chemical Analysis, vol. 17, Wiley, New York, USA, 1967.
- [12] R. Oliveira, M.F. Almeida, L. Santos, L.M. Madeira, Ind. Eng. Chem. Res. 45 (2006) 1266–1276.
- [13] S.D. Crammer, Ind. Eng. Chem. Res. 19 (1980) 300–305.