



Photocatalytic degradation of hydroquinone using HFO supported polymeric material

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ABSTRACT

Photocatalytic degradation of hydroquinone (HQ) has been investigated using polystyrene-divinyl benzene polymeric hybrid ion exchange (HIX) resin. The polymeric material was modified with iron cations and thermally treated at 60°C to produce nano FeOOH species (HFO) supported on the HIX polymer and denoted as Fe-HIX. The obtained material was characterized using X-ray diffraction (XRD) and scanning electron microscope (SEM). The data obtained for the degradation of HQ indicate that the addition of Fe-HIX material to the degraded HQ solution greatly enhance the rate of degradation in the presence of H₂O₂. Since the rate of degradation was found to be governed by the adsorption mechanism, so the adsorption isotherms were established in dark at different pH values and different doses from resin correlated with the obtained data of degradation.

Keywords: HQ; HFO; Photocatalytic degradation; HPLC; IC

1. Introduction

Hydroquinone constitutes one of the most widespread phenolic compounds which is used in several types of industries [1–7]. The degradation of hydroquinone was not extensively investigated, which can be accounted for by the fact that hydroquinone might be produced with the first step of photo degradation process as an intermediate stage.

Advanced oxidation processes have been developed for the removal of organic contaminants. These processes are based on using homogenous or heterogeneous catalysts in the presence of oxygen carrier material for the oxidation of organic contaminates to lower and nontoxic product. For instance, Fenton reagents have been exten-

sively used for the removal of phenols, chlorophenol, dyes, etc. [8–10].

Recent studies have demonstrated the effectiveness of a simple chemical-thermal technique to disperse hydrated iron(III) [Fe(III)] oxide (HFO) particles and magnetite nanocrystals within commercially available ion-exchange resins and polymeric sorbents [11,12]. Such hybrid polymeric-inorganic particles combine the durability of the robust polymer beads with the unique sorption and magnetic properties of iron oxide-based nanoparticles.

The earlier investigation also revealed that HFO particles are irreversibly encapsulated within the gel phase of the ion exchangers but are accessible to dissolved solutes from the aqueous phase [11,12]. On the basis of these observations, it was conceptualized that a single hybrid polymer bead, if appropriately synthesized in accordance with the experimental protocol developed in Sengupta's

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laboratory, can be (i) magnetically active, (ii) selective toward a host of diverse groups of regulated contaminants, and (iii) amenable to efficient regeneration and reuse.

We will try in this work to use a new technique have been used extensively in past for the removal of both organic and inorganic contaminants from polluted water depending on the adsorption phenomena. Our material composed of polystyrene-divinyl benzen polymer modified by Fe loading (HFO) with extremely excess amount that can possess a higher photocatalytic activity. In this paper we will benefit from the excess amount of loaded Fe on the polymeric material to achieve the photo-degradation of hydroquinone in a similar way to Fenton process.

The advantages of this method are:

1. Fe ions can react as a Fenton reagent while its holding the HIX surface, hereby there is no iron in the solution.
2. Fe HIX is durable, resistant to sustainable frictions and amenable to efficient regeneration and reuse.

2. Experimental

2.1. Materials

The following chemicals were analytical reagents and were purchased from Fluka chemical and were used without further purification: hydrogen peroxide (50%), acetonitrile (CH₃CN), hydroquinone [C₆H₄(OH)₂]. C-145 (HIX) cation exchange resin was purchased from Puroite, Inc., Philadelphia.

2.2. Catalyst preparation

The process of magnetization for the polymeric sorbent particles was carried out as that of Sengupta et al. [11]. The obtained materials were dried at 50–60°C.

2.3. Adsorption isotherms

All batch equilibrium experiments were conducted in the dark. Measurements were made on suspensions prepared by 200 ml solution of HQ at neutral pH (6–8) and different pH. The equilibrium concentrations were determined using HPLC, after filtration. The concentration of HQ and the intermediates in the clear filtrate was determined by HPLC analysis.

The amount of adsorbate per gram of HQ (Q_{ads} mol/g) and the maximum number of adsorbed molecules Q_{max} were determined according to the derived Langmuir equation [13] after linearization:

$$Q_{ads} = \frac{Q_{max} \cdot K_{ads} C_{eq}}{1 + K_{ads} C_{eq}} \quad (1)$$

The Freundlich parameters K and n were calculated classically using the results in all the studied of concentrations ($C_{eq} = K C_0^n$)

2.4. Photocatalytic degradation experiments

2.4.1. Photocatalytic degradation cell

The photoreactivity experiments were carried out in a 200 ml cylindrical quartz glass reactor. A 6 W UV light lamps (Cole Palmer E-09815-55, $\lambda_{max} = 254$ nm) were immersed in the photoreactor where the total radiant flux amount (20 m W cm⁻²) was measured using UV radiometer (Digital, UV X 36).

2.4.2. Procedure

200 ml of the hydroquinone (HQ) solutions of different concentrations with the proper catalyst dose was placed in the container of the cell. The starting time of the experiment was determined as soon as the addition of the catalyst was completed. A 5 ml aliquot was then withdrawn after a specific interval which was reported for each experiment and its value was 5 min when no light was used and 2 min when UV light was used.

The collected aliquots at the different intervals were then analyzed using the high performance liquid chromatography (HPLC) and ion chromatograph (IC) instruments.

2.5. Analytical methods

2.5.1. High performance liquid chromatography (HPLC)

The concentration of hydroquinone (HQ) and the photodegradation produced intermediates of aliquots of each experiment were identified and followed using HPLC Dionex 202TP™ C₁₈ column (4.6×250 mm). The mobile phase used was a mixture of acetonitrile : water (60:40), by a pump at a flow rate of 1 ml/min (Dionex p580 pump). This HPLC type has a UV detector and the wave length at which measurements were carried out was 290 nm.

2.5.2. Ion chromatography (IC)

The acetates as an intermediate were measured using ion chromatography (Dionex Ion Pac(R) attached with AS14 column with eluent consisted of 2:7 sodium carbonate: sodium bicarbonate mixture, and the flow rate was 1.2 ml/min. In all cases, air was bubbled through the reaction mixture to ensure a constant dissolved O₂ concentration.

2.5.3. pH measurement

pH values of the samples were measured using Multimeter; WTW (Wissenschaftlich – Technische Werkstätten GmbH) Inolab Multi Level, be 12237de, Germany.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD

XRD patterns of the hybrid ion exchange (HIX) samples which had been modified with Fe cations are presented in Fig. 1b in comparison with that modified by Sengupta et al. (Fig. 1a). The data obtained indicate that the hybrid ion exchange samples possess an amorphous structure due to the absence of any diffraction line characteristic of the crystalline phase and/or Fe-oxide species. This may be due to that the formed FeOOH particles are smaller than the detection limit of the instrument and located in the nano range which cannot be detected by XRD.

3.1.2. Scanning electron microscope

Fig. 2 shows hybrid ion exchange particles modified with Fe cations. Note that the spherical geometry is retained after processing. A number of macropores in the sizes of 20–300 nm can be readily observed. The obtained SEM picture for hybrid ion exchange particles and close physical observation suggest that HFO agglomerates are accessible to dissolved solutes through a network of pores.

3.2. Mechanism of HQ adsorption

No one can deny the important role of adsorption in the catalytic removal of both organic and inorganic contaminants. The adsorption process depends mainly on the surface functional groups which attract the contaminant molecules. In our case the surface of the Fe modified resin contained FeOOH functional group which may be negatively or positively charged depending on the pH of the medium [11,12].

3.2.1. Interaction during HQ sorption onto the polymeric exchanger

The adsorption mechanism can be explain in the light of [11]. Once a HQ molecule enters the exchanger phase and binds to the fixed positive charge, its nonpolar moiety (NPM) tends to be in direct contact with the nonpolar matrix of the ion exchanger. This results in expulsion of polar water molecules from the exchanger phase, which is present primarily due to the osmotic pressure difference between the exchanger phase and the solvent. Fig.3 illustrates a mechanistic interpretation of the foregoing two steps of the sorption process. Note that hydrophobic interactions energetically comprise both NPM solvent and NPM-matrix interactions. Although not explicit, the effect of solvent-matrix interaction is also included in Fig. 3. The weaker the solvent-matrix interaction, the smaller will be the energy required to expel the solvent molecules from the matrix and hence, more favorable will be the sorption process and vice versa.

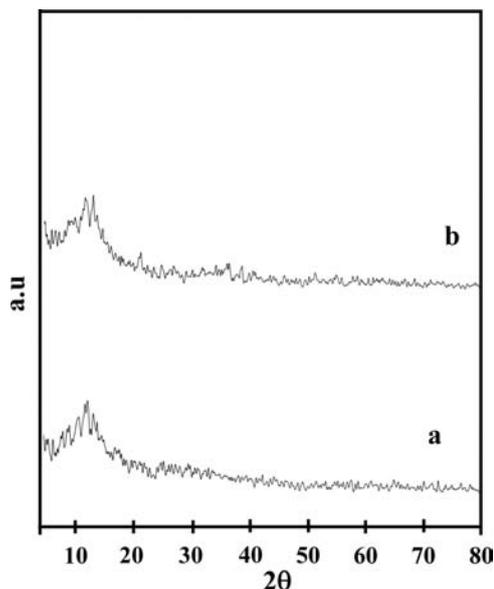


Fig. 1. XRD patterns of different cations modified HIX (a) home (Sengupta et al.), (b) Fe-HIX.

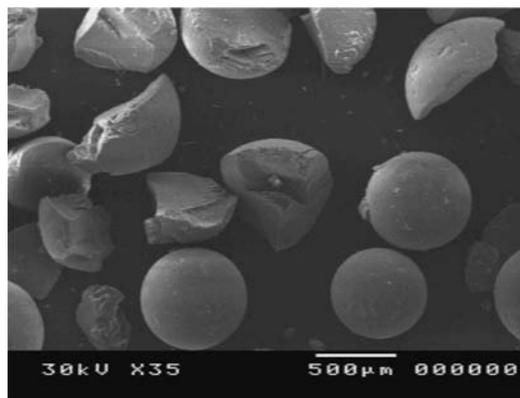


Fig. 2. Scanning electron micrograph of the iron modified polymeric material (C-145).

3.2.2. Adsorption of HQ over Fe loaded hybrid ion exchange (Fe HIX)

Since the rate of most catalytic reactions generally depends on the amount of adsorbed molecules, a series of experiments were carried out in the dark to study the adsorption of HQ on Fe-HIX surface at different doses of the catalyst (0.05, 0.1, 0.15 and 0.2 g/l). An equilibrium adsorption of a Langmuir type was observed.

Eq. (2) represents the linear transformation of Eq. (1) which is expressed by the following equation:

$$\frac{1}{Q_{ads}} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}KC_{eq}} \quad (2)$$

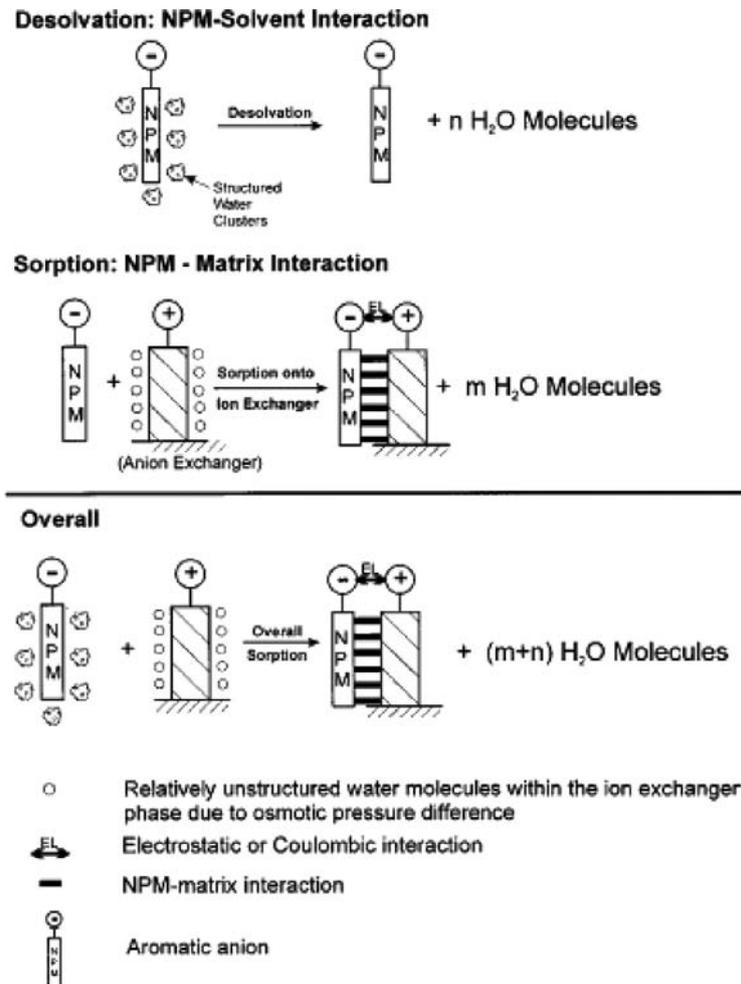


Fig. 3. Schematic illustrating NPM-solvent and NPM-matrix interaction during the adsorption of HQ from the aqueous phase.

Plotting the linear transformation indicate that the ordinate at the origin is equal to the reciprocal of Q_{max} , whereas K can be calculated from the slope (slope = $1/Q_{max}K$).

The adsorption process was carried out using 200 ml HQ solution with different concentrations of catalyst in the dark and kept under constant stirring for different time periods. The data obtained indicate that the increase of the catalyst dose will increase the amount of adsorption. Fig. 4 illustrates the adsorption data of 300 ppm HQ over different amounts of HFO material (0.05, 0.10, 0.15 and 0.20 gm). It is clear that the adsorption process follows the following order $0.20 > 0.15 > 0.10 > 0.05$.

3.2.3. Adsorption of HQ over different loadings of Fe HIX

In order to investigate the most efficient parameter in the adsorption process, different loadings of iron cations were made and the amount of loaded Fe is depicted in Table 1. Fig. 5 illustrates the adsorption data of HQ over Fe-HIX loaded with different concentrations of Fe (200,

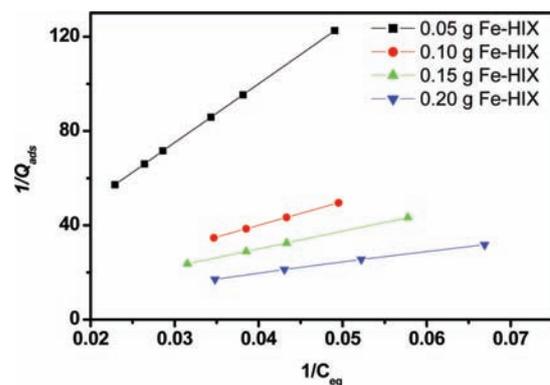


Fig. 4. Adsorption of 300 ppm HQ at different doses of Fe-HIX.

275, 340 and 375 mg Fe/g HIX). The data indicate that the adsorption of HQ reached its maximum value when the concentration of loaded Fe was 200 mg Fe/g HIX (loading 1). Further more, the increase of Fe loading to 275 mg

Table 1
Amount of Fe (mg/g) supported on the polymeric material

Fe content (mg Fe/g HIX)	Loading
200	1
275	2
340	3
375	4

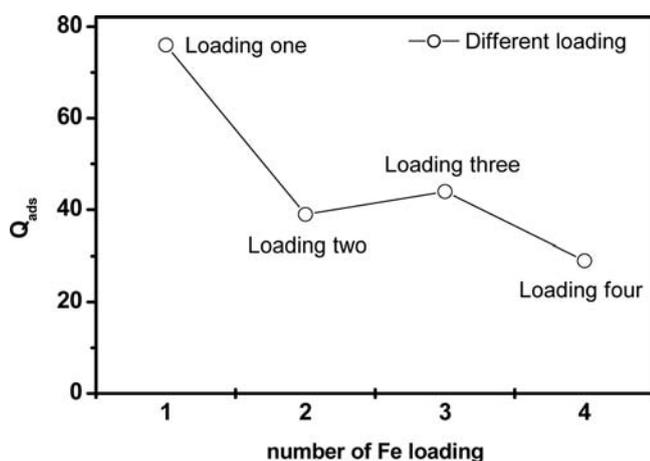


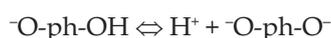
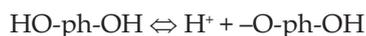
Fig. 5. Effect of different loading of Fe on adsorption of HQ.

Fe/g HIX was found to decrease the adsorbed amount of HQ. The enhancement of adsorption of HQ over Fe modified HIX may be assigned to the newly generated active sites, which were absent in the parent material. The data also reveal that despite increasing of Fe loading to 375 mg Fe/g HIX (loading 4) but shows the lowest adsorption which may be assigned for, the further loaded Fe diffused into the polymeric material matrix reducing the amount of HFO surface responsible for the process of adsorption. The explanation of the above mentioned results may be assumed as follows [11]:

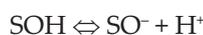
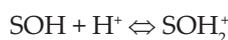
α -FeOOH surface area $45 \text{ m}^2\text{g}^{-1}$

Surface site density [SOH] $5 \times 10^{-4} \text{ mol L}^{-1}$

Solution reactions



Surface reactions



3.3. Degradation of HQ

3.3.1. Photolysis of different concentration of HQ

Direct photolysis is efficiently applied for the removal of phenolic compounds chlorinated hydrocarbons, including hydroquinone amino aromatic compounds, trihalomethanes [13], chlorinated compounds [14,15], nitroaromatic compounds [16] and certain pesticides [17].

When aqueous HQ solutions (50, 100, 200 and 300 ppm) were subjected to UV light, a marked degradation took place as illustrated in Fig. 6. This is due to the formation OH radicals as a result of the interaction between UV and water molecules.

3.3.2. Photocatalytic degradation of HQ with H_2O_2

The addition of H_2O_2 as oxygen carrier material was found to increase the rate of degradation for most organic contaminants [18–21].

In this series of experiments 300 ppm HQ concentration was examined with five different concentrations of H_2O_2 (0.001 M, 0.005 M, 0.01 M, 0.025 M and 0.05 M) in the absence of UV light (Fig. 7a) and in the presence of UV light (Fig. 7b). It is interesting to notice that UV irradiation greatly enhanced the degradation of the 300 ppm HQ solution in the presence of 0.05 M H_2O_2 when compared with the dark condition.

It can also be observed that the degradation rate increased linearly with the increase of H_2O_2 added to reach the optimum value at 0.01 M behind which further addition of H_2O_2 did not affect the rate of degradation.

3.3.3. Photocatalytic degradation of HQ over Fe HIX

Photocatalytic degradation of HQ has been investigated using a newly generated and modified type of polystyrene-divinyl benzene polymer. The modification

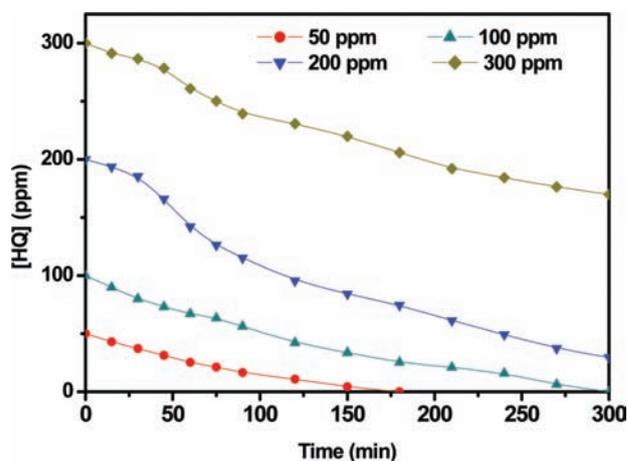


Fig. 6. Degradation of different concentrations of HQ in the presence of UV light.

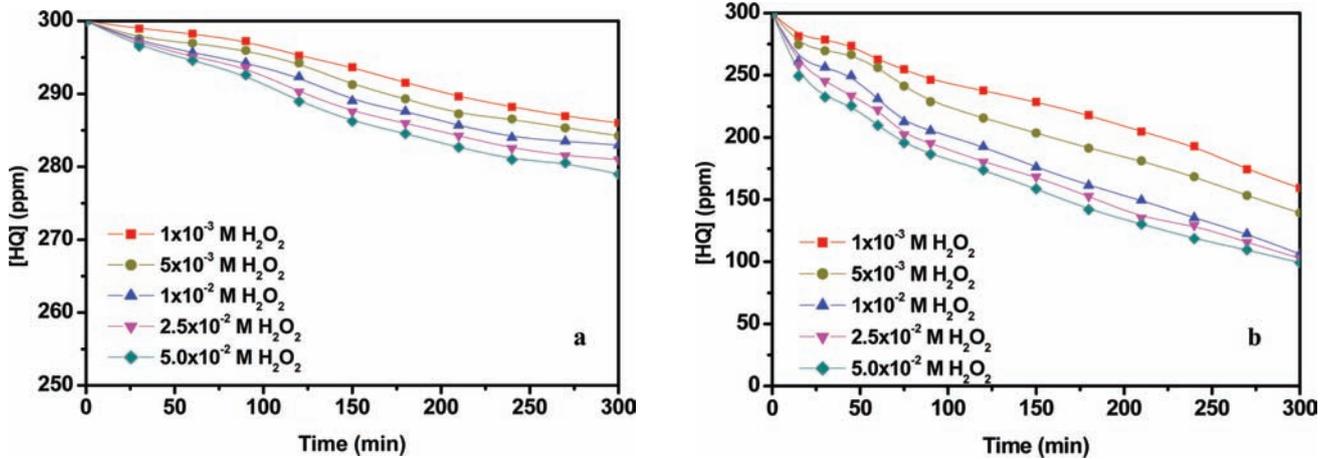
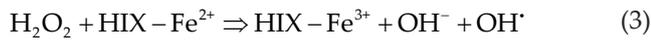


Fig. 7. Degradation of 300 ppm HQ in the presence of different concentrations of H₂O₂ (a) in the absence of UV light (dark), (b) in the presence of UV light.

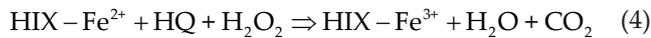
of polymeric material was made using iron cation due to its catalytic activity and photosensitivity toward organic contaminants.

The degradation process in this case is based on Fenton’s reagent, which uses H₂O₂ and iron salts for producing hydroxyl radicals by reaction of H₂O₂ and ferrous ion (Fe²⁺). Hydroxyl radicals are very powerful, effective and nonspecific oxidizing agents.

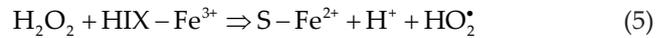
In our case the iron species are held to the surface of HIX material in the form of FeOOH and can react as follows:



The formed hydroxyl radicals will attack the HQ molecules to produce water and carbon dioxide.



- During the optimum reaction sequence with an iron catalyst, ferrous ion (Fe²⁺) is converted to ferric iron (Fe³⁺).
- Ferric ion will not generate the hydroxyl radical but it can be regenerated back to ferrous iron by a subsequent reaction with an additional molecule of H₂O₂ and hereby the degradation reaction will goes on as in Eq. (2).



3.3.3.1. Effect of Fe loading

Photocatalytic degradation of 300 ppm HQ solution was carried out with HIX of different Fe contents under UV irradiation. Samples were taken every 5 min to analyze the remaining HQ and the other degradation products. The data presented in Fig. 8a illustrate the undegraded HQ, before irradiation with UV, with Fe HIX

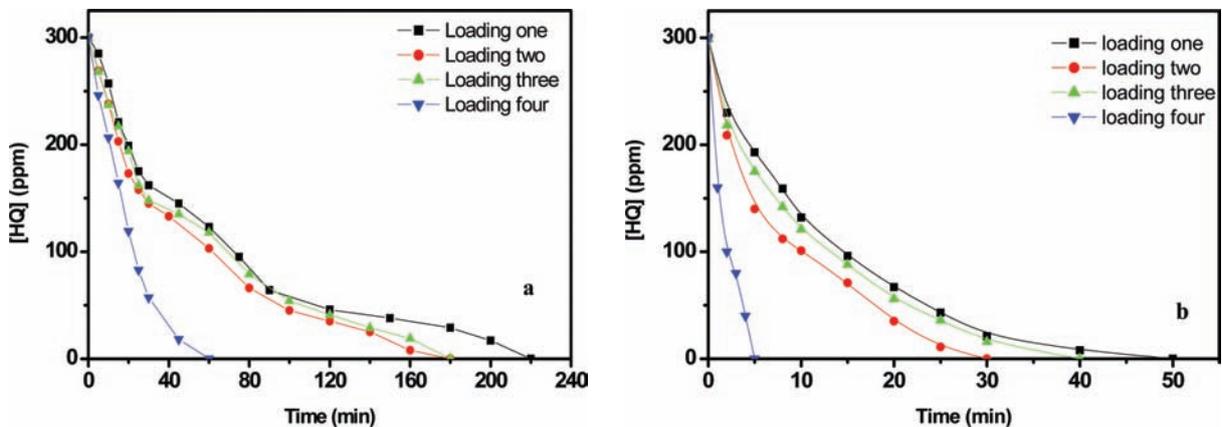


Fig. 8. Effect of different Fe loading on degradation of HQ 300 ppm at fixed 0.01 M H₂O₂ (a) dark, (b) UV.

catalyst and/or H_2O_2 . It was found that HQ decreased sharply and disappeared completely within 60–220 min time range with varying order depending on the Fe loading used. The data also reveal that the degradation rate decreased when the concentration of supported iron was triplicate, which may be assigned for the partial diffusion of surface Fe species within the polymeric matrix of HIX material. Furthermore, with increasing Fe loading to 4 folds the degradation rate increased again due to the dispersion of Fe on the HIX surface and increasing the number of active sites.

Upon applying the UV irradiation the formation of OH radicals was increased and consequently the degradation rate was enhanced giving raise to the complete removal of HQ within 5–50 min time range as depicted in Fig. 8b.

3.3.3.2. Effect of catalyst dose

Investigation of the effect of Fe modified HIX polymeric material dosage has been carried out under different experimental conditions (the presence of Fe HIX and/or UV and H_2O_2). The data obtained revealed that the degradation rate was not greatly affected by increasing the catalyst dose under the applied conditions (Figs. 9a–c) which support the idea of Fe diffusion into the polymeric matrix upon increasing its loading and hence reducing the amount of surface Fe that is responsible for the degradation process.

3.3.3.3. Effect of pH

The role of pH change on the degradation of several organic pollutants has been investigated at different pH values (2, 4, 6, 8 and 10). Figs. 10a–b indicate that the pH change strongly affected not only the adsorption but also the degradation rate of HQ. It is clear that the maximum adsorption was observed with pH 6 and the degradation rate was found to increase linearly with increasing the pH from acidic to basic medium and the most efficient pH was recorded in the basic medium (pH = 8) although it showed extremely weak HQ adsorption. The effect of pH can be explained as follows:

- In acidic medium the HIX surface will be positively charged which hinders the regeneration of Fe^{3+} to Fe^{2+} reducing the amount of produced OH radicals. Furthermore, the ionization of HQ is extremely low so the balance between keto \leftrightarrow enol forms of HQ will be shifted toward the recombination of ionized HQ molecules reducing the easily degraded form (benzoquinon).
- In basic medium the reverse occurs. The surface of HIX will be negatively charged and HQ completely ionized leading to the enhancement of the degradation rate.

Upon the addition of catalyst and H_2O_2 at different pH values the degradation of HQ was observed even in

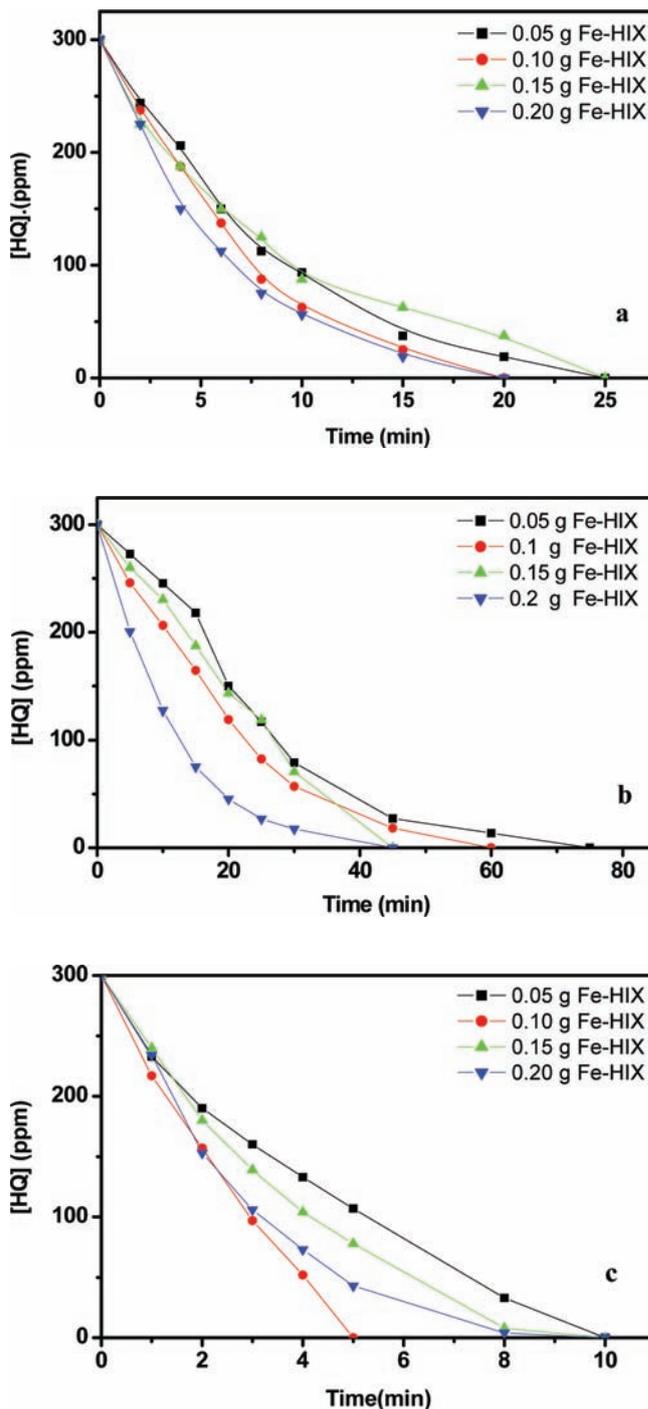


Fig. 9. Effect of Fe-HIX amount on degradation of HQ 300 ppm (a) UV, (b) with H_2O_2 (dark), (c) with H_2O_2 (UV).

the dark. Figs. 11a–b depict the degradation of HQ in the dark, the obtained data reveal that low pH values were found to strongly increase the rate of degradation (pH = 6 and 10). The data also indicate that at pH 10 the reaction was achieved in less than 5 min (during preparation of the experiment) which prevented its follow up.

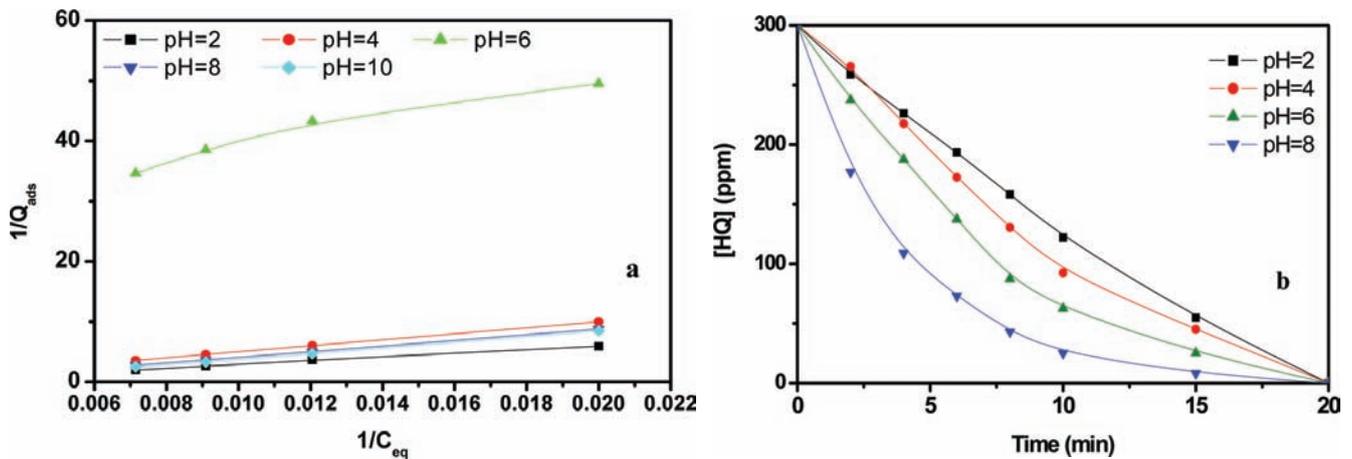


Fig. 10. Effect of different pHs on (a) adsorption of 300 ppm HQ at fixed 0.1 g Fe-HIX, (b) degradation of 300 ppm HQ at fixed 0.1 g Fe-HIX (UV).

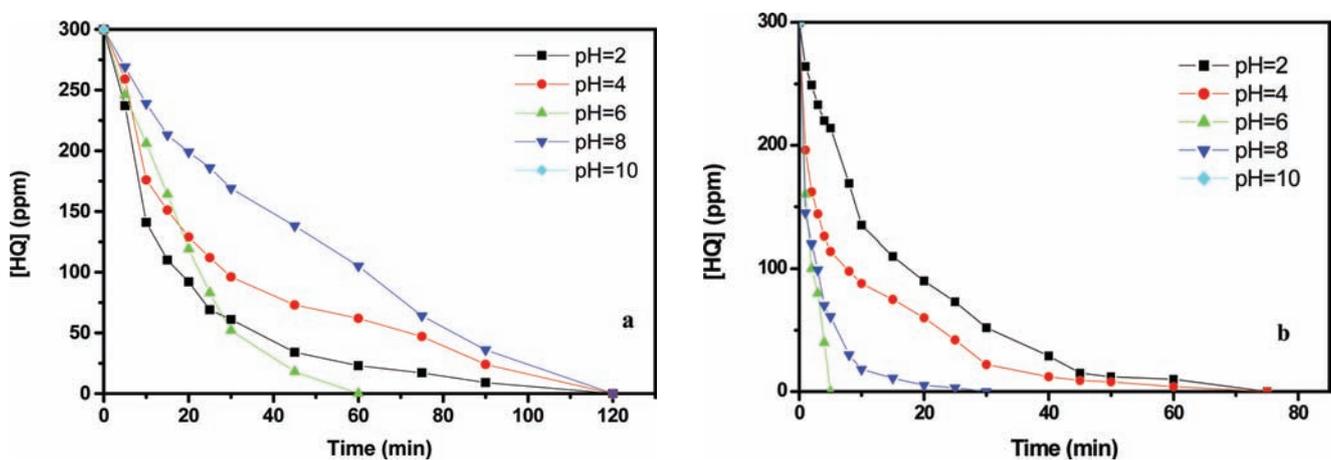


Fig. 11. Effect of different pHs on degradation of 300 ppm HQ at fixed 0.01 M H_2O_2 and 0.1 gm Fe-HIX (a) dark, (b) UV.

4. Conclusion

The degradation of HQ as a model of organic water pollutants have been investigated using HFO supported polymeric materials. The data indicate that the adsorption of HQ as a primary step for the degradation process did not depend on the amount of loaded HFO. The data also indicate the great efficiency of such catalyst when combined with H_2O_2 as oxygen carrier material and pH change for the photocatalytic degradation of HQ.

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Science, Chemistry Department, Al-Azhar University and El-Tebben Institute-Helwan, Egypt.

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