Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20388

67 (2017) 339–345
March

Combined system of natural pomegranate as heterogeneous bioadsorbent and photocatalysis for removal of textile dye herbicide in presence of heavy metals: effect of operating parameters and reaction monitoring

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Received 31 May 2016; Accepted 26 November 2016

ABSTRACT

The photocatalytic degradation of acid orange II (AOII), which is a toxic dye effluent for textile applications, has been studied using natural pomegranate as heterogeneous bioadsorbent in the presence of TiO_2 activated by an external ultraviolet radiation under various conditions. Powder of pomegranate rind and leaves has been tested for heavy metals adsorption. A special attention has been paid to the treatment efficiency of a real dye effluent in the presence of heavy metal, namely zinc (Zn). The experimental results showed that for low values of Zn^{2+} in the solution (40 mg/L), AOII removal kinetics fastened until reaching an optimum, then slowed down for higher concentrations (100 mg/L). This behavior could be explained by the fact that at low zinc concentrations, Zn^{2+} could be incorporated in the photocatalytic process because of its photonic character. At high concentrations, zinc is more susceptible of consuming radicals due to competition effect. On the other hand, results showed that no photocatalytic activity of Zn^{2+} was recorded. The degradation rate was strongly influenced by the presence of heavy metals, initial concentrations of AOII, and amount of crushed powder of pomegranate rind and leaves. Moreover, different ways of adding natural pomegranate in the photocatalytic reactor have been tested in order to keep Zn^{2+} concentration in optimal conditions.

Keywords: Photocatalysis; Natural pomegranate; Organic and inorganic pollution; Combined system; Water treatment

1. Introduction

Water pollution has become an undeniable reality [1]. The problem is now global. In some areas, it has become so acute that the authorities have taken drastic measures. The occurrence of pollutants in rivers mainly from industrial discharge is a major public health issue. Indeed, effluent streams containing dyes have caused serious environmental pollution [2]. Dyes are mainly used in textiles, tanneries, and electroplating industries [1,2]. Dyes are considered as an obnoxious type of pollutants as they impart color to water, which is not acceptable due to esthetic consideration. Hence, the removal of dyes from water and wastewaters is important before they mix up with unpolluted natural water resources. Numerous methods focused on the elimination of dyes from aqueous

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media like advanced oxidation processes (AOP) [3], namely ozonation [4], photo-Fenton processes [5], and photocatalysis [6]. Indeed, this latter is a heterogeneous process between a solid phase (catalyst) containing a semiconductor, usually titanium dioxide (TiO_2), and liquid phase. The catalyst is activated by a photon provided by an ultraviolet (UV) radiation [6]. This technique has proved its ability to mineralize effectively the majority of dyes with low energy consumption [3]. Irradiation of TiO_2 with UV light generates highly reactive electron–hole pairs. The hole subsequently oxidizes the surface hydroxyl groups to form the $^{\bullet}OH$ free radicals [3,6]. Heterogeneous photocatalysis using TiO_2 has several attractions: (i) the catalyst is inexpensive; (ii) it operates at ambient temperature; (iii) the final mineralization by-products are usually CO_2 and H_2O; and (iv) no other chemical reagent is needed.

In addition to dyes, these types of industrial streams contain inorganic pollutants such as heavy metals [2]. Heavy metals in water are well known to damage ecosystems and human health [1,2]. In fact, these metallic ions can be harmful to aquatic life, and water contaminated by toxic metal ions remains a serious public health problem [7,8]. Several existing methods permit removing detrimental metal ions from aqueous solutions. Among them, activated carbon is the most used adsorbent so far. Nevertheless, it is relatively expensive [9,10]. In order to obtain cheaper adsorbents, lignocellulosic and natural materials have been studied [9–13]. Besides activated carbon, other methods have been used in treating heavy metals from aqueous solutions, for example, chemical precipitation, coagulation–flocculation, floatation, and ion exchange, but all these methods need adding some reagents [14].

Thus, adsorption research is directed toward the development of low-cost adsorbents alternatively to activated carbon. In fact, using natural bioadsorption is undoubtedly one of the most suitable techniques for treating wastewater containing organic and inorganic pollutants such as dyes and heavy metals, respectively [15–17]. Over the past years, many low-cost materials have been tested for organic and inorganic pollutants adsorption [18]. Biosorption process has gained wide attention for treating metal or dye bearing effluents. Pomegranate seeds may prove to be efficient, low-cost, and environment-friendly biosorbent for cadmium bioremediation [19]. Previous finding render pomegranate peel powder as an efficient, cost-effective, and environmentally friendly adsorbent for the removal of crude oil from simulated produced water [20]. Agro-wastes from pomegranate rind and leaves have been found to possess high metal binding capacities due to phenolic acids and flavonoid derivatives presence: they contain various functional groups such as amino, hydroxyl, carboxyl, and sulfate, which can act as binding sites for metals [16,18,21,22]. Modification of the pomegranate fruit is often carried out to enhance the bioadsorbent's properties or adsorption performance.

In this context, the main goals of this study were to treat organic and inorganic pollutants by combining photocatalysis, a destructive technology, with adsorption on rust of pomegranate, a recuperative process. Indeed, different adsorption isotherms on different forms of natural pomegranate with acid orange II (AOII) and Zn^{2+} were done in order. Additionally, to understand the kinetic degradation of AOII in the presence of Zn^{2+}, the Langmuir–Hinshelwood (L–H) model was used to study the impact of mineral pollution on the model's constant in order to keep the concentration of Zn^{2+} in optimal conditions.

2. Experimental setup

The experimental units include three major elements: the chemicals, the batch reactor, and the analysis system.

2.1. Chemicals

AOII ($C_{16}H_{11}N_2NaO_4S$; molecular weight (MW) = 350.32 g mol^{-1}, purity = 98%), acquired from Sigma-Aldrich (Saint Louis, USA), was tested with the photocatalysis process. Titanium dioxide (TiO_2; PC500 Anatase, purity > 99%, specific surface area 350–400 m^2·g^{-1}, crystallites mean size = 5–10 nm) was acquired from Millennium Inorganic Chemicals (Thann, France).

Zinc nitrate (zinc nitrate hexahydrate, $Zn(NO_3)_2\ 6H_2O$, MW = 297.49 g mol^{-1}, purity ≥ 98%), acquired from Sigma-Aldrich (Saint Louis, USA), was used in the batch combined pollution experiment.

2.2. Catalyst characterization

The used photocatalyst was PC500 Titania (TiO_2), supplied by Millennium Inorganic Chemicals. It has a crystallite form; the purity of anatase is around 99%; mean crystallite size was 5–10 nm; and its specific area was 320 m^2/g.

Pomegranate (*Punica granatum* L.) fruit and leaves were harvested in October 2015 from Gabes Oasis (southeast of Tunisia: 33°40′ N, 10°15′ E). The sampling was done from different trees of commercial pomegranate variety "Gabsi". Fresh fruits and leaves were stored at room temperature (18°C–20°C) for less than 5 d before processing. The fruits were peeled manually. Good quality peels and leaves were air-dried until complete dehydration. Then, they were ground into powder using electric grinder.

2.3. Setup of photocatalytic experiments

The photocatalysis investigations were conducted in a cylindrical batch reactor, 76 mm as upper diameter and 400 mm of working height, thus accepting up to 1.5 L of the studied solution. A UV lamp was placed inside the reactor. The reactor contains two septa for O_2 bubbling by using an air pump and samples' extractions (Fig. 1). In order to maintain a homogenous partition of the dye and the semiconductor, the solution was maintained in continuous stirring (200 rpm). A weighed amount of natural bioadsorbent was added to dye solutions at different times of experiments.

The effect of initial dye concentration (5–30 mg/L), natural bioadsorbent dose (0.1–1 g/L), and TiO_2 amount (0.1–1 g/L) was tested at neutral pH (around 7) in order to find the optimum conditions for organic and inorganic pollutants treatment. In fact, AOII pKa = 11.2 therefore the increase of the pH inhibit its adsorption. The pH influences both the surface state of TiO_2 and the ionization state of ionizable organic molecules at the same time. For pH higher than the point of zero charge (pzc) of TiO_2, the surface

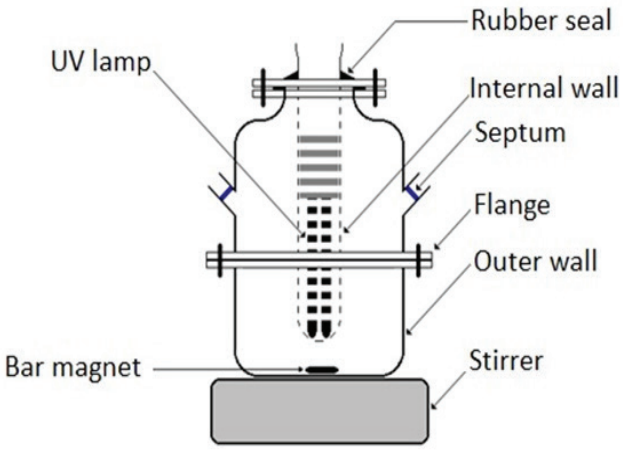

Fig. 1. Composition of the used batch reactor.

becomes negatively charged, and it is the opposite for pH < pzc, according to the following equilibria:

pH < pzc: $Ti–OH + H+ \Leftrightarrow TiOH_2^+$ (1)

pH > pzc: $Ti–OH + OH- \Leftrightarrow TiO^- + H_2O$ (2)

Solution at neutral pH was obtained by adding 0.05 M HCl and/or 0.05 M NaOH solutions.

The AOII concentration was determined by measuring the absorbance at 456 nm using UV-visible spectrophotometer (ThermoSpectronic UV1; Thermo Fisher Scientific, Massachusetts, USA). Small volumes were extracted from the reactor to do the appropriate analysis, and they do not exceed 5% of the total aqueous solution volume present in the reactor. Appropriate dilutions were performed to fit the calibration curve.

2.4. Setup of adsorption experiments

Both experiments were conducted in round bottom flasks at room temperature, at a constant semiconductor dose, and at constant stirring speed (20°C, 1 g/L, and 200 rpm, respectively). Here, Zn^{2+} concentrations were analyzed by using a Shimadzu AA-6200 atomic absorption spectrometry unit (Kyoto, Japan; absorption wavelength = 213.9 nm).

All the experiments were carried out by pouring 100 mL of distilled water at different concentrations of dye and metal.

3. Results and discussion

The experiments, which were repeated twice, showed good reproducibility with 5% standard deviation. This is represented by vertical bars in the experimental results in all figures.

3.1. Adsorption alone

Adsorption isotherm experiments were conducted by equilibrating the adsorbent (untreated and treated) in 200 mL Erlenmeyer flasks. The kinetic study was made for times between 0 and 180 min, and isotherm experiments were performed for initial AOII and Zn^{2+} concentrations varying from 5 to 30 mg/L and from 30 to 100 mg/L, respectively. Different forms of TiO_2 and crushed powder of pomegranate rind and leaves with crude or modified type have been tested for AOII and Zn^{2+} adsorption. After equilibrium, the mixture was then centrifuged at 3,000 rd/min and filtered using 0.45 μm membranes. Adsorption equilibrium data were analyzed by Langmuir isotherm model.

3.1.1. AOII adsorption

The pH of the solution is one of the important factors controlling the adsorption capacity; it influences not only the adsorbent's surface charge but also AOII's solubility. Considering this fact, we have maintained experiment conditions at a neutral pH (pH = 7) in the present study.

Five adsorbents have been tested: raw pomegranate rind (RPR), activated pomegranate rind (APR), raw pomegranate leaves (RPL), activated pomegranate leaves (APL), and TiO_2 in powder form. The isotherm study was conducted by equilibrating organic/inorganic solutions with 0.5 g of adsorbents. After adsorption, the mixtures were filtered, and the filtrates were analyzed for AOII content using UV-visible spectrophotometer (ThermoSpectronic UV1; Thermo Fisher Scientific, Massachusetts, USA).

The adsorption capacity, q (mg/g), was calculated using the following equation:

$$q = \frac{(C_0 - C).V}{m} \quad \text{Eq. (1)}$$

where C_0 (mg/L) and C (mg/L) are concentrations before and after adsorption, respectively; V (L) is the volume of lead solution; and m (g) is the adsorbents weight.

As shown in Fig. 2(a), bioadsorbent in raw form has a high affinity to AOII than modified form. Isotherm simulation with Langmuir model showed that adsorption through a monolayer fixation process is probable. Langmuir model was chosen as it presents a good fit to the experimental data. The maximal uptake capacity "q_{max}" of AOII onto RPR, RPL, APL, APR, and TiO_2 in powder form were summarized in Table 1.

First of all, AOII is weakly adsorbed with TiO_2 powder. Indeed, q_{max} does not exceed 2 mg/g. From these results, it was observed that adsorption capacity with RPR and APL was about 8 mg/g, which is 4 times higher than the one found with TiO_2 in powder form.

3.1.2. Heavy metal adsorption

The batch adsorption experiments were carried out in duplicates, and the results were reported as the average. All chemicals used were of analytical reagent grade. The standard solution of Zn(II) (1,000 mg/L) was purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France). Experimental solutions and the desired lead concentrations were obtained by successive dilutions from the standard Zn(II) solution. The experiments of adsorption were carried out over a pH range of 5–7 to avoid the precipitation of $Zn(OH)_2$. The effects of lead concentration and reaction time were conducted by shaking the adsorbent with Zn(II) solutions (6, 11, 25, 45, and 65 mg/L) at various time intervals (0–120 min). The isotherm study was conducted by equilibrating Zn(II) solutions with 0.5 g of adsorbents. After adsorption, the mixtures were filtered, and the filtrates were analyzed for Zn content using an atomic absorption spectrophotometer (AAnalyst 400 AA, PerkinElmer, USA).

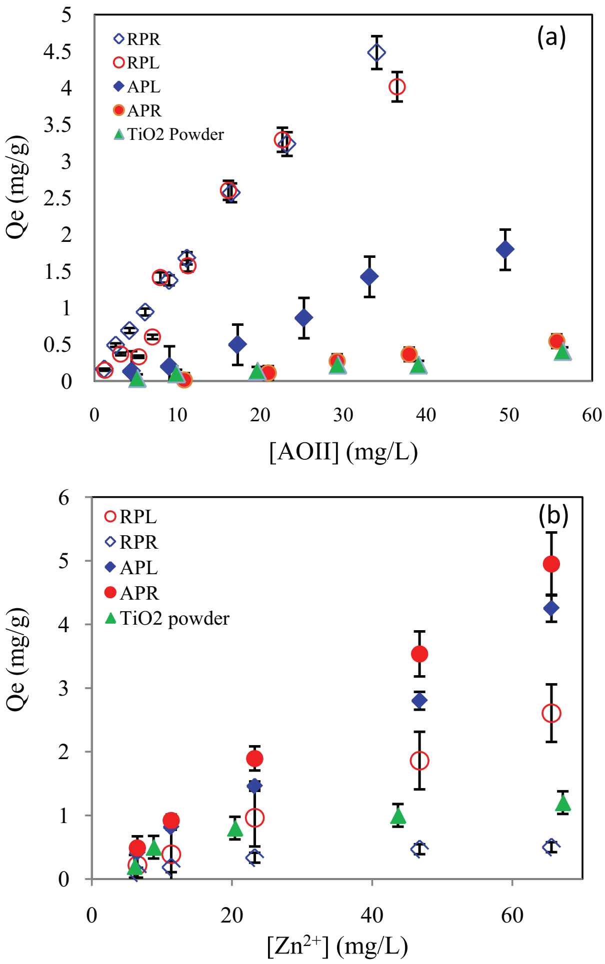

Fig. 2. (a) AOII kinetic adsorption onto different adsorbents ($[Zn^{2+}]$ = 0 mg/L; neutral pH; dose = 0.5 g/L; temperature = 20 ± 2°C) and (b) heavy metal kinetic adsorption onto different adsorbents ([AOII] = 0 mg/L; neutral pH; dose = 0.5 g/L; temperature = 20 ± 2°C).

Table 1
Langmuir model parameters for AOII adsorption onto different adsorbents

	Adsorbent	K (L/mg)	q_{max} (mg/g)	R^2
RPR	Raw pomegranate rind	0.014	08.68	0.9568
RPL	Raw pomegranate leaves	0.025	07.84	0.9854
APR	Activated pomegranate rind	0.051	1.71	0.9520
APL	Activated pomegranate leaves	0.030	04.21	0.9081
TiO_2	TiO_2 powder	0.052	1.69	0.9584

Fig. 2(b) shows that the bioadsorbent in raw form has a lower affinity to Zn^{2+} than the modified form. In fact, q_{max} of RPR doesn't exceed 2 mg/g. However, using the Eq. (1), the adsorption capacity with APR was about 35 mg/g, which is 10 times higher than the one found with TiO_2 in powder form (Table 2).

The APR showed such high affinity for zinc anions, which might be due to the esterification reaction between the functional groups on the surface of pomegranate rind in this raw form and NaOH [21,23–25]. The presence of carboxylate groups on the surface facilitated the binding of cationic pollutants. This observation led to the conclusion that the adsorption of pollutants involved electrostatic interactions between adsorbent and adsorbates [26–28].

This result is similar to the experimental work that demonstrated the adsorption of Cu^{2+} onto chitosan cross-linked with glutaraldehyde (GD), epichlorohydrin (EC), and ethylene glycol diglycidyl ether (EGDE) [29]. It was pointed out that the removal of similar heavy metals such as Cu^{2+} on chitosan cross-linked with GD, EC, and EGDE beads were 59.67, 62.47, and 45.94 mg/g, respectively [29]. We compared this result with that obtained in literature with chitosan because it is well known that chitosan is a good adsorbent for all heavy metals. It is also widely known that the excellent adsorption behaviors of chitosan for heavy metals removal is attributed to: (1) its high hydrophilicity due to high number of hydroxyl groups, (2) its large number of primary amino groups with high activity, and (3) the flexible structure of its polymer chain making suitable configuration for adsorption of metal ions [29,30].

3.2. Photocatalytic degradation of AOII

3.2.1. Effect of heavy metal concentrations

In order to examine and to understand the possible interactions that might occur during the photodegradation of dye in the presence of a heavy metal on the degradation of the AOII, different concentrations of zinc ions were applied. The pollutant's inlet concentration is also varied. In fact, here, kinetic variations for AOII concentration during photocatalysis for default experimental conditions were plotted in Fig. 3(a).

The plot shows that the AOII elimination changed dramatically with its inlet concentration. Indeed, increasing inlet concentration prolongs time needed to achieve pollutant's complete removal due to limited active sites of TiO_2 [3].

To understand the kinetic and the adsorption process of AOII degradation in the presence of a heavy metal, we used

Table 2
Langmuir model parameters for heavy metal adsorption onto different adsorbents

	Adsorbent	K (L/mg)	q_{max} (mg/g)	R^2
RPR	Raw pomegranate rind	0.008	01.96	0.9025
RPL	Raw pomegranate leaves	0.005	06.83	0.9532
APR	Activated pomegranate rind	0.002	34.48	0.9487
APL	Activated pomegranate leaves	0.003	22.83	0.9887
TiO_2	TiO_2 powder	0.006	03.21	0.9589

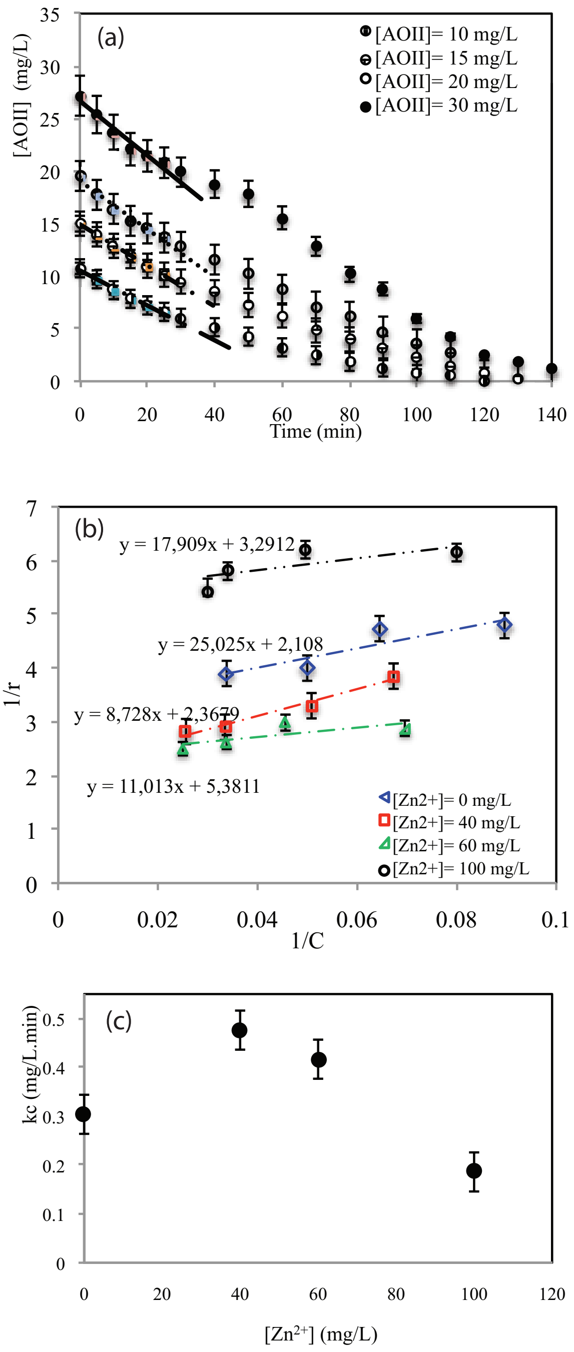

Fig. 3. (a): Evolution of AOII concentration vs. degradation time for the investigated inlet concentrations without inorganic pollution, (b) linear regression using L-H model for AOII for different inlet concretions of heavy metal, and (c) influence of zinc concentration on the degradation rate constant of L–H model.

the L–H model, and the results are gathered in Fig. 3(b). To determine the parameters governing the photocatalytic phenomena, the L–H model was used according to the following equation:

$$r_0 = -\frac{d[\mathrm{AOII}]}{dt} = k_c \frac{K\left[\mathrm{AOII}\right]_0}{1+K\left[\mathrm{AOII}\right]_0} \qquad \text{Eq. (2)}$$

where r_0 (mg/L.min) is the initial photocatalytic degradation; $[\mathrm{AOII}]_0$ is the initial AOII concentration (mg/L); k_c is the kinetic constant (mg/L.min); and K is the adsorption constant (L/mg). Thus, this L–H expression could be linearized and written as follows:

$$\frac{1}{r_0} = \frac{1}{k_c K} \times \frac{1}{\left[\mathrm{AOII}\right]_0} + \frac{1}{k_c} \qquad \text{Eq. (3)}$$

The plotting $1/r_0$ vs. $1/[\mathrm{AOII}]_0$ determines k_c and K values at a value of heavy metal introduced in the photocatalytic reactor (Fig. 3(b)).

According to Fig. 3(b), the kinetic constant (k_c) calculated for all the experiments shows a distinguished pattern, symbolized with an increase when zinc concentrations varies from 0 to 40 mg/L, then a decrease for $[\mathrm{Zn}^{2+}] = 60$ and 100 mg/L (Fig. 3(c)). These results are in agreement with works on photocatalytic degradation of Aniline Blue [18].

For all the experiments performed in batch mode, the heavy metal concentration remained unchanged. The presence of heavy metal has a significant effect on the kinetics of AOII photocatalytic degradation. In fact, many studies have shown the effect of mineral pollution: Devi et al. [18] showed that the rate of photocatalytic elimination of Aniline Blue is enhanced with the amount of Pb(II) concentration. Above a certain threshold, there will be an effect on the degradation rate. In addition, the presence of heavy metal has sometimes no influence for some pollutants. For example, we can cite the case of basic dye [22].

Indeed, referring to Devi et al. [18], the possible reactions that might be occurring in the presence of zinc are:

$$\mathrm{Zn}^{2+} + \mathrm{e}^- \rightarrow \mathrm{Zn}^+ \qquad (3)$$

$$\mathrm{Zn}^+ + \mathrm{O}_2\ (\mathrm{ads}) \rightarrow \mathrm{Zn}^{2+} + \mathrm{O}_2^{-\bullet} \qquad (4)$$

$$\mathrm{Zn}^+ + \mathrm{h}^+ \rightarrow \mathrm{Zn}^{2+} \qquad (5)$$

$$\mathrm{Zn}^{2+} + \mathrm{h}^+ \rightarrow \mathrm{Zn}^{3+} \qquad (6)$$

$$\mathrm{Zn}^{3+} + \mathrm{OH}^- \rightarrow \mathrm{Zn}^{2+} + {}^\bullet\mathrm{OH} \qquad (7)$$

$$\mathrm{Zn}^{3+} + \mathrm{e}^- \rightarrow \mathrm{Zn}^{2+} \qquad (8)$$

According to the previous mechanism, zinc ions enter in reaction with free electrons, then with dioxygen or hydroxide to form free radicals and then regain their initial electronic form [18]. This incorporation at relatively low initial concentrations enhances the degradation of AOII and its mineralization.

On the other hand, when the $[\mathrm{Zn}^{2+}]$ increases, the competitive effect toward the active sites of water becomes predominant. Thus, an optimum Zn^{2+} concentration value is observed for the AOII. This is probably due to the fact that the competitive effect between organic and organic molecules is more important at these conditions. If the “quantity” of the active sites is considered to be constant, it becomes evident that the competitive effect increases by increasing inlet concentrations.

3.3. Combined system

For comparison, two of conventional combined systems experiments were carried out: one-step and two-step systems.

3.3.1. Pollution treatment in a one-step system

The proposed one-step experiments were done by adding a mixture of TiO_2 and APR into the reactor for simultaneous photocatalysis–adsorption under UV light.

The AOII dye degradation by photocatalysis was examined using dye solution of 60 mg/L under optimized conditions of pH and contact time, and the results are presented in Fig. 4. As seen in Fig. 4, in a one-step system, the permanganate dosage decreased the kinetic of photocatalytic degradation of AOII, which could be attributed to a decrease in the surface area and an availability of active sites.

In fact, this behavior can be explained by the fact that TiO_2 actives sites don't absorb enough amount of UV light, thus inhibiting the photocatalytic process. Fig. 5 shows a photograph of the reactor when used with UV light alone and when adding TiO_2 and APR in powder form.

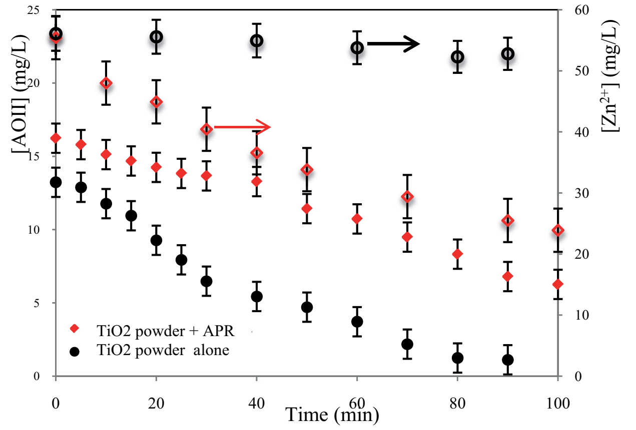

Fig. 4. Simultaneous treatment of AOII and Zn^{2+} with photocatalysis alone and with the one-step system.

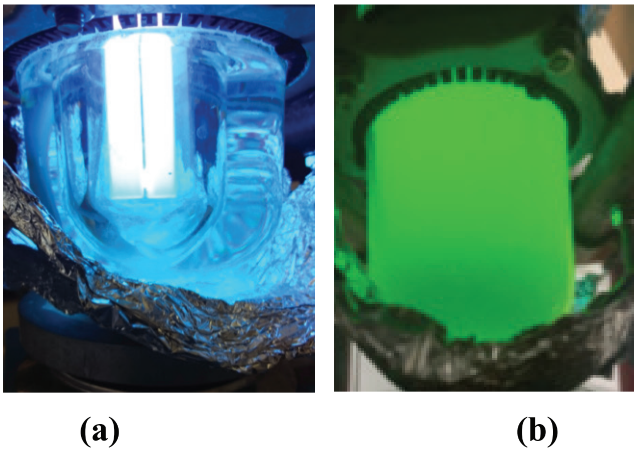

Fig. 5. Photograph of used reactor with (a) UV alone and (b) UV, TiO_2 and APR in powder form.

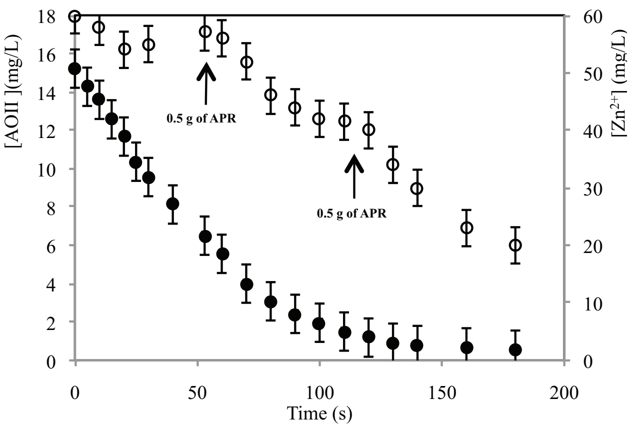

Fig. 6. Simultaneous treatment of AOII and $Zn^{2+}$with the two-step system.

3.3.2. Pollution treatment in a two-step system

For separated photocatalysis and adsorption, AOII with a concentration of 25 mg/L, Zn with a concentration of 60 mg/L, and TiO_2 in powder form were mixed and stirred for 30 min in dark to reach adsorption–desorption equilibrium first, and then the mixture was irradiated under UV light for 180 min. Afterward, APR was added into the reactor to start the adsorption process of mineral pollution at every 60 min of AOII photocatalytic treatment.

The variation of AOII concentration vs. time is shown in Fig. 6. The removal rate of photocatalytic degradation was kept constant with adding the adsorbent (APL).

Experiments on the treatment of total pollution were first conducted in two processes, i.e., photocatalysis and adsorption. In the photocatalysis process, removal of AOII by TiO_2 powder with external UV light was significant (Fig. 6). Since Zn^{2+} adsorption capacity of TiO_2 was very small, AOII gradually reduced in the solution (Fig. 6).

When the dosage ratios of TiO_2 and APR were below 2:1 (i.e., APL 0.5 g L^{-1}), photocatalytic degradation was not affected by adding APR, which concentration is increased with time lapse. The adsorption capacity of APR during this period was very low. When APR dosage increased to 1 g/L, AOII concentration decreased also in the photocatalysis process. In the subsequent adsorption process, total Zn^{2+} concentration sharply decreased from 40 to 20 mg/L. Excellent adsorption performance of APR for Zn^{2+} allowed fast adsorption kinetics, and AOII concentration sharply reduced to less than 4 mg/L after dosage ratios of TiO_2 and APR were below 1:1 (i.e., APR 1 g/L).

4. Conclusion

AOII removal in aqueous solutions using photocatalysis process in the presence of Zn^{2+}, at different experimental physicochemical conditions, was investigated. Organic and inorganic adsorption was studied using a natural bioadsorbent.

RPR, APR, RPL, and APL were investigated as potential bioadsorbents for the treatment of dissolved pollutants in water. Results show that only two natural materials were effective in removing heavy metal ions from water: APL and APR. In fact, APR showed an elimination efficiency of Zn^{2+} = 35 mg/g. Moreover, the Langmuir isotherm model fitted best the adsorption process, dominated by electrostatic interaction between adsorbent and adsorbates.

A combined treatment was also followed by adding different heavy metal concentrations, and the results presented an acceleration in the degradation of AOII at low inorganic concentrations, with high k_c and low K parameters, reaching an optimum at the concentration of $[Zn^{2+}]$ = 60 mg/L. This elevation in degradation process was explained by the possible interference of metal ions in the generation of $^{\bullet}$OH free radicals, favoring the elimination of AOII.

In-situ and ex-situ combining of photocatalysis and adsorption had been tested. The proposed two-step method for removal of AOII and heavy metal with a mixture of TiO_2 and APR was very promising due to significant adsorption without imbibing the photocatalytic activity. The one-step process is not practical due to barrier effect against UV radiation, which affects the TiO_2 function.

Acknowledgment

Authors are grateful to Isabelle Soutrel (ENSC de Rennes, France) for technical assistance with technical measurements. Amrane Abdeltif (Institut des Sciences Chimiques de Rennes) is also gratefully acknowledged for highlighting discussions.

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