

# Decentralized grey-water treatment system based on combined adsorption and electrochemical oxidation

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**Abstract:** Electrochemical technologies for wastewater treatment present several promising characteristics to be used as decentralized systems. In this work, synthetic grey-water (SGW) was treated in a three-dimensional (3D), flow-through electrochemical reactor filled with granular activated carbon (GAC), which enabled simultaneous adsorption of contaminants onto GAC and their electrochemical oxidation. The results show that the main driver for the removal of organic matter is the adsorption onto GAC. However, when a current of  $15 \text{ A m}^{-2}$  is applied, electrochemical regeneration of the bed is achieved, 88% of the Chemical Oxygen Demand (COD) and 85% of the Total Organic Carbon (TOC) adsorbed is degraded, extending the life-time of the GAC bed and oxidizing the pollutants originally present in the water. In addition, a synergetic effect of adsorption and electrochemical oxidation in the 3D system has been observed, which enhances the performance of these two processes operating individually.

**Keywords:** Electrochemical Oxidation, Grey-water, 3D electrochemical system

## Introduction

Due to climate change and population growth experienced today globally, decentralized water production provides an excellent opportunity to supply a growing water demand and complement conventional water supply networks (Shannon et al. 2008). Electrochemical oxidation technologies have been effectively used for water disinfection and organic pollutants removal, and for the treatment of real polluted wastewater, and are suitable to be implemented as decentralized water treatment systems (Radjenovic and Sedlak 2015). The efficiency of a conventional, two-dimensional (2D) electrochemical system can be substantially improved by (1) using a flow-through reactor, and (2) using a bed material inside the reactor (i.e., three-dimensional (3D) electrochemical system), typically a particle, granular or mesh-type material that acts as a third electrode and increases the effective surface area of the electrodes (Zhang et al. 2013, Hussain et al. 2014). In a flow-through reactor, current flow is perpendicular to the flow of contaminated water, which enhances the convective transport of contaminants to the electrode surface. For example, Yang *et al.* (2009) reported up to 161% enhancement of the mass transfer coefficient in a flow-through electrochemical system compared to the conventional flow-by electrochemical reactor (Yang et al. 2009). By adding granular activated carbon GAC as a bed material in a 3D electrochemical system, the effective surface area for electrochemical oxidation can be increased due to the generation of oxidants, such as hydroxyl radicals ( $\cdot\text{OH}$ ), at the surface of the electrochemically polarized GAC (Zhang et al. 2013). Furthermore, when placed in an electric field GAC is regenerated by electrochemical oxidation, thus avoiding its saturation and oxidising the adsorbed pollutants (Zhou and Lei 2006a). Zhu et al (2011) reported that a synergistic effect between GAC adsorption and electro-

oxidation resulted in a better performance than the separate operation of the treatments (i.e., adsorption and electrochemical oxidation).

In this study, 3D electrochemical system with GAC filling was used for the treatment of synthetic grey-water (SGW). The results for the removal of Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), turbidity and colour, and the energy efficiency obtained, have been compared with the treatment of this effluent by adsorption onto GAC, and electrochemical oxidation.

## Material and Methods

### - Experimental setup

The experimental setup is represented in Figure 1.

#### *Figure 1*

Experiments were conducted in a flow-through electrochemical reactor with dimensions 10 x 10 x 3.7 cm. The anode electrode employed was boron-doped diamond (BDD) mesh (dimensions 10 x 10 x 0.13 cm), supplied by Condias (Germany), and stainless steel of the same dimensions was used as the cathode electrode. The inter-electrode distance was 3.5 cm. 50 g of GAC with diameter ranging from 2 to 5 mm (surface area 1000 m<sup>2</sup> g<sup>-1</sup>, density 0.42-0.50 g cm<sup>-3</sup>) was loaded between the two electrodes as a packed bed. The ratio of the volume occupied by GAC and total reactor volume was 0.27.

Five consecutive seven-hour experiments were performed using three different experimental set-ups: (i) experiments with 3D reactor in open circuit (i.e., no current applied), to investigate the adsorption of contaminants onto GAC (GAC system), (ii) experiments with 2D reactor (i.e., no GAC placed between the electrodes), to investigate the removal of contaminants by electrochemical oxidation on BDD anode (2D system), and (iii) experiments with 3D reactor with applied current, to investigate the removal of contaminants by combined adsorption and electrochemical oxidation (3D system). All experiments were performed in duplicate, and the obtained results were expressed as mean values with their standard deviations. Electrolysis experiments were conducted galvanostatically, at a constant current of 150 mA, using a VSP Modular 5 channels Potentiostat/Galvanostat (Bio-Logic SAS, US). An Ag/AgCl reference electrode (3 M KCl, 0.210 V vs. SHE) was placed in the proximity of the anode and used to control and measure the applied current and potential. 2L of low-load SGW, with a composition comparable with combined wastewater from showers and washing basin, was recirculated through the reactor at a flow rate of 35 L h<sup>-1</sup> (NFS 2011). In order to achieve an electrical conductivity close to 1000 μS cm<sup>-1</sup>, 0.67 mg L<sup>-1</sup> of sodium sulphate (Ajax Finechem) was added to the prepared SGW. The reactor and reservoir bottle were covered with aluminium foil to avoid the light degradation of the pollutants. Samples were taken after 0, 1, 3, 5 and 7 h and analyzed for COD, TOC, turbidity and colour.

Desorption experiments were conducted using the GAC from the previous experiments (i.e., (i) GAC system and (iii) 3D system). The procedure is based on Zhu *et al.* (2011) experiments. In a 250 mL conical flask, 30 g of the GAC and 100 ml of Milli-Q water were added. The flask was shaken for 48 h at ambient temperature, and then ultrasonicated for 30 min (40 kHz, 120 W). Samples were filtrated using a 0.22 μm Millipore syringe unit, and soluble COD and TOC were analysed.

### **- Chemical analysis**

COD was determined using the COD tube test range 25-1500 mg L<sup>-1</sup> (Merck) by spectrophotometric method. TOC was analysed by Shimadzu TOC-L CSH Analyser. Turbidity was measured using a Turbidimeter Turbicheck (0.1-2000 NTU) Lovibond. True colour of the filtered sample (0.22 µm) was analysed by UV-Visible spectrophotometry (Cary 50 Bio, Varian) at 475 nm.

## **Results and Discussion**

### **- SGW characterization**

The SGW prepared for these experiments was characterised and the results are summarised in the table below and compared with reported values obtained from literature (Table 1) (NRMMC-EPHC–NHMRC (Natural Resource Management Ministerial Council 2006, Morel and Diener 2006, Eriksson et al. 2002, Li et al. 2009).

*Table 1*

COD and TOC of the SGW used are within the limits reported by literature. In addition, the levels of chloride are lower which may incur in a lower potential formation of toxic disinfection by-products during electrochemical oxidation. It should be noted that the sulphate that was added to increase the conductivity of the water is within the limits reported by literature for real grey-water.

### **- Comparison between GAC adsorption, 2D and 3D electrochemical systems**

The results obtained for the degradation of COD, TOC, colour and turbidity when treating 2 L of SGW during 5 consecutive experiments are illustrated in the Figure 2.

*Figure 2*

From Figure 2 it can be inferred that when GAC is added as a bed material in the 3D system, the mineralization and oxidation of organic matter occurs at a higher rate than in a 2D electrochemical system. This tendency is in accordance with the study of Kong et al (2006), who reported an enhanced COD removal after adding modified kaolin particles as a third electrode to the electrochemical system. Due to the presence of the bed material in an electric field, a 3D system experiences an increase of the electroactive surface area and a decrease in mass transfer limitations, which may increase the treatment efficiency (Zhang et al. 2013). When potential is applied to the cell, the particles may be polarized and act as “microelectrodes”, each of them presenting a positively and a negatively charged side which can induce electrochemical reactions on the bed material, thus leading to the generation of strong oxidizing agents (i.e., <sup>•</sup>OH radicals) (Zhang et al. 2013, Kong et al. 2006, Zhou and Lei 2006b, Polcaro et al. 2000, Yasri et al. 2015). Zhang et al (2013) attributed the enhanced removal of pollutants to 2 factors: (1) adsorption and electrosorption on the bed material (Ban et al. 1998), (2) catalysis on the surface of the bed material that enhances the production of oxidants and thus the degradation of the adsorbed pollutants, regenerating the active sites of the GAC (Zhang et al. 2013, Polcaro et al. 2000). Moreover, GAC can catalyse the decomposition of hydrogen peroxide, formed during the electrolysis of water, to <sup>•</sup>OH radicals, which can then oxidize the pollutants (Zhou and Lei 2006a, Lücking et al. 1998).

Although adsorption onto GAC is a fast process, 3D system with electrochemically polarized GAC enhances the removal efficiencies of COD, TOC turbidity and colour for up to 30%, 18%, 31% and 41%, respectively.

In addition, the kinetic parameters of the degradation of COD and TOC were compared for all the experiments. They were determined by better fitting the normalised concentrations to the pseudo-first order kinetic equation and are summarised in Figure 3. Kinetic constants  $k_1$ ,  $k_2$ , and  $k_3$ , correspond to the removal rate constants of the experiments of (i) GAC, (ii) 2D and (iii) 3D systems, respectively.

In the experiment with no current applied (i.e., GAC system), the pollutants are removed by adsorption to the GAC. In a 2D electrochemical system, pollutants can be decomposed by direct electrochemical oxidation on the anode surface, or by indirect electrochemical oxidation mediated by reactive oxygen species (ROS), particularly  $\cdot\text{OH}$  radicals generated at the BDD anode. In a 3D electrochemical system, adsorption and electrochemical oxidation occur simultaneously. In addition, when GAC is placed in an electric field, its polarization may lead to the electrosorption of the pollutants on its surface and the electrochemical regeneration of the bed material (Kong et al. 2006, Zhu et al. 2011).

Synergy between these two processes (i.e., adsorption and electrochemical oxidation) can be calculated using the following equation (Equation 1) (Zhu et al. 2011):

$$\text{Synergy (\%)} = \frac{k_3 - k_2 - k_1}{k_3} \quad \text{Equation 1}$$

This value illustrates an enhancement in the removal of contaminants in the 3D reactor compared to the sum of their removals by adsorption and electrochemical 2D treatment separately and together with the kinetic constants are represented in the Figure 3.

### **Figure 3**

As expected, the apparent rate constants of COD and TOC removal in a 2D system (i.e.,  $k_2$ ) remained constant in all the consecutive trials, demonstrating the robustness of the electrochemical cell. However, constants  $k_1$  and  $k_3$  observed for GAC and 3D systems, respectively, decrease in the first two trials due to the initial saturation of GAC, and then remain stable. Given that fresh GAC was used at the beginning of each series of experiments, the removal of COD and TOC was faster in the first two cycles. Nevertheless, it should be noted here that full saturation of GAC has not been achieved during the 5 consecutive experiments conducted.

Synergy values represent the enhanced effect of the combination of adsorption and electrochemical oxidation compared to the performance of these two processes separately. The positive value of this parameter,  $21.1 \pm 4.3\%$  and  $23.3 \pm 6.6\%$  for COD and TOC removal respectively, means that the combination of both processes (i.e., GAC adsorption and electrochemical oxidation) enhances the performance of the system compared to GAC adsorption and electrochemical oxidation operating separately and superposed.

### **- Desorption experiments**

Desorption experiments were performed in order to identify the amount of the remaining organic matter on GAC and electrochemically polarized GAC, and thus evaluate the degree of electroregeneration of GAC (i.e., degradation of the adsorbed organics due to the electrocatalysis occurring at the surface of GAC in a 3D ELOX system).

Table 2 summarises the results obtained from desorption experiments treating the GAC from the GAC and the 3D systems.

### **Table 2**

It can be observed that the organic and inorganic matter and colour desorbed from the GAC used in the 3D electrochemical system was considerably lower than that from the GAC used in the adsorption experiment. This result is in accordance with the study by

Zhu et al (2011). The results suggest that GAC used in the 3D reactor has been regenerated. Due to polarisation of the GAC in the 3D system, capacitive deionization of the water can occur besides the adsorption capacity of the GAC, concentrating the ions and charged pollutants on its surface. The adsorbed compounds are degraded by ROS formed through electrochemical oxidation and catalytic reactions on the surface of the GAC.

### - Energy consumption

The energy efficiency of the system was expressed as specific energy consumption ( $E_{SP}$ ) per kg of COD removed.

$$E_{SP} = \frac{1}{3600} \frac{F V_{CELL}}{8 ACE_{COD}} \quad \text{Equation 2}$$

Where  $F$  is the Faraday constant ( $96487 \text{ C mol}^{-1}$ ),  $V_{CELL}$  is the total cell potential (V),  $8$  is the equivalent mass of oxygen ( $32 \text{ g O}_2$  per  $4 \text{ mol e}^-$ ), and  $ACE_{COD}$  is the average current efficiency of COD removal (Radjenovic and Sedlak 2015).

The electrical energy per order ( $E_{EO}$ ), defined as the number of kWh of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in  $1 \text{ m}^3$  of contaminated water is calculated using the expression:

$$E_{EO} = \frac{P t 1000}{V 60 \log(C_0/C)} \quad \text{Equation 3}$$

Where  $P$  is the input power (kW),  $t$  is the treatment time (min),  $V$  is the volume of water treated (L) and  $C_0$  and  $C$  are the initial and final COD concentration ( $\text{mg L}^{-1}$ ) (Behnajady and Modirshahla 2006).

As summarized in Table 3, when anodic current density of  $15 \text{ A m}^{-2}$  is applied, the working electrode potential (i.e., BDD Anode) remained stable at  $3.70 \text{ V vs SHE}$ . Due to the presence of the GAC interlayer, the  $V_{CELL}$  was higher in the 3D system (i.e.,  $13.3 \text{ V}$ ) than in the 2D system (i.e.,  $8.1 \text{ V}$ ).

The  $E_{SP}$  and  $E_{EO}$  are significantly lower in the 3D system than in the 2D system, demonstrating that the treatment efficiency of the 2D system is enhanced when GAC is added as a bed material.

**Table 3**

Same tendency has been described by Kong et al (2006), who reported that the energy efficiency of the 2D system is lower than the 3D system for the removal of surfactants in an electrochemical system using  $\text{Ti/Co/SnO}_2\text{-Sb}_2\text{O}_3$  electrodes and modified kaolin particles as a bed material. The energy consumed per kg of COD removed by the 2D system was up to  $960 \text{ kWh kg}^{-1} \text{ COD}$ , while in the 3D system was  $790 \text{ kWh kg}^{-1} \text{ COD}$  (Kong et al. 2006). The presence of a bed material inside the reactor contributes to decrease the mass transfer limitations and reduces the energy consumption of the system (Wei et al. 2010).

### Conclusions

A flow-through 3D electrochemical system using GAC as a bed material was used for the treatment of SGW. Adsorption onto GAC leads the removal of COD, TOC, turbidity and colour. However, the removal efficiencies of these parameters were improved by up to 30%, 18%, 31% and 41% respectively in the 3D system. In addition, positive values of synergy for COD and TOC removal (i.e., 28% and 30% respectively) demonstrate that the combination of adsorption and electrochemical oxidation triggers electroadsorption and electrocatalytic reactions at the surface of GAC, showing a better performance than their superposed operation.

Higher values of the true colour, soluble COD, TOC, TIC and TC, released in the desorption experiments from the GAC used in adsorption and 3D electrochemical oxidation experiments demonstrated electrochemical regeneration of GAC due to the production of oxidant species at the surface of GAC.

$E_{SP}$  and  $E_{EO}$  were significantly lower in the 3D system indicating that it was more energy-efficient than the 2D system.

Further research is necessary on the saturation capacity of the GAC when current is applied in the 3D system, to determine the regeneration efficiency of 3D system.

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## Figures and Tables

**Table 1** Characterization of SGW

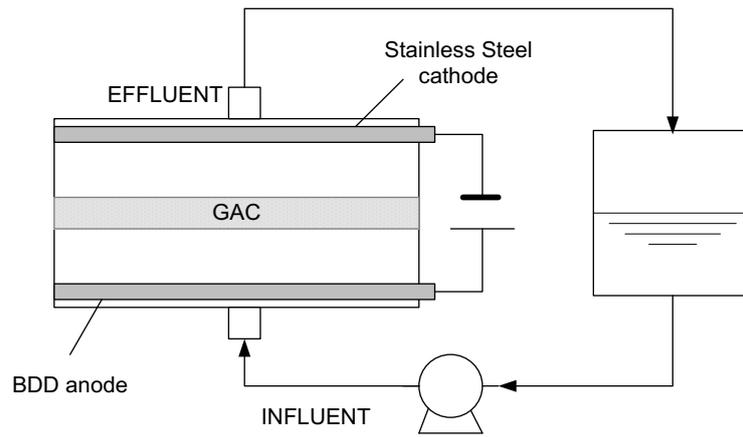
Parameter	Unit	SGW	Reported
pH		5.0 ± 0.3	5.0-10.0
Electric Conductivity	μS cm <sup>-1</sup>	1144.4 ± 75.3	82-2721
True colour	mg L <sup>-1</sup> Pt-Co	8.2 ± 1.1	60-100
Turbidity	NTU	24.8 ± 5.7	28-240
COD	mg L <sup>-1</sup>	273.8 ± 16.5	100-633
TOC	mg L <sup>-1</sup>	66.9 ± 5.3	30-104
Chloride	mg L <sup>-1</sup>	12.7 ± 0.8	3.1-136
Sulphate-S	mg L <sup>-1</sup>	146.7 ± 3.9	4-168

**Table 2** Desorption experiments

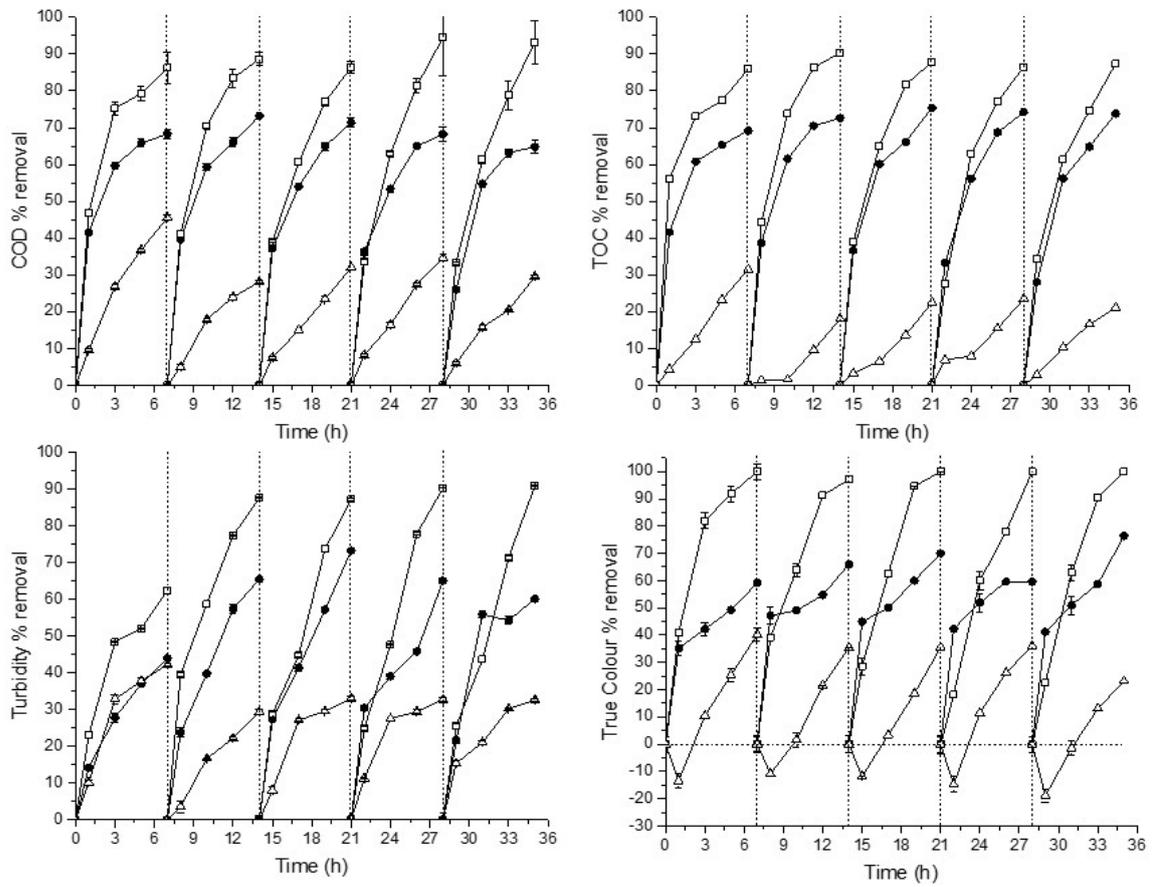
Parameter	Units	GAC <sub>AC-System</sub>	GAC <sub>3D-System</sub>
True Colour	mg L <sup>-1</sup> Pt-Co	105.8 ± 17.1	48.3 ± 8.7
COD soluble	mg L <sup>-1</sup>	14.0 ± 0.8	2.9 ± 0.4
TOC soluble	mg L <sup>-1</sup>	6.5 ± 0.4	4.9 ± 0.6
TC soluble	mg L <sup>-1</sup>	32.4 ± 1.2	9.9 ± 1.9
TIC soluble	mg L <sup>-1</sup>	26.0 ± 1.6	5.0 ± 1.3

**Table 3** Performance parameters related to energy consumption in 2D and 3D electrochemical configurations

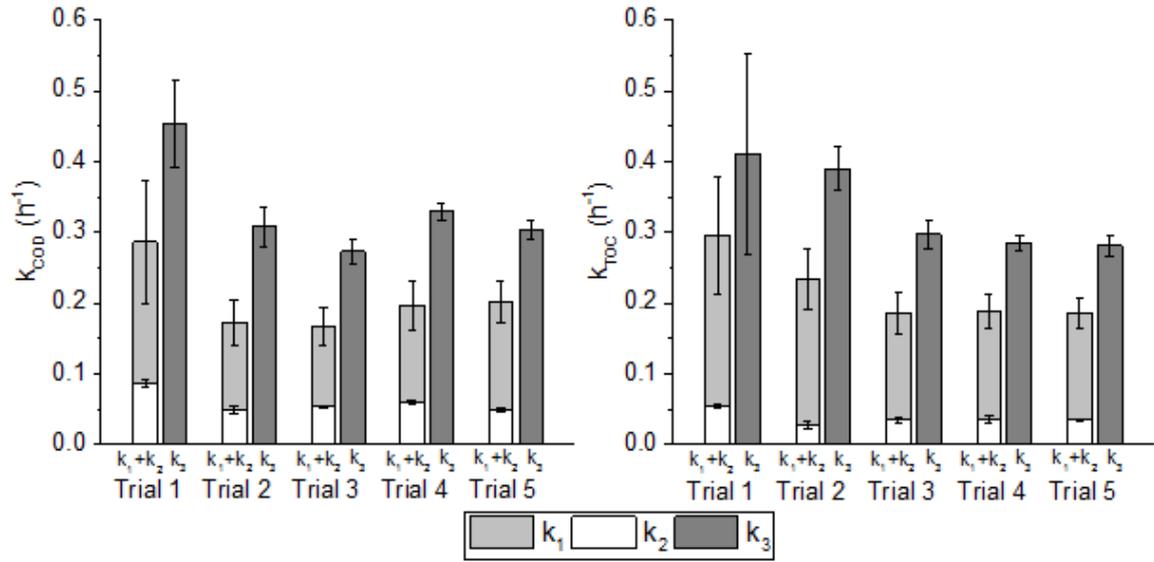
	2D system	3D system
COD removal (%)	35.3 ± 3.5	84.4 ± 4.1
TOC removal (%)	25.4 ± 2.8	84.0 ± 1.9
Working electrode potential vs. SHE (V)	3.8 ± 0.1	3.8 ± 0.1
V <sub>CELL</sub> (V)	8.1 ± 0.1	13.3 ± 0.6
E <sub>SP</sub> (KWh kg COD <sup>-1</sup> )	45.9 ± 5.6	30.2 ± 1.2
E <sub>EO</sub> (kWh m <sup>-3</sup> order COD <sup>-1</sup> )	7.7 ± 1.0	2.9 ± 0.3



**Figure 1** Experimental setup



**Figure 2.** Removal of COD, TOC, turbidity and colour over the time. (●) GAC adsorption, (Δ) 2D electrochemical system, and (□) 3D electrochemical system.



**Figure 3.** Apparent removal rate constants (h<sup>-1</sup>) for COD and TOC removal