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A Comparative Study for Electrochemical Oxidation of Aromatic Compounds in the Absence and in the Presence of Granular Activated Carbon (GAC)

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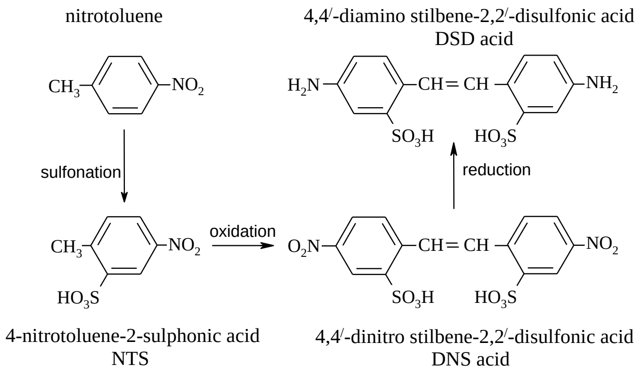
Electrochemical oxidation of aromatic compounds existed in 4,4$^{/}$-diaminostilbene-2,2$^{/}$-disulfonic (DSD) acid manufacturing wastewater was comparatively performed on PbO_2/Ti anode in the absence and in the presence of granular activated carbon (GAC). If less current density is applied across the two systems, the initial zero-order kinetics and the subsequent first-order model should be used for the overall description of chemical oxygen demand (COD) variation. While higher applied current density results in application of the homogeneous first-order model due to the reactions exceed the mass transport limitation. The experimental results illustrate larger current efficiency and lower power consumption could be effectively obtained during DSD wastewater treatment in the presence of GAC, which is of obvious superiority to anodic oxidation without GAC. As a result, the power consumptions of 19.1 and 9.4 kW·h/kg COD as well as COD removal efficiencies of were achieved at reaction time of 5.0 h and 2.5 h in the absence and in the presence of GAC, respectively, which directly confirms the excellent electrode performance of employing GAC as particulate electrode.

Keywords: Electrochemical oxidation; 4,4$^{/}$-diaminostilbene-2,2$^{/}$-disulfonic (DSD) acid manufacturing wastewater; Kinetics; Granular activated carbon (GAC)

1. INTRODUCTION

The lower production yield or reaction efficiency during 4,4$^{/}$-diaminostilbene-2,2$^{/}$-disulfonic (DSD) acid manufacturing (see scheme 1) [1] brings about non negligible amounts of raw materials (i.e. nitrotoluene), intermediate products (e.g. 4-nitrotoluene-2-sulphonic acid and 4,4$^{/}$-dinitro stilbene-2,2$^{/}$-disulfonic acid) and the target production (i.e. DSD acid) scattered in the discharge, causing the characterization of DSD acid manufacturing wastewater by high value of chemical oxygen demand (COD) and abundant salinity (Na_2SO_4). Restricted by high concentration of salinity and poor biodegradability, conventional biological processes are rarely considered to treat such kind of wastewater. It has come to our knowledge that only extraction [2], ion-exchange [3] and multiple-evaporation [4] were reported to deal with the wastewater in industrial scale. However, the mentioned technologies suffer inherent disadvantages in terms of their high cost and difficulties of control, reliability and efficiency. Considering environmental compatibility, economics, easy applicability to automation and scale of wastewater purification operations, electrochemical method is in preferential development among all kinds of physicochemical processes and has been found to be the most suitable candidate [5].



Scheme 1. Synthesis of DSD acid

Recently, main types of electrochemical techniques such as anodic oxidation and packed-bed electrode (filled with activated carbon) have been extensively employed in treating phenolic compounds [6], olive mill wastewater [7] and dyestuff effluent [8, 9]. Among these reports, higher COD removal, increasing current efficiency and less energy consumption were obtained. These achievements are for the generation of hydroxyl radical (·OH) on anodes possesses high oxygen over-potential, leading to the rapid oxidation of organic compounds to CO_2 and H_2O. In addition, peroxodisulfates also could be generated by sulfate radicals and involve in the bulk electrolysis [10]. Thus, existence of these oxidants with high oxidation ability causes obvious reduction of organic contaminants in solutions. As far as theoretical analysis is concerned, first-order kinetics was usually used to describe the overall decreases of COD during electrochemical oxidation in the absence and in the presence of GAC [11-13]. However, poor agreement is obviously observed in initial reaction stage between experimental and theoretical when using this homogeneous model. Perhaps, there should be existed a completely different mechanism from current theories during these electrochemical processes.

Herein, we propose a novel theoretical approach to estimate the electrochemical performance for oxidation in the absence and in the presence of granular activated carbon (GAC) at a continuous flow mode based on Faraday's law. It is known that current can be fully utilized when the reaction is in electron transfer controlled regime and a zero-order kinetic could well define the behavior of the reactions [14]. The reduction of COD in solution enhances the diffusion flux of organic matter to the anode and side reaction such as oxygen evolution occurs, then the accumulation of the gas at the electrode surface minimizes the number of active site of the electrode [15] and thus the mass transfer limitation causes an exponential reduction of COD at the subsequent stage. Although the same kinetics reported by several authors [16, 17], the essential differences of this work from the previous literatures are in two aspects: one is the distinction of electron transfer and mass transfer controlled regimes by numerical description of the mass transport properties; the other is establishment of the overall models for theoretical estimation of COD, current efficiency and power consumption evolutions.

This paper is focused on the proposal of a novel kinetics to accurately predict electrochemical performances and the evaluation of the merits and drawbacks in the absence and in the presence of GAC during electrochemical treatment of refractory organic pollutants in DSD acid manufacturing wastewater. In addition, the presented models were checked in detail by experimental data under different applied current densities.

2. EXPERIMENTAL SECTION

2.1 Electrochemical systems

The experimental system consists of a 30 L reservoir, 10 rectangular electrode chambers made of polymethyl methacrylate with 10 cm×10 cm×5 cm in each and a power supply with a maximum output of 300 A and 12 V. A micropore plate is fixed at the bottom of each electrode chamber for even distribution of solution in the reactor. PbO_2/Ti anode and stainless steel cathode with an active area of 0.01 m^2 (10 cm×10 cm) were arranged closed to the inner walls of each chamber with an inter-electrode distance of 5 cm. Raw wastewater with flow rate of 1.0 L/h (2.78×10^{-7} m^3/s) was pumped into each chamber with a metering pump having 12 channels connected to the reservoir. A constant temperature (25 °C) for experiments was controlled through circulating water recycled from a water bath and monitored with glass thermometers immersed in the exit and inlet of each chambers. The process was schematically described in our previous works [18, 19].

The experiments were carried out with and without GAC packed between anode and cathode in each chamber. Commercially available GAC used for the experimentation has a specific surface of 826 m^2/g and a specific weight of 752 g/L. Prior to the experiments, the carbon was washed with deionised water several times and dried in an oven at 105 °C for 48 hours to a constant weight.

2.2 Wastewater characterization

The target solution was collected from a DSD acid manufacture plant, located in North China. The physicochemical characteristics of the wastewater are shown in Table 1. The contents of pH value and conductivity were recorded by using instruments modeled pHSJ-5 and DDSJ-319L, respectively, which were purchased from INESA Scientific INstrument Co.,Ltd (China). The quantities of sulfate and sodium anions were determined by an ion chromatograph (IC) with model of ICS-1600 (USA). As can be seen, the effluent is characterized by low pH value (2.0-5.5), high COD value (18000-26000 mg/L) and little suspended solid (10-50 mg/L). Further, the high concentration of sulfate and sodium anions causes a high value of the electrical conductivity, permitting the application of electrochemical oxidation without dosage of any supported electrolyte.

Table 1. Characterization of DSD manufacturing wastewater used in this work

Items	range	average
pH	2.0-5.5	4.4
conductivity (mS/cm)	125.6-218.3	185.0
COD (mg/L)	18000-26000	24000
suspended solid (mg/L)	10-50	26
sulfate (mg/L)	37860-66260	50700
sodium (mg/L)	18150-31750	24300

2.3 Analytical methods

The COD content of all samples was determined based on the standard methods [20] and each sample was analyzed at least 2 times, so each result is expressed as an average to minimize the deviation.

The cost of electrolysis is directly determined by the power consumption (*E*, kW·h/kg COD) and the following equation was used for the calculation of values of this parameter:

$$E = 1000 \times \frac{UI}{Q(\mathrm{COD}_0 - \mathrm{COD}_t)} \qquad (1)$$

where *U* is applied voltage (V), *I* the current (A), *Q* the flow rate (m^3/s), COD_0 and COD_t (mg/L) the initial and the COD value at a given reaction time *t*.

3. RESULTS AND DISCUSSION

3.1 GAC stable experiments

The effect of adsorption by GAC should be fully considered during electrochemical oxidation of organic compounds. From Fig. 1, we can observe that the continuous running of the combined system under applied current densities *i* of 200-400 A/m^2 is remarkably stable. Theses results of 20 days continuous experiments demonstrate that the elimination of organics was not for the adsorption ability of GAC, but rather owing to the completely direct or indirect oxidation on the anodes and these particles. That is to say, the important role played by GAC is to expand the electrode area, and the total removal quantity of organics of 5503.6, 7994.0 and 8278.5 g after 20 days operation under 200, 300 and 400 A/m^2, respectively, which are more than the weight of GAC of 3760.0 g packed in the electrode gap, can prove this conclusion.

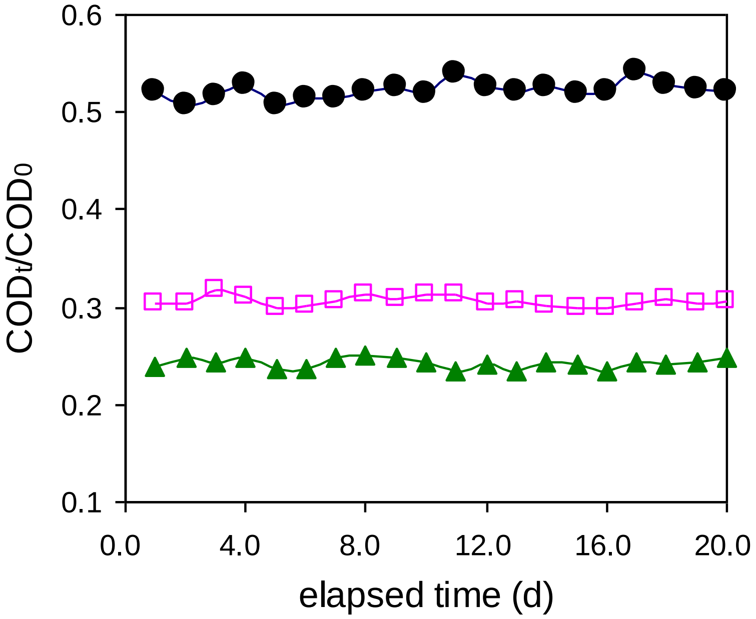


Figure 1. The variation of effluent COD with 20 days continuous operation of PBEC under applied current density (● 200 A/m^2; □ 300 A/m^2; ▲ 400 A/m^2) at a constant temperature of 25 °C.

3.2 COD evolution

In view of the effect of the current density on rate constant and mass transfer, electrochemical oxidation of target organics in DSD acid wastewater was carried out by varying the applied current density in the range 200-400 A/m^2 in the absence and in the presence of GAC, respectively. Fig. 2 shows the relations between the applied current density and COD removal under a constant flow rate. From curves in this figure, we can observe that larger current density results in higher COD removal, leading to the decrease of residential pollutants in solution. In addition, the COD removal with GAC under the same reaction time was about 3 times larger than that of without GAC when the same applied current density was used. Furthermore, Fig. 2a shows the increment between 300 A/m^2 and 400 A/m^2 was much less than that of 200 A/m^2 and 300 A/m^2 without GAC. Similar phenomena have been reported in previous literatures [21-23], and these are due to the existence of mass transport limitation, which makes the increase of side reactions (e.g. water decomposition) when a higher current density is applied. While obvious decrease of the increment from 200 A/m^2 to 300 A/m^2 and the initial stage of 400 A/m^2 are not found in the presence of GAC (see Fig. 2b), maybe this is for the decrease of the effective volume of reactor so as to increase the mass transfer of organic matters to electrode related to the limiting current density (i_{lim}),

$$i_{\mathrm{lim}} = nFk_m c \qquad (2)$$

where n is electron transferred during electrochemical oxidation, F the Faraday's constant (96485 C/mol), k_m the mass transfer coefficient (m/s) and c the concentration of organics in solution (mol/m^3).

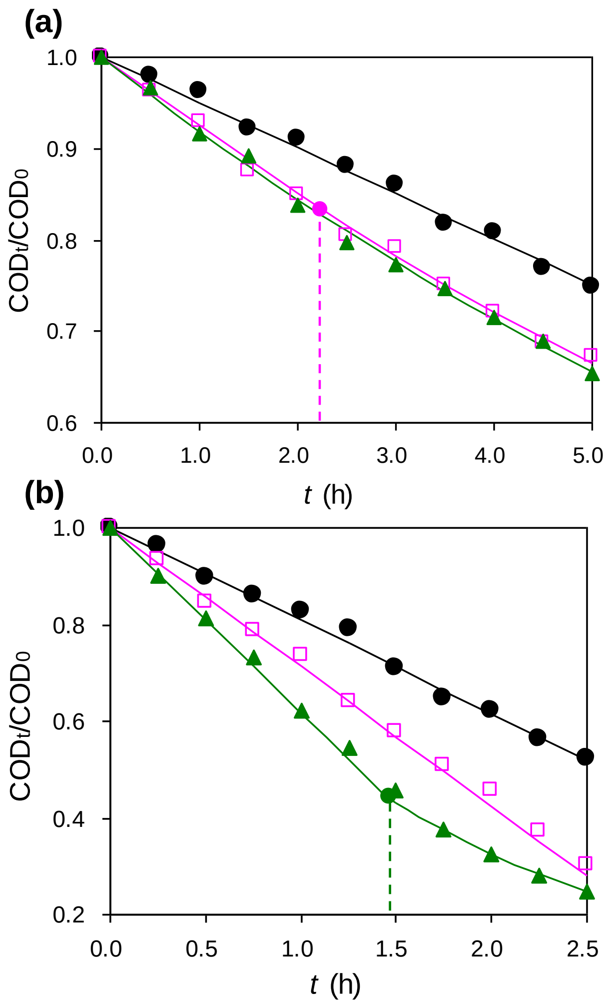


Figure 2. Effect of the applied current density (● 200 A/m^2; □ 300 A/m^2; ▲ 400 A/m^2) on the variation of COD$_t$/COD$_0$ in the absence (a) and in the presence (b) of GAC under flow rate of 1.0 L/h at a constant temperature of 25 °C. The solid curves represent the model prediction using Eqs. (11) and (12).

In many literatures, first-order kinetics is usually used to describe the variation of COD [11-13]

$$\frac{\mathrm{COD}_t}{\mathrm{COD}_0} = \exp(-kt) \qquad (3)$$

Using Eq. (3), the COD values could be calculated by means of the initial COD value (COD$_0$), the rate constant (k, h^{-1}) and the reaction time t. It should be pointed out that the precondition for the employment of this equation is the oxidation should exceed the mass transfer limitations [24]. However, if operated at lower applied current density, the reaction would be determined by electron transfer. Under this condition, mass balance can be conducted using Faraday's law

$$Q(c_0 - c_t) = \frac{I}{nF} \qquad (4)$$

If the concentration c (in mol O_2/m^3) is expressed in unit of g/m^3, Eq. (4) can be rewritten as

$$Q(\mathrm{COD}_0 - \mathrm{COD}_t) = \frac{8I}{F} \qquad (5)$$

The relationship between flow rate and reaction time is as following

$$V = Qt \tag{6}$$

where V is the effective volume of electrochemical reactor (m^3). In the absence of GAC, a linear change of COD could be describe the character of the electron transfer controlled regime at a steady state by substituting Eq. (6) into Eq. (5)

$$\frac{\mathrm{COD}_t}{\mathrm{COD}_0} = 1 - \frac{8I}{VF\mathrm{COD}_0}t \tag{7}$$

As far as GAC is concerned, numerous evidences confirm the GAC particles could be easily isolated and polarized, acting as bipolar microelectrode because of high contact resistance each other [25, 26]. For the parallel character between GAC particles and electrolytic solution, only Faradaic current, which is associated with the values of by-pass resistance (r_2) and Faradaic resistance (r_1), can give full scope to oxidation [27]. The fraction of the Faradaic current (β) to the total cell current is calculated by [28]

$$\beta = \frac{r_2}{r_1 + r_2} \tag{8}$$

Because part of the total current is applied across the particulate electrode, the mass balance analysis in the presence of GAC is expressed as

$$Q(\mathrm{COD}_0 - \mathrm{COD}_t) = \frac{8(1+\beta)I}{F} \tag{9}$$

Substitution of Eq. (6) into Eq. (9) leads to

$$\frac{\mathrm{COD}_t}{\mathrm{COD}_0} = 1 - \frac{8(1+\beta)I}{\varepsilon VF\mathrm{COD}_0}t \tag{10}$$

where ε refers the void fraction of packed bed. Based on Eqs. (7) and (10), the reaction rate constant k in the absence and in the presence of GAC can be calculated from the slope value of the plot t versus $\mathrm{COD}_t/\mathrm{COD}_0$.

The critical time (t_{Cr}) between zero-order and first-order models without and with GAC could be obtained by solving the equations as following

$$\begin{cases} \dfrac{\mathrm{COD}_t}{\mathrm{COD}_0} = 1 - \dfrac{8I}{VF\mathrm{COD}_0}t \\ \dfrac{\mathrm{COD}_t}{\mathrm{COD}_0} = e^{-kt} \end{cases} \tag{11}$$

$$\begin{cases} \dfrac{\mathrm{COD}_t}{\mathrm{COD}_0} = 1 - \dfrac{8(1+\beta)I}{\varepsilon VF\mathrm{COD}_0}t \\ \dfrac{\mathrm{COD}_t}{\mathrm{COD}_0} = e^{-kt} \end{cases} \tag{12}$$

The regression analysis listed in Table 2 by Eqs. (11) and (12) illustrates that first-order kinetics is not always applicable. In case of lower current density, application of linear kinetics is superior to the first-order model, perhaps this is because the electrochemical reactions are far below the mass transfer limitations. However, when the oxidation exceeds the limiting current density calculated by Eq. (2), the first-order kinetics is suitable. Seen from the trends of curves in Fig. 2, linear kinetics causes the rapid decrease of COD, while the first-order model leads to the relatively less reduction of COD under the same interval of reaction time. Fig. 2 also shows the rather higher agreement between experimental data and model simulation. The linear decrease (Eqs. (7) or (10)) could be used to describe the COD variations under 200 A/m^2 and 200 A/m^2, 300 A/m^2 in the absence and in the presence of GAC, respectively, while the oxidation at 400 A/m^2 without GAC should be estimated by the exponential trend. From the comparison of Fig. 2a and 2b, we can observe that the mass transfer limitation of anodic oxidation is easily arrived even at a small applied current density, but slow transition of the limitation is shown even in the same geometric configuration reactor when GAC is used. During the experiments, the linear kinetics and first-order model are used to describe electrochemical oxidation with critical time of 2.25 h without GAC when current density of 300 A/m^2 was employed. At the same time, the critical time of 1.45 h with GAC between linear kinetics and first-order model was obtained at applied current density of 400 A/m^2. The phenomenon can be interpreted as follows: a higher current density relates to a larger value of COD, which makes a less COD removal; however, even under a higher current density at anodes, expanding of electrode area by GAC brings about the decrease of the overall current applied across to the whole system, which is associated with a less value of COD.

Table 2. Summary of linear and first-order regression data for lab-scale rates of electrochemical oxidation under different applied current density in the absence and in the presence of GAC

	Without GAC				With GAC			
	linear		first-order		linear		first-order	
i (A/m^2)	k (h^{-1})	r^2	k (h^{-1})	r^2	k (h^{-1})	r^2	k (h^{-1})	r^2
200	0.0497	0.9935	0.0551	0.9849	0.1920	0.9934	0.2412	0.9735
300	0.0746^a	0.9979	0.0816	0.9966	0.2881	0.9984	0.4119	0.9580
400	0.0995	0.9895	0.0845	0.9968	0.3841^b	0.9987	0.5431	0.9867

[a,b] The linear kinetics end at 2.25 h and 1.45 h, then the process start by first-order model with k=0.0817 (r^2=0.9916) and k=0.5606 (r^2=0.9995) in the absence and in the presence of GAC, respectively.

The above analysis is conducted based on the experimental data, especially for the achievement of the t_{Cr} value. According to electrochemical theory, the linear kinetics last until the applied current is equal to the limiting current, hence, after the combination of Eqs. (2) and (7) or (10) we can obtain

$$t_{\mathrm{Cr}} = \frac{V}{8}\left(\frac{F\,\mathrm{COD}_0}{I} - \frac{8}{Ak_m}\right) \tag{13}$$

$$t_{\mathrm{Cr}} = \frac{\varepsilon V}{8(1+\beta)}\left(\frac{F\,\mathrm{COD}_0}{I} - \frac{8}{Ak_m}\right) \tag{14}$$

where A is the geometric area of anode. To accurately predict the oxidation by the proposed model, determination of the k_m value becomes an important issue in distinguishing the electron transfer (linear kinetics) and mass transfer (first-order model) controlled regimes. The theoretical equation for mass transport properties are shown by Eqs. (15) and (16) in the absence and in the presence of GAC [29, 30].

$$k_m = \sqrt{\frac{2.54 iD(\mathrm{Re}\cdot\mathrm{Sc})^{0.35}}{nFc_0 d(H_R / y_0)^{3.29}}} \quad (15)$$

$$k_m = \sqrt{\frac{i\,\mathrm{Sc}^{1/3} D}{nFc_0 \varepsilon d(H_R / y_0)^{1.27}}(0.765\,\mathrm{Re}^{0.18} + 0.345\,\mathrm{Re}^{0.614})} \quad (16)$$

where D is the diffusion coefficient, d the equivalent length of cell or particle diameter, H_R the hydraulic radius, y_0 the length of anode; Sc (Sc=υ/D) and Re (Re=dv/υ) refer to Schmidt and Reynolds numbers, respectively, here v and υ are the linear velocity and kinematic viscosity of solution.

According to Eqs. (15) and (16), the k_m under 300 A/m^2 and 400 A/m^2 in the absence and in the presence GAC were obtained with values of 1.14×10^{-6} m/s and 2.96×10^{-6} m/s. Substituting the k_m values into Eqs. (13) and (14), the t_Cr values of 2.26 h and 1.46 h under the two condition could be obtained, which are equal to the experimental ones (calculated by Eqs. (11) and (12)). Consequently, quantitative determination of the mass transport coefficient leads to theoretical prediction of current efficiency and power consumption during electrochemical oxidation.

3.3 Calculation of the average current efficiency

The average current efficiency (η) for the electrochemical mineralization could be calculated according to the COD reduction measured at a given reaction time

In the absence of GAC, $\eta = \dfrac{FQ(\mathrm{COD}_0 - \mathrm{COD}_t)}{8I}$ (17)

In the presence of GAC, $\eta = \dfrac{FQ(\mathrm{COD}_0 - \mathrm{COD}_t)}{8(1+\beta)I}$ (18)

The value of η would be 1.0 when the oxidation is in electron transfer control ($t<t_\mathrm{Cr}$) but its value is determined by applied current density if the reaction exceeds the mass transfer limitation [31] and the theoretical description of η in the absence and in the presence of GAC is given by [32]

for $t \geq t_\mathrm{Cr}$, $\eta = \dfrac{8ikt_{Cr} - Fk_m\mathrm{COD}_0(e^{-kt} - e^{-kt_{Cr}})}{8ikt}$ (19)

where i is the applied current density of each chamber. If reaction time is larger than the critical time (t_{Cr}), the average current efficiency could be obtained by substitution of k values simulated by using Eq. (3) and k_m values calculated from Eqs. (15) and (16). From Fig. 3, it can be seen that the experimental data are in high agreement to the theoretical results under these applied current densities, and a significant relevance is displayed when the reaction is in mass transfer control. On the other hand, the oxidation with and without GAC differs in the terms of values of current efficiency (see Fig. 3a and Fig. 3b) and the degradation in the presence of GAC tends to remain relatively higher values of η than those without GAC even under a higher applied current density.

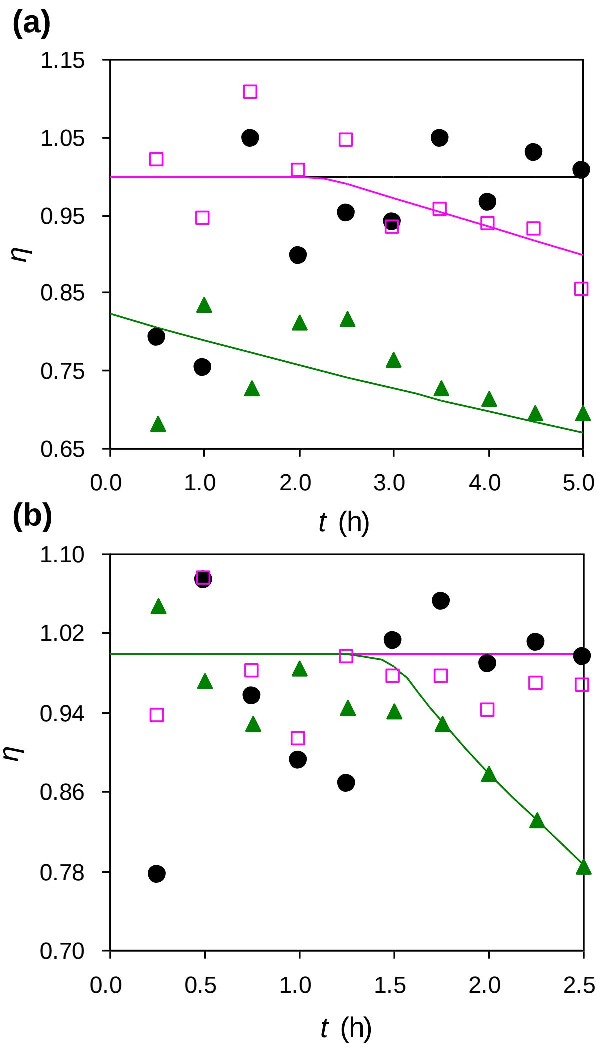


Figure 3. The variation of average current efficiency during electrochemical oxidation at applied current densities of 200 A/m^2 (●), 300 A/m^2 (□) and 400 A/m^2 (▲) in the absence (a) and in the presence (b) of GAC under flow rate of 1 L/h at a constant temperature of 25 °C. The solid curves represent the model prediction using Eq. (19).

3.4 Power consumption

The operation cost is another key parameter to evaluate the feasibility of the treatment process in industrial scale-up and the power consumption can be used as the integrative measurement index.

Taking into account the average current efficiency, one can obtain the following equations through rewriting Eqs. (17) and (18)

$$I = \frac{FQ(\mathrm{COD}_0 - \mathrm{COD}_t)}{8\eta} \tag{20}$$

$$I = \frac{FQ(\mathrm{COD}_0 - \mathrm{COD}_t)}{8(1+\beta)\eta} \tag{21}$$

The combination of Eq. (1) and Eq. (20) or (21) arrives at

$$E = \frac{FU}{3600 \times 8\eta} \tag{22}$$

$$E = \frac{FU}{3600 \times 8(1+\beta)\eta} \tag{23}$$

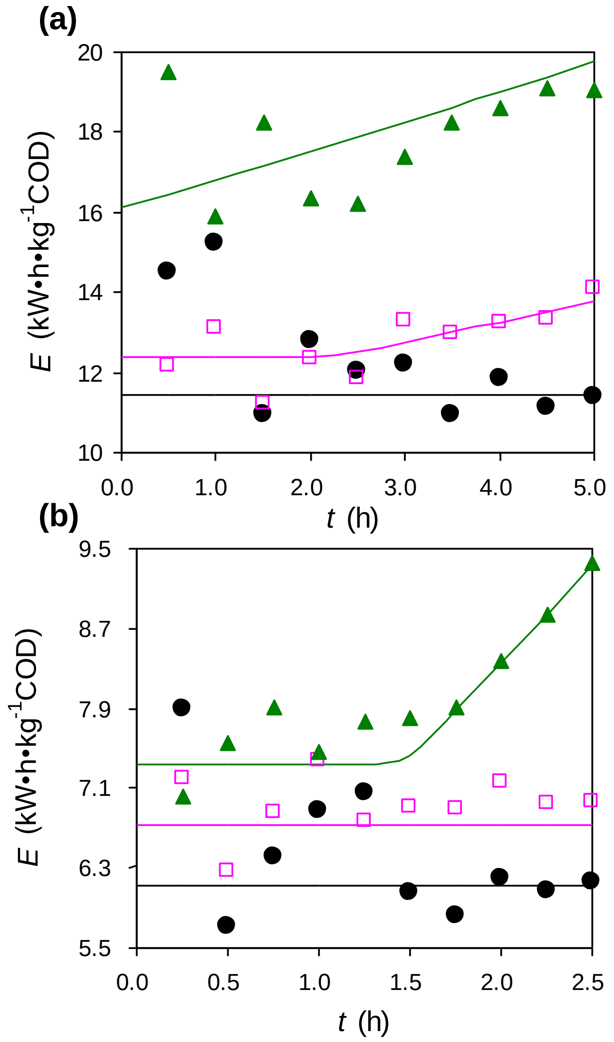


Figure 4. The variation of power consumption during electrochemical oxidation at applied current densities of 200 A/m^2 (●), 300 A/m^2 (□) and 400 A/m^2 (▲) in the absence (a) and in the presence (b) of GAC under flow rate of 1 L/h at a constant temperature of 25 °C. The solid curves represent the model prediction using Eqs. (22) and (23).

Eqs. (22) and (23) could be used to calculate the theoretical power consumption in the absence and in the presence of GAC, respectively. When operated under current density of 200 A/m^2 at reaction time , the power consumptions without and with GAC all remain constant value of 11.5 and 6.2 kW·h/kg COD, and there is around 2 times of the former to the latter (see Fig. 4). Furthermore, the increase of current density causes a sharply enhancement of power consumption, e.g. under current density of 400 A/m^2, the power consumption are 19.1 and 9.4 kW·h/kg COD at reaction time of 5.0 h and 2.5 h in the two systems, respectively. Fig. 4 shows the power consumptions of oxidation with GAC are significant lower than those without GAC although the applied voltage of the former is slightly larger than the latter (Table 3) and there is a higher agreement between the experimental and the theoretical ones. Hence, these experiments performed in this study confirm that employment of GAC as particulate electrode is a preferred access to increase COD removal, enhance current efficiency and reduce power consumption.

Table 3. The applied voltages under different current density in the absence and in the presence of GAC

i (A/m^2)	Without GAC (V)	With GAC (V)
200	3.42	3.53
300	3.70	3.88
400	3.96	4.23

4. CONCLUSION

Kinetics was proposed for prediction of electrochemical oxidation in the absence and in the presence of GAC and the presented model was checked by treatment of 4,4$^{/}$-diaminostilbene-2,2$^{/}$-disulfonic (DSD) acid manufacturing wastewater. The results show the employment of GAC could effectively enhance COD removal efficiency and current yield, as well as reduce power consumption. By using the regression analysis, we can observe the model estimation could satisfactorily match the experimental data when DSD acid wastewater was treated under applied current densities of 200 A/m^2, 300 A/m^2 and 400 A/m^2. The proposed kinetics could provide a different perspective on the evolution of academic approach in electrochemistry, especially for completely electrochemical treatment of high concentrated wastewaters.

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