Experimental investigation on the removal of phenol from simulated wastewater by reverse electrodialysis reactor

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ABSTRACT

The removal of phenol from simulated wastewater by a reverse electrodialysis reactor (REDR) wastewater treatment system is experimentally investigated in independent or synergetic degradation circulation mode under specific conditions. Results demonstrated that the total degradation efficiencies ($\eta_{de,tot}$) and the total chemical oxygen demand (COD) removal efficiencies ($\eta_{COD,tot}$) in an independent degradative circulation mode were better than those in a synergetic degradative circulation mode. After 2 h of treatment, the $\eta_{de,tot}$ of phenol reached 100% and 99.7%, and $\eta_{COD,tot}$ reached 59.6% and 51.3%, under two circulation modes, respectively. However, the synergistic degradation cycle mode achieved a balance between hydrogen ion production and consumption during the wastewater treatment process. When the synergetic circulation mode was applied, the pH of the wastewater was always maintained at around 3 without the addition of acid, which reduced the wastewater treatment costs. Moreover, the general current efficiency and the energy consumption of REDR in the synergetic degradative circulation mode were 51.1% and 168.8 kWh/kgCOD, respectively, after 2 h. Therefore, the implementation of REDR with a suitable circulation mode and operating conditions offered a viable alternative to achieve a win-win situation for both energy and the environment.

Keywords: Reverse electrodialysis; Salinity gradient energy; Phenol; Energy efficiency; Electrochemical advanced oxidation processes

1. Introduction

In recent decades, the occurrence of phenol in natural water has received increasing attention as a persistent organic pollutant. Phenol with high toxicity and poor biodegradability is a common compound in lots of industries, mainly including coke production, pharmaceutical plants, oil refineries, textile processing and several other chemical plants [1]. Once entering natural waters, it will not only cause damage to the ecosystem but also pose a serious threat to human health [2]. The World Health Organization has limited phenol concentration in drinking water to 1 mg/L [3]. Therefore, the development of an effective and safe disposal method for phenol wastewater is nowadays of paramount importance to solve the problem of phenol pollution in natural water bodies.

Currently, the most common methods used in the treatment of phenol-containing wastewater include adsorption [4], supercritical water oxidation [5], catalytic wet oxidation [6], and some biological treatment methods [7]. Each

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of these treatment methods has recognized advantages and disadvantages. For example, the adsorption method has the advantages of simplicity and no secondary pollution, but the adsorption process is difficult to desorb after saturation and the adsorbent is difficult to regenerate. So, it is not suitable for treating high concentrations of phenol wastewater [8]. The traditional biological methods are easy to operate, low cost and flexible, but factors such as influent concentration and temperature can affect the growth of microorganisms, reducing the treatment effect [9]. In these cases, electrochemical advanced oxidation processes (EAOPs) have received great attention in the removal of pollutants from refractory organic wastewater.

EAOPs are based on the electrochemical generation of powerful reactive species, such as hydroxyl radical, on the surface of electrodes, which are then able to destroy organics up to their mineralization [10]. Compared with other traditional wastewater treatment methods, major advantages of the EAOPs are provided as follows [10–12]: (1) high degradation efficiency; (2) no need for additional chemical reagent, which means the process does not require the transportation and storage of oxidants or reductants; (3) mild operating conditions and high environmental compatibility on trials; (4) affordable operating costs. Based on these advantages, EAOPs have been widely applied in the pretreatment and advanced treatment of phenol wastewater.

Mu'azu et al. [13] used direct electrochemical oxidation to degrade phenol at low concentrations and optimized this process via response surface methodology. Results indicated that optimal operating conditions yielded complete oxidation of phenol with an average current efficiency of 19.89% and a specific energy consumption of 329.52 kWh/kg-phenol. An et al. [14] investigated the degradation efficiency of phenol in the three H_2O_2-based EAOP systems (electro-Fenton, photo-electro-Fenton, and photo-electro-generated H_2O_2). Results showed that all three EAOPs were able to remove more than 97% of phenol within 1 h at 10 mA/cm^2.

Even so, the use of EAOPs technology to treat organic wastewater requires a large amount of electrical energy, leading to high costs for wastewater treatment [15]. To solve this problem, an alternative method, namely the reverse electrodialysis reactor (REDR) technology, has been proposed [16]. REDR is a process for power generation from salinity gradient energy (SGE), based on the use of many pairs of alternating anion and cation exchange membranes (AEM/CEM) [17]. Various strong oxidants will be produced at the two electrodes of REDR through appropriate redox processes. Since SGE comes from nature (sea or salt lake water and river water), by-products of desalination plants (concentrated seawater and natural seawater) or waste heat conversion [18,19], low-cost wastewater treatment can be achieved by using REDR technology.

Scialdone et al. [20,21] first proposed the REDR wastewater treatment technology powered by SGE and verified the feasibility of this technology by experiments. Results showed that the Cr(VI) or Acid Orange 7 in wastewater could be successfully abated using SGE and proper redox processes in REDRs. With the conversion of redox reactions, the authors also developed a microbial reverse electrodialysis cell and an assisted reverse electrodialysis to degrade

Cr(VI) and formic acid [22,23]. The results revealed that the selection of electrochemical routes could accelerate the removal rate of pollutants in comparison with the conventional REDR. Zhou et al. [17] used anodic indirect oxidation by REDR to treat ammonia nitrogen wastewater. The results showed that the maximal ammonia degradation rate and output power density of REDR under optimal conditions reached 98% and 0.06 W/m^2, respectively.

The works mentioned above only investigated the reaction mechanism of the anode or cathode respectively. The synergistic effect of redox reactions was not addressed. In this context, Xu et al. [24,25] experimentally investigated the decolorization efficiency of Acid Orange 7 simulated wastewater in synergistic or independent degradation cycle mode. The results indicated that the interference of anodic/cathodic products in a synergetic degradative circulation mode would reduce the decolorization efficiency of azo dye wastewater.

A review of open literature shows that only a few papers have been published on the REDR wastewater treatment technology to date. The removal of simulated phenol wastewater by REDR has not been studied before. For further expanding the application of REDR in the field of wastewater treatment, phenol, a typical phenolic compound, will be explored in this work. The ability to degrade simulated phenol wastewater and the energy efficiency of REDR will be investigated by experiments in two circulation modes. The research verifies the feasibility of REDR to treat phenol-containing wastewater and investigates its performance in terms of removal rate and energy, which provides some valuable experimental guidelines for the practical application of REDR.

2. Experimental material and procedure

2.1. Experimental system

Fig. 1 shows a REDR wastewater treatment system in a synergetic degradative circulation mode, in which Fig. 1a is a flowchart of the experimental system and Fig. 1b is a photo of the actual experimental system. In the system, there are two big peristaltic pumps to push concentrated solution (CS) and diluted solution (DS) flowing through REDR. The volumetric flow rates of CS and DS are 96 mL/min. A small peristaltic pump is used to push wastewater or electrode rinse solution (ERS) flowing through two electrode channels of REDR with a volumetric flow rate of 128 mL/min. Five tanks are used to contain CS feeding solution, DS feeding solution, CS effluent, DS effluent and ERS respectively. Specifications and characteristics of instruments and devices used in the experimental system are shown in Table 1.

Since oxygen is consumed at the cathode of REDR to produce oxygen peroxide (oxidant), an air pump is used to blow air into the cathode channel with a volume flow rate of 800 mL/min. A pH meter is used to determine the pH value of wastewater or ERS. An electrochemical workstation is employed to measure the electrochemical parameters of REDR and control the output current of REDR. The current output by REDR is controlled at 0.2 A during experiments. A pair of mercury-mercurous sulfate reference electrodes
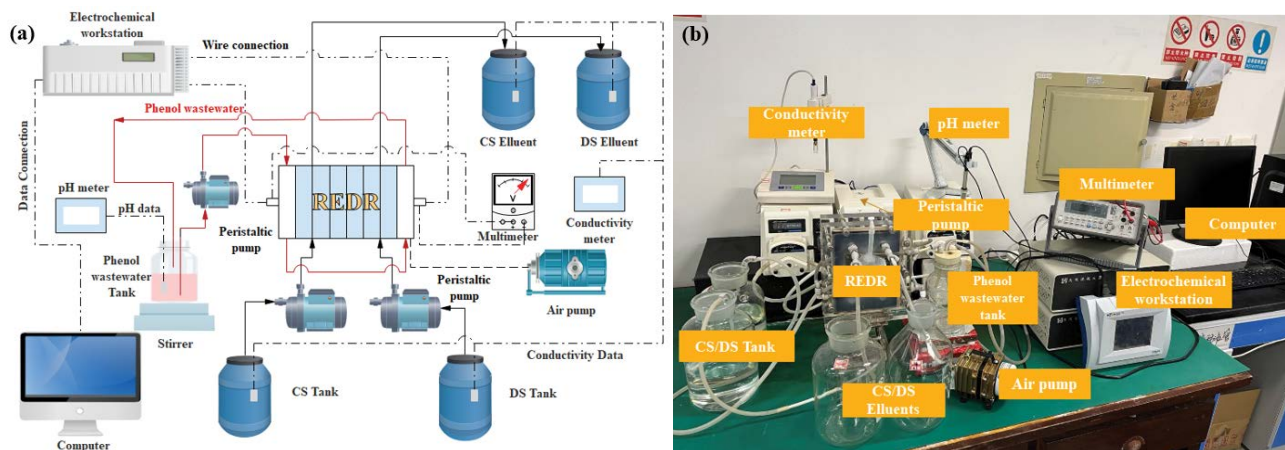
Fig. 1. REDR phenol wastewater treatment experimental system (a) system flowchart and (b) photo of the actual experimental system.

Table 1
Specifications and characteristics of instruments and devices used in the experimental system

Equipment	Manufacturers	Type	Precision
Electrochemical workstation	CH Instruments, Inc., USA	CHI660E	0.2%
CS and DS pumps	Longer, UK	BT100-2J	0.1 r/min
Electronic scale	G&G Measurement, China	JJ1023BC	±0.001 g
UV Spectrophotometer	Shimadzu, Japan	Shimadzu UV-1780	±0.002
pH meter	Lei Ci Instrument Co., China	PXSJ-226	0.001 pH
Air pump	SunSun, China	CT-201	—
ERS pump	Kamoer, China	KCP PRO2-N40	2%
Digital multimeter	Tektronix, USA	Keithley 2110-220	±0.012% DV
Conductivity meter	Mettler Toledo, Switzerland	FiveEasy Plus™ + InLab® 710	±0.5%
COD digester	Lianhua Company, China	5B-1F(V8)	–
COD detector	Lianhua Company, China	5B-3C(V7)	±5%

are used to determine the potential loss of the electrode system (E_{ele}) [26]. The voltage or potential loss is measured by a precise digital multimeter. U-tube manometers are used to measure the pressure drops of working fluids and ERS flowing through REDR.

2.2. Reverse electrodialysis reactor

The key device in the system is a self-made REDR. A lab-scale REDR with 40 membrane pairs/cells is implemented in this work and its structure is shown in Fig. 2. Two external membranes are CEMs rather than AEMs, which is different from previous reports in the literature [22,24,25]. The purpose of using CEMs as the external membranes is to avoid the migration of chloride ions from the working solutions through the ion-exchange membranes (IEMs) into the ERS (wastewater). Active chlorine generated at the anode is avoided, thus preventing the production of toxic organochlorines during the oxidation and degradation of organic pollutants. The IEMs used in REDR are mainly purchased from Fuji Company (7-3, Akasaka 9-chome, Minato-ku, Tokyo 107-0052, Japan) (Type 2) but

only two external membranes (CEM) are purchased from AGC (Selemion, 5-1, Marunouchi 1-chome, Chiyoda-ku, Tokyo 100-8405, Japan). A piece of carbon felt is used as the cathode and its size is 100 mm³ × 100 mm³ × 4.0 mm³. A titanium mesh coated with lead dioxide (Ti/PbO$_2$) is used as the anode and its size is 100 mm³ × 100 mm³ × 3.5 mm³. Ti/PbO$_2$ anode is a non-active anode with a high O$_2$ evolution over-potential. The thicknesses of the anode and cathode channels are 5 and 6 mm, respectively.

As shown in Fig. 2, when the working fluids (DS and CS) flow their respective channels in REDR, a membrane potential will be created owing to the difference in the concentration of anions and cations on both sides of the membrane. Under the action of this membrane potential, two electrodes of REDR will occur redox reactions to produce different oxidants.

2.2.1. Oxidative reaction at the anode

When wastewater or ERS without any chorine ions flows through the anode channel of REDR, a direct oxidative reaction (DO) will be created at the anode coated with

metallic oxide (MO_x) to produce a strong oxidant, adsorbed hydroxyl radical [$MO_x(^{\bullet}OH)$] [27]. Hydroxyl radicals can efficiently destroy organic pollutants in wastewater [28]. The DO process is [27]:

$$MO_x + H_2O \rightarrow MO_x\left(^{\bullet}OH\right) + H^+ + e^- \quad \text{(Non-active anode)} \quad (1)$$
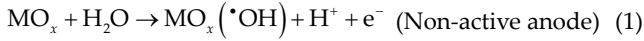
2.2.2. Reduction reaction at the cathode

When acid wastewater or ERS containing ferrous ions flows through the cathode channel of REDR and oxygen or air is injected into it simultaneously, an electro-Fenton reaction (EF) will be created at the cathode to produce a strong oxidant, hydroxyl radical ($^{\bullet}OH$). The EF process is [29]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (3)$$

Fig. 2. Schematic structure and operating principle diagram of reverse electrodialysis reactor (REDR).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

2.3. Degradative circulation modes

When wastewater flows through the anode or cathode channel of REDR, organic pollutants in it can be removed by oxidative degradation reactions. Therefore, two degradative circulation modes, independent and synergetic degradative circulation modes, can be adopted during the wastewater treatment process. Fig. 3 shows the flow diagrams of the independent and synergetic degradative circulation modes respectively. The flow pattern of working solutions in both modes is identical (as shown in Fig. 1a) and is not illustrated here. In this work, the degradation efficiency of simulated phenol wastewater in the two modes will be investigated and compared by experiments.

In an independent degradative circulation mode, there are two separate wastewater loops. The wastewater in the two loops is treated independently and does not interfere with each other. The wastewater in the anode loop will be acidified due to producing plenty of hydrogen ions during the DO process. But the wastewater in the cathode loop will be alkalized due to a large number of hydrogen ions consumed by the EF reaction. Therefore, some acid (sulfuric acid) must be added to the wastewater in the cathode loop to meet the requirement of hydrogen ion concentration or pH for the EF reaction during experiments.

In a synergetic degradative circulation mode, there is only one wastewater loop and the wastewater is treated synergistically by DO and EF reactions at two electrodes. The advantage of this mode is that the hydrogen ions generated at the anode are just equal to the ions consumed at the cathode. The treated wastewater is neither acidified nor alkalized. Any acid is not consumed during the wastewater treatment process, which can reduce wastewater treatment costs.

2.4. Materials

The working fluids (CS and DS) are NaCl aqueous solutions prepared artificially. The concentrations of CS and DS are 3 and 0.03 mol/kg (concentration ratio is 100)
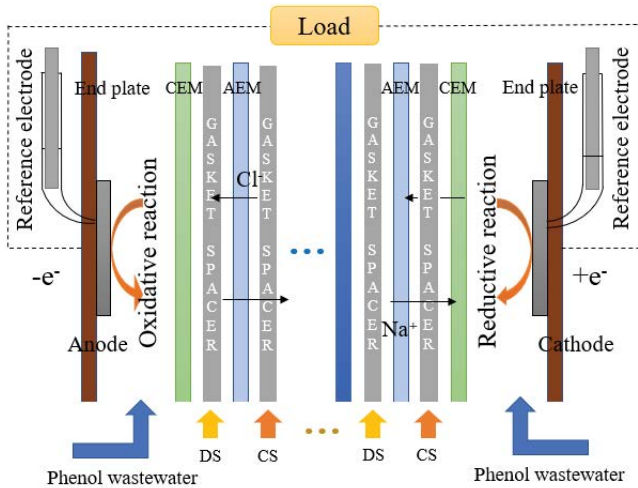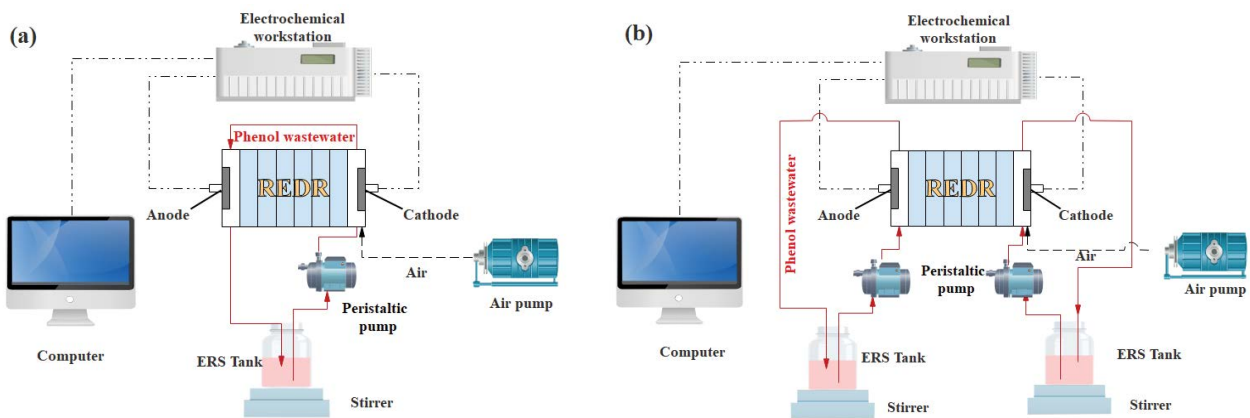

Fig. 3. Flow diagrams of (a) independent circulation mode and (b) synergetic circulation mode.

respectively, and the volume of each is 12 L. Wastewater with phenol concentration of 50 mg/L is also prepared artificially. The properties of phenol are listed in Table 2.

The actual organic wastewater is often accompanied by various impurities of metal salts and the conductivity of the wastewater is large. Therefore, when formulating the simulated organic wastewater, in addition to adding organic substances to the deionized water, a small amount of supporting electrolyte and catalyst (called ERS) should be added and the pH of the simulated wastewater should be adjusted to suit the redox reactions. In this experiment, $NaSO_4$ and $FeSO_4$ are used as the supporting electrolyte and catalyst, respectively. The operation conditions in the two degradative circulation modes are shown in Table 3.

The purities of all reagents or electrolytes used for preparing working fluids and ERS are of analytical grade and are supplied by DAMAO Company (North Yubao Industrial Zone, Huaming Town, Dongli District, Tianjin, China). Deionized water is used as the solvent.

2.5. Measurement and analysis methods

During the experiment, wastewater samples are taken from the ERS tanks at 10 min intervals in the first hour and at 20 min intervals in the second hour. The phenol concentration in the simulated wastewater and chemical oxygen demand (COD) value is measured by 4-aminoantipyrine spectrophotometry and COD rapid determination method. For phenol concentration measurement, the absorbance of the samples is tested by using the UV-1780 Spectrophotometer. Afterwards, the concentration of phenol is deduced according to the standard curve. It should be noted that the wavelength of spectrophotometry to measure phenol is 510 nm. For the measurement of COD values, the samples are placed in the COD digester for digestion after adding a certain amount of potassium dichromate and catalyst. And the COD value can be obtained by the

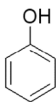test of the COD tester. The degradation efficiency (η_{de}) of phenol and COD removal efficiency (η_{COD}) are calculated by Eqs. (5) and (6), respectively [30,31]. All experiments are repeated in triple and the error bars are reported on the corresponding figures.

$$\eta_{de} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{5}$$

$$\eta_{COD} = \left(1 - \frac{COD_t}{COD_0}\right) \times 100\% \tag{6}$$

where C is the concentration of phenol wastewater, mg/L; COD is the COD value of wastewater, mg/L. Subscript: 0 and t denote the initial and t moments of the processing, respectively.

2.6. Energy consumption

Energy consumed by REDR is the SGE of the working fluid during the wastewater treatment process. SGE is a maximal variation of Gibbs freedom energy of working fluids when they are mixed reversibly. It is [32]:

$$SGE = 2RT\left(Q_{CS}x_{CS}\ln\frac{x_{CS}}{x_m} + Q_{DS}x_{DS}\ln\frac{x_{DS}}{x_m}\right) \tag{7}$$

$$x_m = \frac{(Q_{CS}x_{CS} + Q_{DS}x_{DS})}{(Q_{CS} + Q_{DS})} \tag{8}$$

where R is the universal gas constant, 8.314 J/mol·K; T is the temperature of working fluids, K; x is the molarity of salt in the working fluids, mol/L; Q is the volumetric flow rate of working fluids, L/s. Subscript: CS, DS and m present concentrated, diluted and mixed solutions, respectively.

Energy consumption (EC) and general current efficiency (GCE) of REDR during the wastewater treatment process are [33,34]:

$$EC = \frac{(SGE_{in} - SGE_{out} - P_{net})t}{[(COD_o - COD_t)V_{tot}]} \tag{9}$$

$$GCE = \frac{(COD_0 - COD_t)V_{tot}F}{(8It)} \tag{10}$$

where P_{net} is the net output power of REDR, W; V is the volume of ERS or wastewater, L; F is Faraday constant,

Table 2
Properties of phenol

Molecular formula	C_6H_5OH
Molecular structure	OH
Molecular weight (g/mol)	94.11
Peak absorption wavelength (nm)	510
COD value of phenol with 50 mg/L	119

Table 3
Operating conditions in the two degradative circulation modes

Mode	Redox reactions		Phenol, mg/L	Volume, mL	$NaSO_4$, mol/L	$FeSO_4$, mmol/L	Initial pH	ERS flow rate, mL/min	Current, A	Aeration rate, mL/min
Independent degradative circulation mode	Anode	DO	50	500	0.1	1.0	7.4	128	0.2	–
	Cathode	EF	50	500	0.1	1.0	3	128	0.2	800
Synergetic degradative circulation mode	DO + EF		50	1,000	0.1	1.0	3	128	0.2	800

96,487, C/mol; 8 is the oxygen equivalent mass, g/eq; I is the output current of REDR, A; t is the treatment time, h. Subscript: in and out present the inlet and outlet of REDR; tot donates the total.

Net power output by REDR is [35]:

$$P_{net} = P_{output} - P_{pump} = IU - P_{pump} \qquad (11)$$

Power consumed by pumps (P_{pump}) is [35]:

$$P_{pump} = \frac{\sum_i \left(\Delta P \times \dfrac{Q}{1000} \right)_i}{\eta_{pump}} \qquad (12)$$

where U is the output or terminal voltage of REDR, V; ΔP is the pressure drop of the working fluid or ERS flowing through REDR, Pa; η_{pump} is the pump efficiency (It is set as 0.75). Subscript: i presents the ith pump.

Power consumed by the electrode reactions of REDR (P_{ele}) is:

$$P_{ele} = E_{ele}I \qquad (13)$$

where E_{ele} is the potential loss caused by the electrode compartment, V.

3. Results and discussion

3.1. Independent degradative circulation mode

Fig. 4 shows the variations of degradation efficiency (η_{de}) and COD removal efficiency (η_{COD}) of phenol in wastewater with treatment time in the independent degradative circulation mode. It can be seen from Fig. 4a that phenol in wastewater can be degraded rapidly in both loops, and the η_{de} in the cathode loop is better than that in the anode loop. It implies the EF process is superior to the DO process

for phenol degradation, which is consistent with previous reports [36]. After 2 h of treatment, the η_{de} in the two loops can reach 93.4% and 99.9%, respectively.

Actually, during the phenol degradative processes, the phenol is first decomposed into some intermediate products such as hydroquinone, p-benzoquinone, catechol, and then continues to be degraded into small molecular carboxylic acids, before complete mineralization [1]. Since the mineralization rate of some intermediate products may be relatively low, the value of η_{COD} is always much lower than the value of η_{de} in the phenol wastewater treatment process by REDR (Fig. 4b).

However, it is worth noting that the η_{COD} of the wastewater in the anode loop is higher than that of the cathode loop during the first 80 min of the wastewater treatment process. Then, the η_{COD} of the anode loop is lower than that of the cathode loop. The reason for this phenomenon is that the hydroxyl radicals adsorbed on the surface of the anode react directly with organic pollutants in wastewater during the DO degradation process. When the concentration of pollutants in the wastewater decreases, the mass transfer kinetics [$MO_x(^\bullet OH)$] between the pollutants and the oxidant decreases, which leads to a decrease in the removal rate of the anode loop with increasing treatment time. For the EF degradation process in the cathodic loop, the homogeneous hydroxyl radicals in the ERS react with the organic pollutants in wastewater. The removal rate is hardly controlled by the mass transfer kinetics. Thus, the phenol mineralization rate in the cathodic loop varies almost linearly with the treatment time. After 2 h of treatment, the η_{COD} in the anode and cathode loops are 51.8% and 62.8%, respectively.

3.2. Synergetic degradative circulation mode

In this section, different combinations of anode and cathode reactions will be investigated to explore an optimal combination of redox reactions and operating conditions.
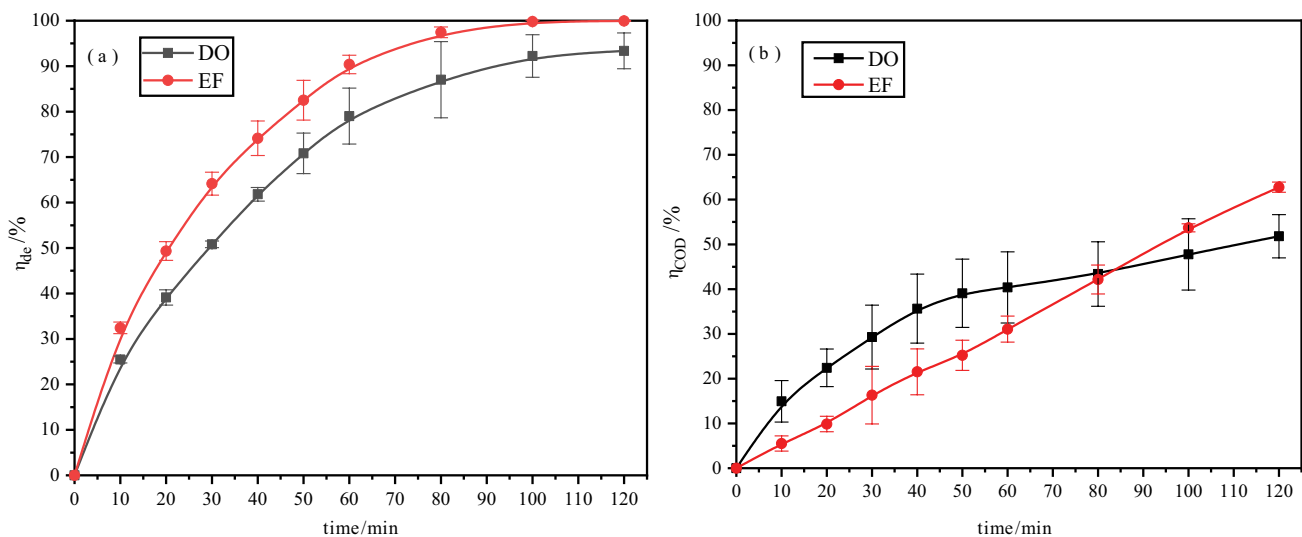

Fig. 4. Variations of (a) degradation efficiency (η_{de}) and (b) COD removal efficiency (η_{COD}) of phenol in wastewater with treatment time in the independent degradative circulation mode.

These combinations include DO-EF, DO-H$_2$O$_2$ and DO-blank processes. In a DO-EF process, both DO and EF reactions are created when ERS flows through two electrode channels in series by adding ferrous catalysts and air to ERS. In a DO-H$_2$O$_2$ process, a DO reaction and a reduction reaction of electro-generated H$_2$O$_2$ are created when ERS flows through two electrode channels in series by only injecting air into ERS. And in a DO-blank process, neither ferrous catalysts nor air is added to ERS. Only a DO reaction occurs when ERS flows through the two electrode channels in series. Fig. 5 shows the η$_{de}$ and η$_{COD}$ of phenol in wastewater at a current of 0.2A in different combinations of anode and cathode reactions.

Fig. 5a shows that although phenol in wastewater can be successfully degraded in different combinations of anode and cathode reactions, the values of η$_{de}$ are different for the same treatment time. The experimental results show that the sorting order of η$_{de}$ for the three treatment processes is DO-EF process > DO-H$_2$O$_2$ process > DO-blank process at the same treatment time. After 2 h of treatment, the η$_{de}$ of DO-EF, DO-H$_2$O$_2$ and DO-blank processes is 99.7%, 93.4% and 81.7%, respectively.

It is obvious that the degradation efficiency of phenol wastewater in the DO-EF process is the highest among the three treatment processes. This is because the oxidation potential of hydroxyl radicals is higher than that of hydrogen peroxide (H$_2$O$_2$). Additionally, H$_2$O$_2$ is easily decomposed into O$_2$ and hydrogen ions again during the wastewater treatment process as shown in Eq. (14) [37]. Under the condition of ERS without dissolved hydrogen, the reduction reaction at the cathode is mainly a hydrogen evolution reaction and almost no oxidant is produced. Therefore, the degradation efficiency of phenol wastewater in the DO-blank process is the lowest.

$$H_2O_2 \rightarrow O_{2(g)} + 2H^+ + 2e^- \qquad (14)$$

Fig. 5b shows the η$_{COD}$ also rises with increasing treatment time in all three treatment processes. It can be seen from the figure that the η$_{COD}$ for the three treatment processes is ranked as follows: DO-EF process > DO-H$_2$O$_2$ process > DO-blank process for the same treatment time. After 2 h of treatment the η$_{COD}$ values of DO-EF, DO-H$_2$O$_2$ and DO-blank processes are 51.3%, 40.1% and 31.9%, respectively. It can also be seen from the figure that the variation of η$_{COD}$ with treatment time for the DO-EF process is almost linear. During the first 40 min of treatment time, the curves of η$_{COD}$ with treatment time for the DO-EF and DO-H$_2$O$_2$ processes overlap. But, as the treatment time increases, the η$_{COD}$ values of the DO-EF process are higher than those of the DO-H$_2$O$_2$ process. This further proves that the concentration of hydroxyl radicals in wastewater increases with treatment time in the EF process [38], which keeps the COD removal rate of wastewater constant (discuss in Section 3.1 – Independent degradative circulation mode). Since the oxidation and degradation reactions occurring between organic matter and H$_2$O$_2$ oxidant are controlled by mass transfer, the COD removal rate reduces as the concentration of organics in the wastewater decreases.

3.3. Comparison of two modes

For comparing the strengths and weaknesses of two degradative circulation modes, the total degradation efficiency of phenol (η$_{de,tot}$) and the total COD removal efficiency (η$_{COD,tot}$) are introduced. They are:

$$\eta_{de,tot} = \left[\frac{\sum_i (c_{0,i} - C_{t,i})V_i}{\sum_i (c_{0,i}V_i)} \right] \times 100\% \quad i = a,c \qquad (15)$$

$$\eta_{COD,tot} = \left[\frac{\sum_i (COD_{0,i} - COD_{t,i})V_i}{\sum_i (COD_{0,i}V_i)} \right] \times 100\% \quad i = a,c \qquad (16)$$

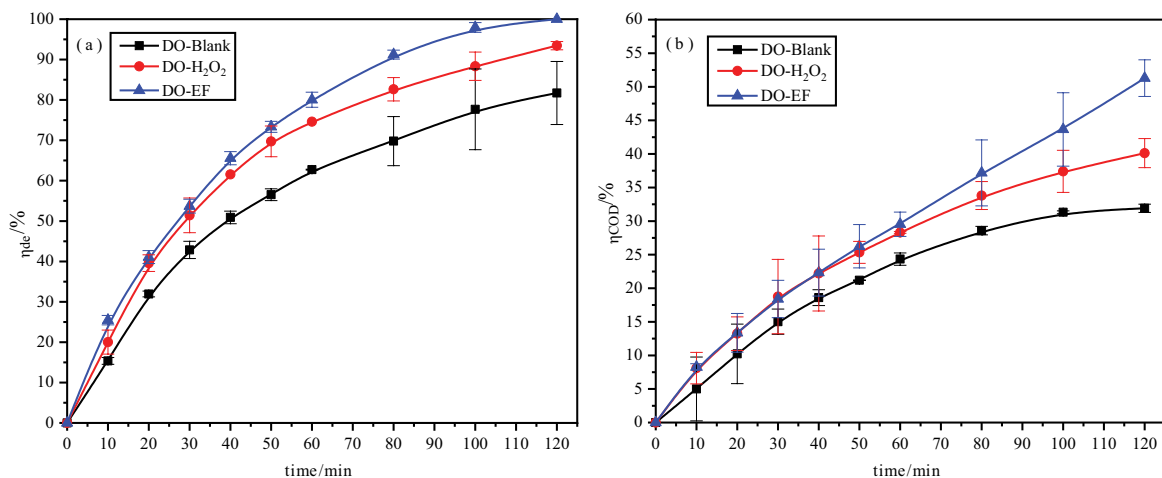where a and c are the anode and cathode loops, respectively.

Fig. 5. Variations of (a) degradation efficiency (η$_{de}$) and (b) COD removal efficiency (η$_{COD}$) of phenol in the wastewater with treatment time at a current of 0.2 A in different combinations of anode and cathode reactions.

Fig. 6a illustrates the variations of total degradation and COD removal efficiencies ($\eta_{de,tot}$ and $\eta_{COD,tot}$) with treatment time in two degradative circulation modes under the given redox processes and operating conditions. The given redox processes are a DO reaction at the anode and an EF reaction at the cathode. And the operating conditions are initial phenol concentration of 50 mg/L, air flow rate of 800 mL/min, Na_2SO_4 concentration of 0.1M, $FeSO_4$ concentration of 1.0 mM and current of 0.2 A.

Experimental results show that phenol in wastewater can be almost fully decomposed in both degradative circulation modes after 2 h of treatment. $\eta_{de,tot}$ can reach 100% in the independent degradative circulation mode and 99.7% in the synergetic degradative circulation mode. $\eta_{COD,tot}$ is 59.6% in the independent degradative circulation mode and 51.3% in the synergetic degradative circulation mode. Obviously, $\eta_{COD,tot}$ is always lower than $\eta_{de,tot}$ regardless of the mode applied. This is consistent with the results obtained in Section 3.1 – Independent degradative circulation mode.

It also can be seen from the figure that both $\eta_{de,tot}$ and $\eta_{COD,tot}$ in the independent degradative circulation mode are superior to those in the synergetic degradative circulation mode. The main reason is that in the synergetic degradative circulation mode, the reaction between hydroxyl radicals and ferrous ions or hydrogen peroxide leads to a decrease in the concentration of strong oxidants. The reaction equations are given by [39,40].

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{17}$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \tag{18}$$

Although $\eta_{de,tot}$ and $\eta_{COD,tot}$ in the independent degradative circulation mode are superior to those in the synergetic degradative circulation mode, the disadvantages of the independent degradative circulation mode are also obvious. Fig. 6b illustrates the pH of wastewater or ERS with treatment time in the two degradative circulation modes under the same conditions. It can be found from this figure that the wastewater or ERS of the anode loop in the independent degradative circulation mode is acidized due to the occurrence of reaction (1). The pH decreases from 7.4 to 2.1 when the treatment time increases from 0 to 120 min.

In addition, it is clear from Eqs. (2)–(4) that the EF reaction is an acid-consuming process in the cathode loop. Therefore, a dynamic equilibrium of the hydrogen ions is achieved with the synergistic effect of the synergistic degradation cycle mode. As shown in Fig. 6b, the pH of the wastewater or ERS in the synergistic degradation cycle mode is kept around 3 during experiments. The absence of acid in the wastewater or ERS is very important to simplify the experimental process and reduce the cost of wastewater treatment.

3.4. Energy analysis

The application of a REDR wastewater treatment system aims to reduce electrical power consumption and costs in the wastewater treatment process by utilizing SGE from nature, by-products from desalination plants, or waste heat conversion. In this section, an in-depth energy analysis of the synergetic degradative circulation mode will be presented to further explore the application value of the system.

3.4.1. Current efficiency and energy consumption

Two performance indexes, the general current efficiency (GCE) and energy consumption (EC) are used to evaluate the energy efficiency of the REDR wastewater treatment system. The former indicator is defined as a ratio of charges used for the oxidation and degradation of phenol compound to the total charges passed during the treatment process [41]. And the latter one presents the SGE consumption of removing 1 kg COD from phenol wastewater [42]. Fig. 7 shows the variation of GCE and EC in the system with the DO-EF process in a synergetic degradative circulation mode.
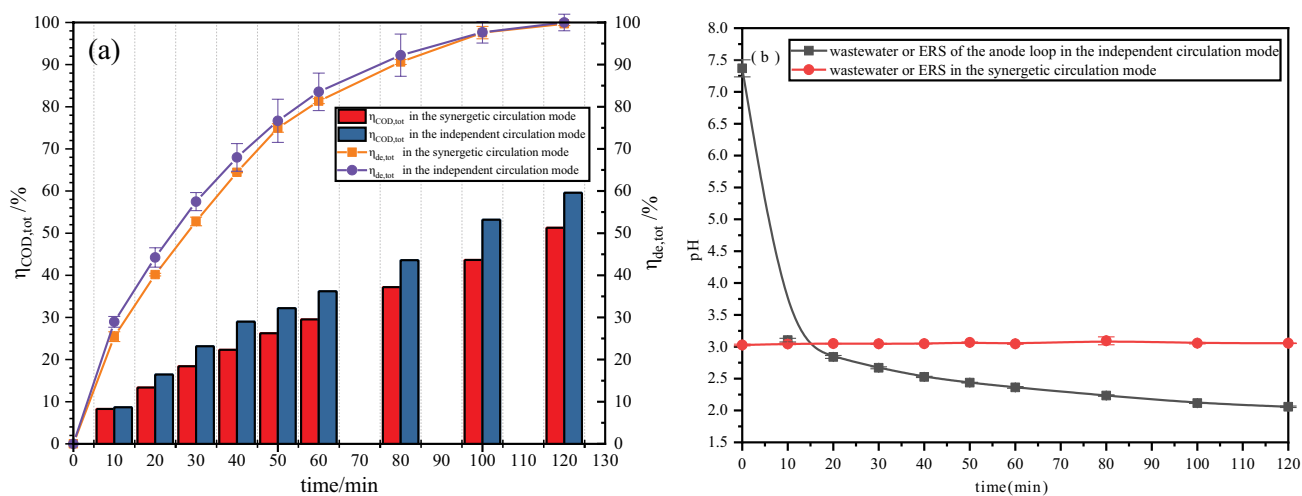

Fig. 6. Variations of (a) total degradative and COD removal efficiencies ($\eta_{de,tot}$ and $\eta_{COD,tot}$) and (b) pH of wastewater with treatment time in two degradative circulation modes under the given redox process and operating conditions.

As shown in Fig. 7, the GCE drops and EC rises with the increase of treatment time. It is easy to understand that the decrease of GCE means that partial charges exchanged at the two electrodes are not involved in the degradation reactions of organic pollutants in wastewater; accordingly, the energy consumed by the system is used to generate some side reactions, which leads to the increase of the EC value. Moreover, it can be seen from the figure that the value of GCE can reach 100% within the first 10 min of a 2-h treatment. This is because more phenol molecules enter the reaction zone near the electrode surfaces under the conditions of high phenol concentration. The charge exchanged at the electrode surface is completely used to generate hydroxyl radicals to degrade organic matter. The degradation reaction is controlled by the current in this period [43].

However, as the treatment time increases and the concentration of organics in the wastewater decreases, the reaction kinetics will shift to mass transfer control, and the GCE value in this period is below 1. Experimental results show that GCE drops from 100% to 51.1% and EC rises from 87.1 to 168.8 kWh/kgCOD when the treating time rises from 10 to 120 min. Therefore, from the point of view of reducing energy consumption, the REDR wastewater treatment system is suitable as a pretreatment method for treating a high concentration of refractory organic wastewater.

3.4.2. Energy consumption distribution

Fig. 8 illustrates the energy consumption distribution of the REDR system with the DO-EF process after 2 h of treatment in the synergistic degradation cycle mode. The SGE consumed by REDR in the system is a salinity difference of the working fluids (CS and DS) flowing through REDR. During the energy conversion process, SGE is converted into oxidative degradation energy or electrode system energy (E_{ele}), net output electrical energy (E_{net}) and various energy losses (E_{loss}). The energy losses are caused by the internal resistances of REDR, the co-ions and solvent (water) crossing the IEMs, etc. [44]. It can be seen from Fig. 8 that various energy losses account for most of the SGE, close to 88.2% of the SGE. So, reducing the various energy losses of REDR is an effective way to improve the energy conversion efficiency of REDR.

A voltage loss of the REDR electrode system originates from the theoretical redox reaction potential, over-potential and concentration polarization potential [26]. Since the concentration polarization potential loss is much less than theoretical redox reaction potential and over-potential losses, the voltage electrode system loss is mainly caused by theoretical redox reaction potential and over-potential losses. It can be seen from Fig. 8 that the effective energy (E_{ef}) supplied by REDR is only 0.628 W in the consumed SGE, of which a net output electrical energy is 0.173 W and electrode system energy is 0.455 W.
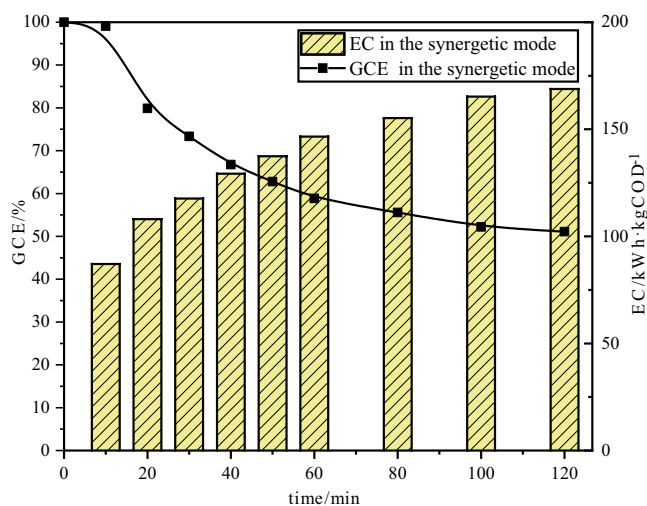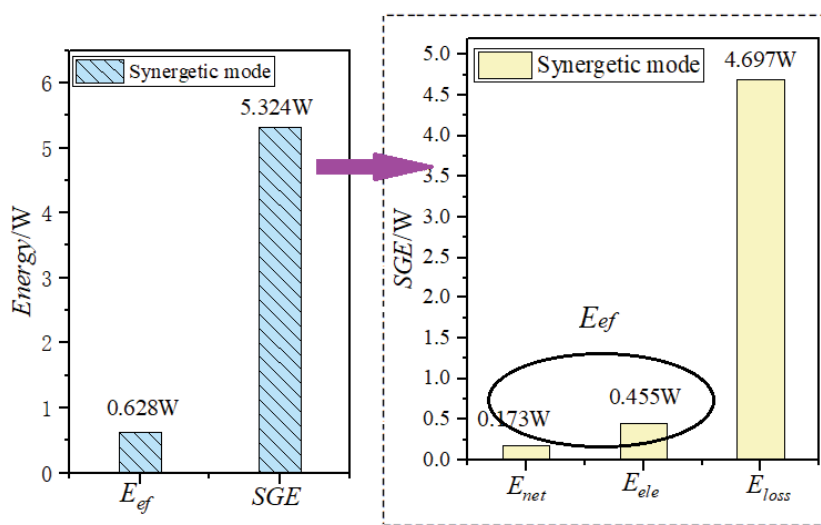

Fig. 7. Variations of general current efficiency (GCE) and energy consumption (EC) of a REDR wastewater treatment system with DO-EF process with treatment time in a synergetic degradative circulation mode.

Fig. 8. Energy distribution with DO-EF process in the synergetic degradative circulation modes after 2 h of treatment.

Table 4
Comparison of the performance indicators of various phenol wastewater treatment methods

Methods	Current density/Concentration of pollutants (time)	COD removal (%)	Energy consumption (kWh/kgCOD)	General current efficiency (%)	References
Photo-electrocatalytic oxidation	30 A/m²/30 mmol/L (180 min)	35.0	228.0	3.5	[45]
Anodic oxidation	30 A/m²/100 mg/L (60 min)	49.1	200.0	–	[46]
DO-H₂O₂	33.3 A/m²/100 mg/L (120 min)	13.0	700.0	4.0	[47]
Electrochemical oxidation	30 A/m²/100 mg/L (120 min)	52.1	219.0	–	[34]
Synergetic degradative circulation mode	20 A/m²/50 mg/L (120 min)	51.3	168.8[a]	51.1	This paper

[a]Salinity gradient energy.

3.5. Comparison with other technologies

The performance indicators of various EAOPs reported in the literature for phenol wastewater treatment are listed in Table 4. It can be seen from the table that whether COD removal efficiency or energy efficiency, the performance indicators of REDR system with DO-EF process in a synergetic degradative circulation mode outperform those of other EAOPs. It is because the redox reactions at both electrodes of REDR can be simultaneously applied to degrade phenol in wastewater, which gives the REDR wastewater treatment system a relatively high current efficiency and low energy consumption during the wastewater treatment process. Moreover, the energy source that drives the REDR system is cheap SGE rather than expensive electrical energy.

In summary, the removal of phenol using REDR has the advantages of high current efficiency, low energy consumption, and low operating cost, which achieves a win-win situation for both energy and the environment. However, the energy conversion efficiency of REDR is still low, especially due to the limitations of IEMs and electrodes, such as the low selective permeability coefficients of the membranes or the high reactivity of the electrodes. To improve the energy conversion efficiency of REDR, exploring suitable IEMs and electrode materials is urgent.

4. Conclusions

In this paper, an experimental investigation of phenol in simulated wastewater removed by a REDR system was carried out and an energy analysis of the system was done. Some conclusions can be drawn as follows:

- An appropriate degradative circulation mode is of significance to reduce the costs of wastewater treatment. Under the given conditions, the total degradation efficiency ($\eta_{de,tot}$) and total COD removal efficiency ($\eta_{COD,tot}$) in an independent degradative circulation mode are slightly higher than those in a synergetic degradative circulation mode. However, the synergetic degradative circulation mode can balance the generation and consumption of hydrogen ions, which eliminates the need for the addition of acid during the wastewater treatment process.
- In an independent degradative circulation mode, the EF process in a cathodic loop facilitates the removal of

phenol from simulated wastewater compared to the DO process in an anodic loop. The η_{de} is 93.4% and 100%, and the η_{COD} is 51.8% and 62.8%, respectively in the anode and cathode loops after 2 h of treatment.

- In a synergetic degradative circulation mode, the ranking orders of degradation efficiency for the three combinations of redox reactions are DO-EF process > DO-H₂O₂ process > DO-blank process at the same treatment time. Within 2 h of treatment time, η_{de} and η_{COD} in the DO-EF process reach a maximum value of 99.7% and 51.3%, respectively.
- Extended treatment time is not conducive to improving current efficiency and reducing energy consumption in REDR wastewater treatment systems. Experimental results show that the general current efficiency drops from 100% to 51.1% and the energy consumption rises from 87.1 to 168.8 kWh/kgCOD when treatment time increases from 10 to 120 min under the restricted conditions.
- The energy conversion efficiency of the system is relatively low. Under specific conditions, various energy losses account for about 88.2% of the SGE consumed by the system. Reducing various energy losses becomes one of the key measures to improve the energy conversion of REDR wastewater treatment systems.

Declaration of competing interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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