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# Treatment of cooling tower blowdown water by using adsorption-electrocatalytic oxidation: Technical performance, toxicity assessment and economic evaluation

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ABSTRACT

An eco-friendly process was adopted to treat cooling tower blowdown water (CTBD) and the toxicity of correspondingly produced water/eluate was evaluated using the transcriptional effect level index (TELI) based on toxicogenomics. The objective of the work is to provide a feasible treatment loop including adsorption to remove organics and phosphorus from CTBD, electrocatalytic oxidation to improve the biodegradability of the eluate after desorption. Results showed that PANI/$TiO_2$ was a promising adsorbent in the removal of organics and phosphorus from CTBD and exhibited a satisfied regeneration ability beyond 30 times of reuse. During the electrocatalytic oxidation process the biodegradability of desorption eluate was gradually increasing and $BOD_5$/COD of the oxidized eluate reached 0.4 after 4.8 h of treatment, indicating that the treated wastewater could be returned to the biological treatment loop for further processing. The analysis of the quantitative toxicogenomics assay revealed that the toxicity of CTBD was mainly caused by oxidizing biocides of trichloroisocyanuric acid (TCCA), leading to a significant membrane stress response of bacteria. And the toxicity level of CTBD decreased after adsorption treatment while the desorption eluate experienced increase and then decrease during the electrocatalytic oxidation, meaning that certain oxidation duration was needed to keep the eluate safe for biological treatment. According to economic analysis, the operation cost of treatment loop was estimated at around 0.6 dollars/$m^3$, ensuring high reuse water quality and safe eluate for further biological treatment.

## 1. Introduction

Annually, huge amounts of freshwater globally are used for cooling tower systems [1,2]. For China, the industrial circulating cooling water consumption is up to 100 billion cubic meters, accounting for 60–80% of the total industrial water consumption [3]. A great deal of chemicals, such as scale inhibitors, corrosion inhibitors, biocides etc., are added into the cooling water to maintain the system chemically and biologically stable [4]. Due to evaporation, salts are condensed and need to be discharged regularly [5,6]. In this regard large volumes (10–20% of the consumed water) of the cooling tower blowdown water (CTBD) rich in chemicals (dozens to hundreds mg/L), phosphorus (several mg/L) and other organics (dozens mg/L) need to be discharged and handled, which otherwise would bring severely negative impact on the accepting water bodies or wastewater treatment plants (WWTPs).

In the CTBD water, the contaminants are mainly synthetic chemicals and a mixture of solvable microbiological products (SMP) and natural organic matter (NOM), contributing to COD, nutrients (e.g. phosphorus) and leading to toxicity. Regarding corrosion and scale inhibitors, the most widely used agents in most countries (e.g. China) are still phosphorus series [7,8], such as nitrilotrimethylene triphosphonic acid (ATMP, $C_3H_{12}NO_9P_3$), hexanediamine tetramethylene phosphonic acid (HDTMP, $C_{10}H_{28}N_2O_{12}P_4$), etc. which bring organics and nutrients to the water body when incorrectly discharged and would lead to severe

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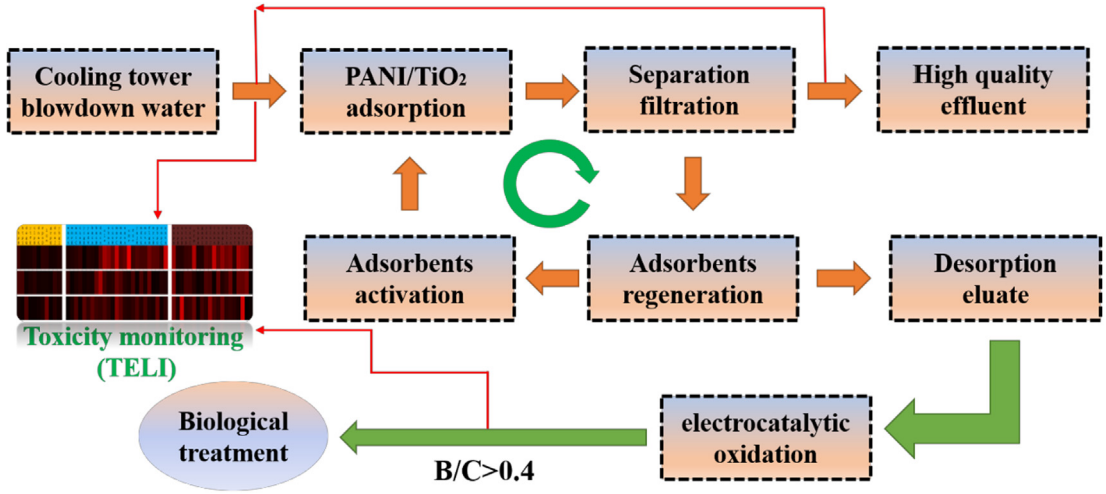


**Fig. 1.** Flow chart of CTBD water treatment process.

contamination and eutrophication [9,10]. Besides, anti-bacteria reagents such as trichloroisocyanuric acid (TCCA, $C_3N_3O_3Cl_3$) are commonly used in cooling water as oxidizing biocide. Some WWTPs accepting discharged CTBD containing biocides often complained collapse of the microbiological system for wastewater treatment and thus severely dropped treatment efficiency. Some studies showed that the decomposed products of biocides (e.g. TCCA) are readily to react with organics in water and form toxic disinfection by-products (DBPs) which would increase the risks of cytotoxicity, neurotoxicity and genotoxicity [11–13] due to the use of such contaminated water. In general, although the aforementioned chemicals exhibit good corrosion, scale and bactericidal inhibition efficiency, they are usually environmentally unfriendly and lead to toxicity for organisms and the ecosystem. Therefore, effective wastewater treatment technology is urgently needed to remove COD and nutrients and reduce the toxicity.

At present, the common technologies for CTBD treatment include flocculation, membrane filtration, etc., but the problems of high investment cost, poor stability and secondary pollution have to be considered [14,15]. From both economy and effectiveness perspectives, adsorption is considered as a promising technology for simultaneous removal of organics and phosphorus [16–18]. The thus treated wastewater could be either discharged or reused. Among candidate adsorbents polyaniline-modified $TiO_2$ (PANI/$TiO_2$) is a novel composite adsorbent designed by Wang et al., which showed outstanding performance in the removal of dyes, phosphorus and effluent organic matters from treated wastewater [19,20]. In addition, the adsorbent exhibited excellent regeneration ability [21]. Considering its high efficiency and regeneration ability, PANI/$TiO_2$ was selected in the present work for the treatment of CTBD.

CTBD treated by adsorption would produce desorption eluate which is rich in contaminants [19]. COD of the eluate could usually exceed 10,000 mg/L accompanied by high ion concentration (to the level of g/L). Till present, treatment of eluate has not got enough attention in previous studies while the efficacy of the adsorption itself was always the focus. Among advanced treatment technologies handling such heavily contaminated water electrocatalytic oxidation is one of the most suitable processes for its high efficiency in removing recalcitrant pollutants and the property of easy to use [22–26]. Usually, Ti/$PbO_2$ is considered as a promising anode material and has been successfully used in electrocatalytic oxidation process due to its strong oxidation ability, low cost and easy for preparation [27–29]. From economic perspective the refractory eluate does not need to be fully mineralized, but to achieve certain level of biodegradability and then discharged to biological WWTPs [30,31]. The integration of adsorption, electrocatalytic oxidation could thus form a thorough treatment loop [19].

In such a loop it is necessary to assess the toxicity of the liquid formed in each step, to understand its possible impact on human healthy and the bacteria in accepting water bodies or WWTPs. Among a number of toxicity test methods, transcriptional effect level index (TELI) is a novel, feasible and cost-effective quantitative toxicogenomics-based toxicity assessment method [32,33]. It could quantify toxicity and simultaneously analyze toxic mechanisms within 2–4 h. It is important to note that TELI is a quantitative evaluation criteria for toxicity level, which exhibited a dose-response relationship and allowed for linking the transcriptional level effects to conventional toxicity endpoints [32]. At present, this method has been successfully applied in some fields for toxicity analysis [34–36]. Toxicity assessment is important for risk evaluation but has usually been neglected by studies focusing mainly on the treatment efficiency as a sole consideration.

In this work, the combination of treatment processes including adsorption of CTBD and electrocatalytic oxidation of thus formed eluate, were presented to deal with such kind of wastewater. The performance of PANI/$TiO_2$ on the removal of organics and phosphorus was evaluated, the effectiveness of electrocatalytic oxidation on the treatment of desorption eluate regarding COD decrement and biodegradability improvement was proved. TELI method was applied to assess the toxicity of the wastewater quantitatively and understand the toxic mechanisms regarding the activation/deactivation of certain genes after certain treatment processes. In addition, we also evaluated the economic cost of the whole treatment process. The purpose of the present work is to provide an efficient, economical and eco-friendly treatment process for CTBD.

## 2. Materials and methods

### *2.1. Illustration of the adsorption-desorption and electrocatalytic oxidation treatment loop*

The flowchart (Fig. 1) shows the specific processes of the overall CTBD-related treatment: firstly, PANI-$TiO_2$ was used to remove organic pollutants and phosphorus from CTBD. The high-quality water with low COD and P contents was obtained by filtration to separate the solid adsorbents from it. Secondly, the used PANI-$TiO_2$ was desorbed and activated by using acidic-alkaline. Finally, the desorbed and concentrated eluate was electrocatalyticaly oxidized to achieve COD removal and biodegradability improvement, so as to meet the requirement for subsequent biological treatment. The toxicity of effluent or concentrated eluate was evaluated during the whole treatment process.

**Table 1**
List of CTBD water quality.

| Parameters | Value |
|---|---|
| TP | 5.6–6.3 mg/L |
| COD | 63.2–68.7 mg/L |
| pH | 8.1–8.5 |
| EC | 3120–3209 μs/cm |
| TH | 462–471 mg/L |
| TA | 189–493 mg/L |

*Note:* Circulating cooling system: Luoyang Petrochemical No.1 circulating water field; Capacity is 6000 $m^3$/h, source water is from groundwater or reclaimed water, concentrating ratio of circulating cooling water is around 3.8; The main chemicals used for keeping the stability of the water are trichloroisocyanuric acid (abbreviated as TCCA) and chemicals containing zinc-phosphorus (abbreviated as CCZP). Discharge requirements: COD < 50 mg/L, TP < 1.0 mg/L.

### 2.2. CEBD water sample and water quality analysis

The conventional water quality parameters including total phosphorus (TP), Chemical oxygen demand (COD), pH, electrical conductivity (EC), total hardness (TH) and total alkalinity (TA) were determined using a TP auto-analyzer (IL500P, HACH, US), potassium dichromate method, pH probe (STARTER 2100, Shanghai Precision Science Instrument Co., Ltd., China), conductometer (HQ30d, HACH, US) and titration method, respectively. The CTBD was collected from petrochemical enterprises in Luoyang, China, which had basic water quality information as follows in Table 1:

### 2.3. Experimental procedure

(1) Adsorption-desorption process

i. Adsorption

Firstly, the fresh adsorbent PANI/$TiO_2$ were soaked in ultra-pure water and cleaned in 0.1 mol/L NaOH solution for 5 min. Then, 0.1 mol/L HCl was used to acidify the adsorbent for activation. Detailed operational process could be found in the literatures[20]. The adsorbent was separated from the liquid by centrifugation at a centrifugal speed of 8000 r/min for 10 min and filtered using filter membrane with 0.45 μm pore size, then dried in room temperature and ready for adsorption experiments. Add a fixed amount of adsorbents into 1000 mL of targeted wastewater and then mix them by stirring at 200 r/min for 120 min at 25 °C. After that, the treated wastewater and adsorbents were separated by centrifugation and filtration, preparing for further adsorbents desorption/regeneration or water quality analysis.

ii. Desorption and regeneration

The used adsorbent was immersed into 0.5 mol/L NaOH solution and shook in a shaker for 10 min at 25 °C. The corresponding pollutants would be desorbed and produce desorption eluate. Then the adsorbent PANI/$TiO_2$ was separated by a vacuum filter (SHZ-DIII, Gongyi Yuhua Instrument Co., Ltd., China) for subsequent adsorbent regeneration.

The separated adsorbent was acidified using 0.1 mol/L HCl solution for activation. The mixture was then centrifuged at a speed of 8000 r/min for 10 min and separated by a vacuum filter. At this point, the adsorbent would be regenerated and the regenerated adsorbents were continuously used for the next adsorption-desorption cycle.

(2) Electrocatalytic oxidation

The eluate was concentrated from 1 $m^3$ of CTBD by using the same alkali liquor for desorption treatment until its COD reached 10,000 mg/L. The electrocatalytic oxidation process was carried out in a circulating system containing 300 mL of the concentrated eluate. $PbO_2$-PVDF (i.e. polyvinylidene fluoride modified lead dioxide electrode) [37] with 10 × 7 cm in size was acted as anode and copper sheet of the same size was used as a cathode. The anodic current density was maintained at 100 mA/$cm^2$ during the whole process. Inductively coupled plasma emission spectrometer (ICP-E9000) was used to analyze the concentration of Ca and Mg in the eluate. Variation of $BOD_5$ and COD were measured by analyzing the samples taken from the oxidation tank each hour, to determine the biodegradability and COD level of the treated eluate. Changes in molecular weight distribution and fluorescent signal were also analyzed by LC-OCD system (DOC-LABOR Dr. Huber, Germany) and fluorescent excitation-emission matrixes (FEEMs, FluoroMax-4, HORIBA, US) to understand the variation of the organics in detail. The quality parameters of the concentrated eluate can be seen in Table S4.

Note: LC-OCD is an analysis system of size-exclusion chromatography coupled with organic carbon detector, which can separate the natural organic matters (NOMs) into five fractions (i.e. biopolymer, humics, building blocks, LMW acids and LMW neutrals) mainly based on their molecular weight. Meanwhile, the corresponding content and proportion of these five fractions can also be acquired by using ChromCALC (DOC-LABOR, Karlsruhe, Germany).

(3) Evaluation of the toxicity of oxidized eluate using TELI method

During the adsorption and electrocatalytic oxidation processes, a high-throughput mechanistic toxicity assay method was employed (GFP-fused whole-cell array of Escherichia coli K12, MG1655) [38]. And the transcriptional effect level index (TELI) was used to quantify the magnitude of the affected gene(s) and their expression level upon the exposure to toxicants [32]. All of the samples were neutralized to pH ~7 prior to enrichment by lyophilization (Freezone 4.5, LABCONCO, Kansas City, MO) at −42 °C under a 0.1 Torr vacuum. Lyophilization was adopted because it has a higher recovery of nonvolatile substances than solid phase extraction [39]. All tests were conducted in triplicate.

### 2.4. Characterization and performances evaluation of PANI/$TiO_2$ and $PbO_2$-PVDF electrode

Scanning electron microscopy (SEM, SNE-3200 MB, SEC Co., Ltd, Korea) was used to observe the morphology. X-ray diffraction (XRD, PAN alytical, Holland) using Cu $K_\alpha$ source ($\lambda$ = 0.15416 nm) was adopted to analyze crystal structure. The scanning angle (2θ) ranges from 10° to 90°.

In the process of adsorption, COD and TP in CTBD were detected to evaluate its adsorption performance. In order to evaluate the regeneration of PANI/$TiO_2$, 30 cycles of the adsorption–desorption tests were carried out (dosage 1.5 g/L; reaction time 30 min). In addition, COD and $BOD_5$ were also measured during the electrocatalytic oxidation. Furthermore, the LC-OCD system and FEEMs were used to analyze the change of molecular weight distribution and fluorescent signals for more in-depth analysis of the water samples.

### 2.5. Chemicals and reagents

All reagents used in the experiments were obtained from Sinopharm Chemical Reagent Xi'an Co., Ltd and were of analytical grade without further purification. The aqueous solutions were deionized water (18 MΩ cm). In this experiment, the $PbO_2$-PVDF electrode with high catalytic oxidation ability and stable performance was used. The preparation of electrode can be referred to our previous work [37]. The composite adsorbent PANI/$TiO_2$ was synthesized using a one-pot chemical oxidative polymerization method according to Wang et al.'s work [40]. The detailed preparation steps and basic characterizations of PANI/

$TiO_2$ can be found in the supplementary material (Information S1, Fig. S1 and Table S1).

## 3. Results and discussion

### 3.1. Performance of PANI/$TiO_2$ for CTBD treatment

Fig. S2 shows the performance of PANI/$TiO_2$ in removing COD and TP from CTBD at different dosages and reaction times. With the increment of adsorbent dosage, the removal of both COD and TP increased quickly till to the dosage of 1.5 g/L, and above which the improvement became minor. Under the dosage of 1.5 g/L, the removal of COD and TP reached 58 and 90% within 60 min, respectively. The results indicated that a dosage of 1.5 g/L adsorbent could be reasonable for the treatment of CTBD and more adsorbent dosing will be unnecessary to achieve the requirement of the discharge standard. According to Fig. S2, 30 min of adsorption duration was selected as the process achieved its plateau.

The adsorption kinetics for COD and TP were fitted by the pseudo-first-order model and pseudo-second-order model (1.5 g/L). The fitting plots and corresponding fitting parameters were shown in Fig. S3 and Table S2. By comparing the correlation coefficients ($R^2$), pseudo-first-order kinetic model was more suitable for the description of COD and TP removal, indicating that the adsorption process was mainly controlled by the diffusion step of the substances [41–43]. Equilibrium adsorption capacity ($q_e$) of COD and TP was 23.70 ± 0.25 mg/g and 4.15 ± 0.07 mg/g, respectively in CTBD. The correctness of the kinetic model was verified by contrasting the fitting data and the experiment data (Table S2). For the commonly used ion exchange resin (e.g. IRA 402Cl and IR 120H), the adsorption capacity of COD and P in industrial wastewater was only around 5.37 mg/g and 0.02 mg/g after 60 min, respectively [44]. Compared with the aforementioned ion exchange resin, PANI/$TiO_2$ exhibited superior removal capacity (or adsorption rate) of COD and P. Meanwhile, previous studies has demonstrated that PANI/$TiO_2$ also exhibited superior adsorption capacity and regeneration ability for organics or P compared with $TiO_2$[20,21]. The above studies indicated that the PANI/$TiO_2$ was a potential and suitable adsorbent for the CTBD treatment.

Fig. 2 and Table 2 show the changes of size fractioned dissolved organic carbon (DOC) before and after adsorption of CTBD. It could be seen the macromolecular substances such as biopolymers (23% of DOC), humic substances (40% of DOC) and building blocks (14% of DOC), account for a large proportion of the raw CTBD. After adsorption they were all removed significantly. Paying attention to the biopolymers (molecular weight > 20 kDa [45]), which were decreased from 3.83 to 0.42 mg/L, reaching 89% of removal. This is consistent to our previous observations in treated wastewater[19]. At the same time, humic substances, building blocks and small molecule substances (acids and neutrals) were all well removed, leading to a DOC reduction from 16.24 to 4.73 mg/L (Table 2), which confirmed the promising performance of PANI/$TiO_2$.

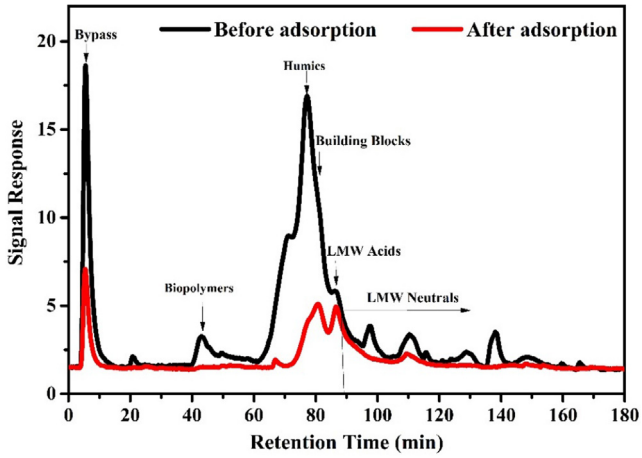


**Fig. 2.** LC-OCD spectrum before and after adsorption of CTBD.

The fluorescent excitation-emission matrixes (FEEMs) of water samples were presented in Fig. 3. With PARAFAC analysis, three components were extracted from the FEEMs (Fig. S4). Compared with the location of FEEM peaks based on literature reports [46,47], these three components belonged to fulvic acid-like (Component A, peak at $\lambda_{Ex/Em}$ = 250/400), humic acid-like (Component B, peak at $\lambda_{Ex/Em}$ = 330/425) and soluble microbial byproduct-like (Component C, peak at $\lambda_{Ex/Em}$ = 280/325) substances, respectively. After adsorption, PARAFAC results and $F_{max}$ showed that the fluorescence intensity of the three components (Component A ~ C) decreased by 77.2, 87.5 and 52.7%, respectively, which exhibited an excellent adsorption capacity for fluorescent substances using PANI/$TiO_2$.

Fig. 4 shows the removal capacity of PANI/$TiO_2$ on COD and TP in 30 cycles of adsorption-generation. Compared to the initial removal of COD and TP to 56.9 and 92.8%, respectively, that after 30 times of regeneration dropped to 43.9 and 86.1%. These results proved the impressive regeneration capacity and stable performance of PANI/$TiO_2$ in treating the CTBD. SEM and XRD analysis (Fig. S5 and Fig. S6) showed no obvious change in the morphology and crystalline phases of the adsorbent along with the increasing regeneration cycles. From the results of LC-OCD and FEEMs during multiple cycles (Fig. S7, Fig. S8 and Table S3), it can also be found that PANI/$TiO_2$ still had considerable adsorptive capacity after 30 regeneration cycles. In practical application of printing and dyeing wastewater treatment, the adsorbent can be recycled for more than 100 times (the specific data was not shown). Based on the above results, it was proved that the adsorbent of PANI/$TiO_2$ exhibited much better recycling capacity than the traditional activated carbon [48]. Meanwhile, pH of the wastewater decreased slightly from 8.1 ~ 8.3 to 7.3 ~ 7.6 after treatment, but it still remained in the near neutral range, which would not hinder the discharge of the treated water based on relevant discharge standards.

### 3.2. Electrocatalytic oxidation of the desorption eluate

Fig. 5a showed that COD decreased from 12,316 to 6269 mg/L after 6 h of oxidation. Correspondingly, $BOD_5$ increased from 969 to 3505 mg/L. $BOD_5$/COD value (abbreviated as B/C) increased gradually and reached 0.4 after 4.8 h. The increased B/C implies that concentrated eluate was much more biodegradable than that before the treatment (0.08) [49]. The treated eluate could be a source providing carbon source with small-molecule weights (Fig. 6) and phosphorus to the biological treatment process. Energy consumption analysis shows that the average power consumption in the whole electrocatalytic oxidation process was about 80 kW·h/kg COD, which lied within an acceptable range for practical application.

It can also be found that after 6 h of electrolysis, the concentration of TP in the eluate decreased from 652 to 407 mg/L, achieving a removal of 37.6% (Fig. 5b). Simultaneously, the concentration of Ca and Mg in the eluate also decreased from 274 and 76 mg/L to 148 and 52 mg/L, respectively (Fig. S9). Therefore, the reason for TP removal could be accounted for the formation of precipitates such as calcium phosphate or magnesium phosphate under the electrocatalytic treatment [50].

The variation of the LC-OCD chromatogram of the eluate during the electrocatalytic oxidation was presented in Fig. 6. As shown, organic substances with a molecular weight greater than 500 Da (Retention time < 83 min), including biopolymers, humic substances and building blocks, account for 71% of DOC in the eluate. During 6 h of electrocatalytic oxidation the organics with $M_w$ > 500 Da was declining and decreased from 2315.6 to 935.5 mg/L (Table S5). Interestingly, it shows a trend of declining-rising-declining for the small molecule substances ($M_w$ < 350 Da, Retention time: 100–115 min)

**Table 2**
Analysis of LC-OCD results before and after adsorption of CTBD (mg C/L).

| Water sample | *DOC | Bio-polymers | Humic substances | Building Blocks | LMW Neutral | LMW Acids |
|---|---|---|---|---|---|---|
| Before adsorption | **16.24** | 3.83 | 6.46 | 2.36 | 3.59 | n.q |
| After adsorption | **4.73** | 0.42 | 0.91 | 1.57 | 1.61 | 0.22 |
| Removal efficiency | **70.9%** | 89.0% | 85.9% | 33.5% | 55.2% | – |

*Dissolved organic carbon, quantifed using LC-OCD system.
n.q: not quantifiable, concentration < 0.001 mg C/L.

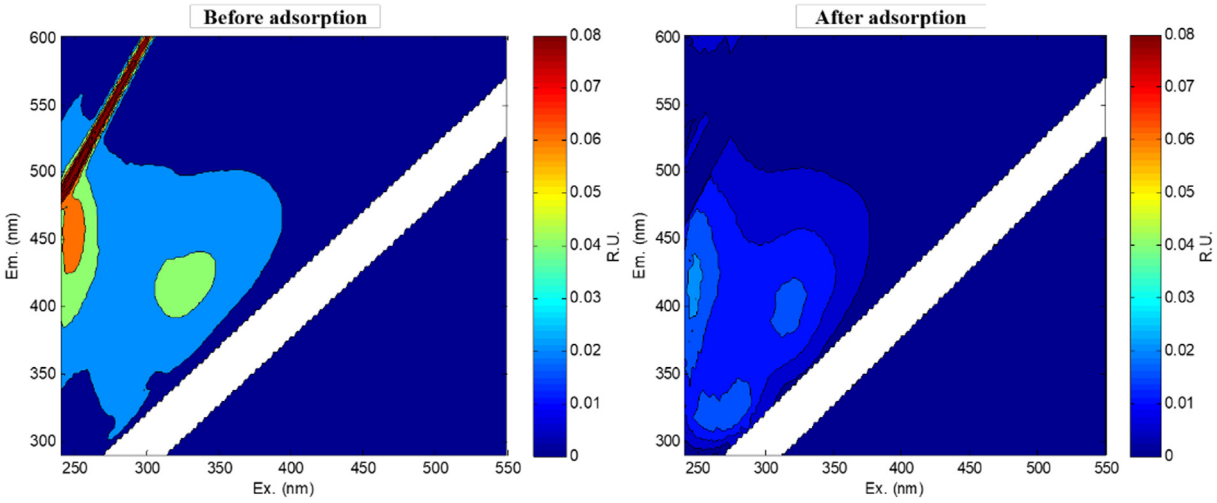


**Fig. 3.** FEEM spectrum before and after adsorption of CTBD.

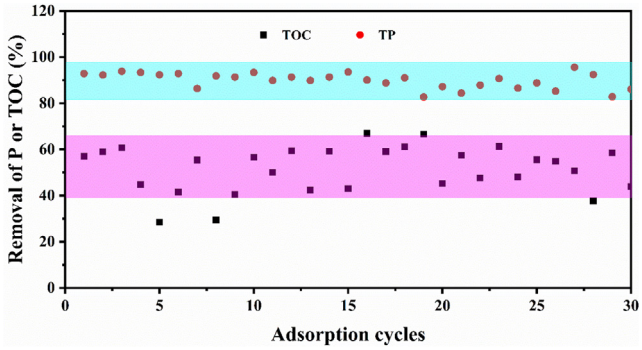


**Fig. 4.** Multiple adsorption-desorption tests in the removal of COD and TP.

along the oxidation process, indicating that the macromolecular was firstly decomposed into smaller ones, and they were further mineralized with extended oxidation duration. From FEEMs result of Fig. S10, the variation of the intensity of fluorescence demonstrated a trend of weakening of all the components and the maximum removal occurred in component A (fulvic acid substances, 88.1%), while for the other two the removal reached 61.1% and 49.3%, respectively.

### *3.3. Toxicity assessment in the adsorption-electrocatalytic oxidation process*

Fig. 7 shows that the total toxicity of CTBD was reduced after PANI/$TiO_2$ adsorption (Af-ad for short) as the TELI index decreased from 2.0 to 1.6. The TELI index of 1.6 was close to the molecular endpoint of $TELI_{1.5}$ value, which is considered as the level of non-toxicity according to ISO8692 water quality determination methods, indicating the toxicity was nearly completely eliminated after adsorption[34]. Along with the electrocatalytic oxidation of the eluate, the total toxicity of the sample increased first and then decreased. The $TELI_{Total}$ of water sample reached its maximum 3.0 after 2 h of electrolysis (Equivalent to the toxicity level of 50 mg/L triclosan solution [51]), indicating that some more toxic intermediates were generated during the process. Thereafter, the toxicity level of eluate decreased gradually. The wastewater with low toxicity exhibited weak inhibition on microbial activity, which was more conducive to the consumption of organic matter by microorganisms. Our previous work also proved that the reduction of wastewater toxicity could promote higher biodegradability [31]. Therefore, electrolysis needs to last for an appropriate period of time to reduce the toxicity of the eluate and ensure low adverse effect on subsequent microorganisms.

The toxicity leads to five grouped stresses, namely oxidative stress, protein stress, membrane stress, general stress, and DNA stress [32]. In which the membrane stress got always the highest score in all the cases, indicating that some organics in the water samples could cause membrane damage although the treatment processes were employed. The other two stresses, general stress and protein stress, are also on the top of the severity of responses. As mentioned in Section 2.2, the main chemicals used in the industrial cooling water are TCCA and CCZP. For TCCA, it can hydrolyze to produce highly oxidized chlorine which can attack the peptide bond on cell membrane and lead to cell membrane damage, it can thus penetrate the microbial cell membrane rapidly, promote the malfunction of enzymatic transport systems and then kill the bacteria [52,53]. In practice, TCCA could stay in cooling water and be concentrated further, it is not surprising that they are functioning in the present test even after days of sampling. With respect to CCZP, although it exhibits also high toxicity level, it can easily precipitate in the form of $Zn(OH)_2$ and lose its toxicity [54]. Through the toxicity test of pure TCCA and CCZP (Fig. S11), it was found that the toxicological effect of TCCA was similar to that of the wastewater (Membrane stress response was the strongest, followed by protein stress and general stress). For CCZP, DNA stress was the most obvious, which was totally different from the toxicological effect of wastewater. Therefore, it could be preliminarily determined that the toxicity of wastewater mainly caused by TCCA related chemicals.

To understand the development of the toxicity, more in-depth examination of 110 genes stresses under the five groups was carried out

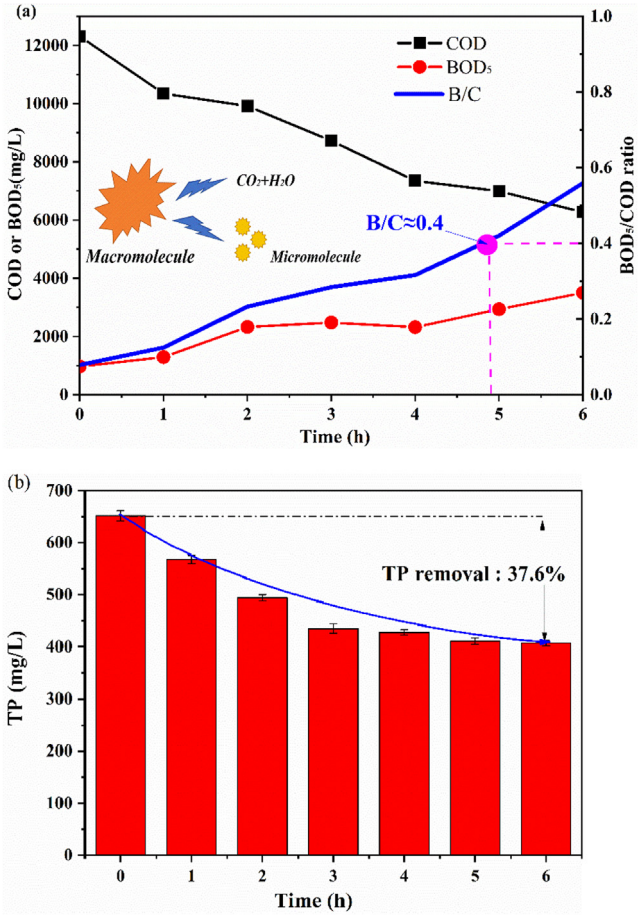


**Fig. 5.** Variation of COD, $BOD_5$, B/C ratio (a) and TP (b) during electrocatalytic oxidation.

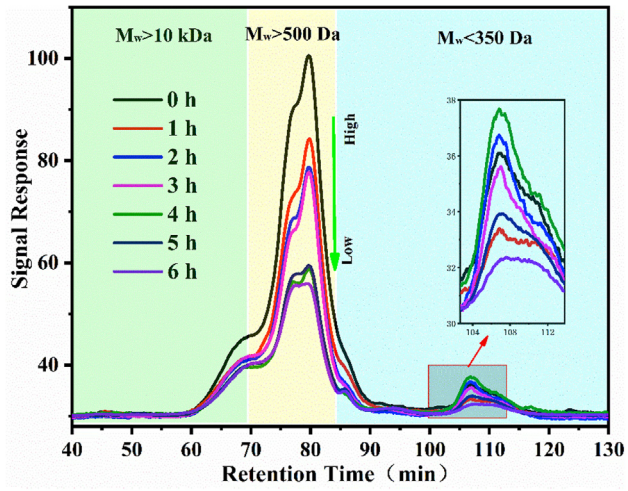


**Fig. 6.** LC-OCD chromatogram of eluate during electrocatalytic oxidation.

(Fig. 8). The main focus was addressed on the genes related to membrane stress, general stress and protein stress as they are the most significant responses TELI presented (Selected genes with significant stress response (TELI > 2.0) were shown in Fig. S12). The results show that under membrane stress the genes of *amiC, cueR, yedW, dacA, cls, marC, cmr, zntA* were most strongly expressed, while *uspA, uspB, crp, dinJ, inaA, ydgL, slyA, osmE, yfjG, ssrA* were the activated ones under general stress group. In the protein stress the gene expression of *degQ, lon, dnaJ* were all upregulated. Based on the library of stress response genes

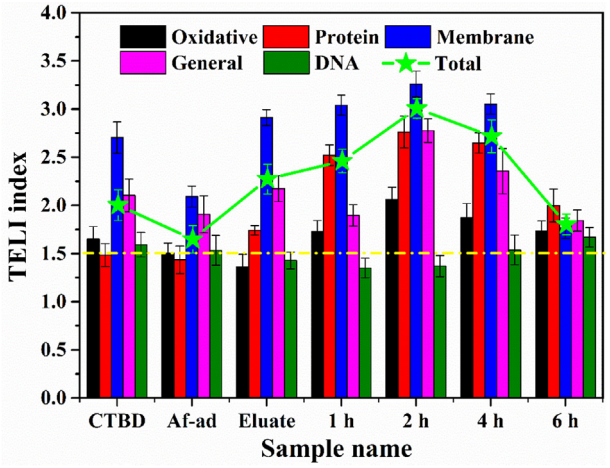


**Fig. 7.** Histogram of different grouped stress responses induced during the adsorption-electrocatalytic oxidation process.

(www.ecocyc.com), it could be concluded that most of the genes above mentioned are related to protein synthesis and secretion, drug resistance, phospholipid synthesis of the cell membrane, and intracellular physical-chemical homeostasis. A more detailed gene description can be referred to Information S2. In addition, observed from the DNA stress group, it could be seen that three genes, namely *recN, ftsK* and *uvrD*, which are closely related to DNA synthesis, replication and repair, were strongly activated. According to the function and stress level of the aforementioned genes, it can be inferred that the organics in water samples are mainly result in the hindrance of protein synthesis, cell membrane dysfunction and imbalance of intracellular metabolism.

Through principal component analysis (PCA) on the TELI values of the 110 genes in water samples (Fig. 9), it was found that the cosine value of the angle between CTBD and Af-ad loading became larger after adsorption, which means that there was a high correlation between the two samples. But the correlation between the CTBD and the concentrated eluate was weaker, showing that the characteristics of samples were quite different. The reason may be attributed to the selective adsorption of PANI/$TiO_2$ on the removal of the substances (chemicals or other substances) in CTBD, or the hydrolysis reaction between the substances and the alkali liquor in the desorption process, which results in the large difference of characteristics between the eluate and CTBD. In addition, it was noticed that with the increase of electrolysis time, the angle between the oxidized sample (1–6 h) and the original eluate gradually increased, indicating that the correlation between the samples gradually weakened during electrolysis and the altering of the property of organics in water became more significant. Thus, it can be summarized that the toxicity of the samples was constantly changing during the adsorption-electrocatalytic oxidation process. From the 95% confidence ellipse of the five genomes, the data distribution of DNA stress group was the most centralized, and the covariance between these data points was small, meaning the variation is mostly limited with respect of the types of responds, e.g. up/down regulation of DNAs. For general stress, the maximum 95% confidence ellipse mirrored that the data points in the genome were the most discrete, implying the responses could be more separated in terms of characteristics.

### 3.4. Economical evaluation

The total operation cost of CTBD wastewater treatment mainly lies on two parts: the adsorption process and the electrocatalytic oxidation process. For the adsorption process, the related cost is mainly determined by the price of adsorbent, hydrochloric acid, sodium hydroxide, etc. Power consumption is the main economic cost in the electrocatalytic oxidation process. Information about the price of PANI/

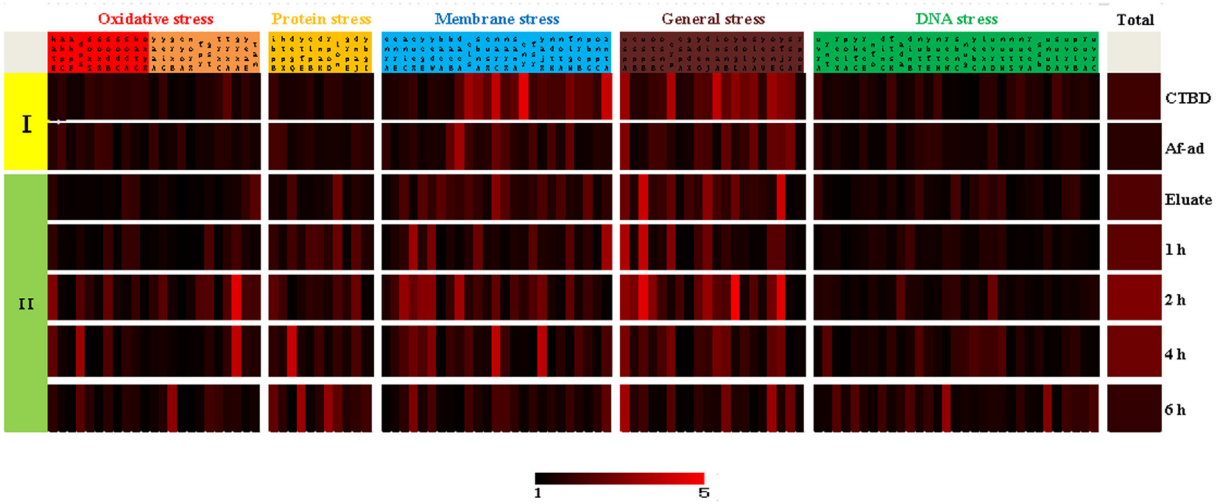


**Fig. 8.** Heatmap of TELI index of 110 genes divided under five stress groups (Black: low toxicity; Red: high toxicity).

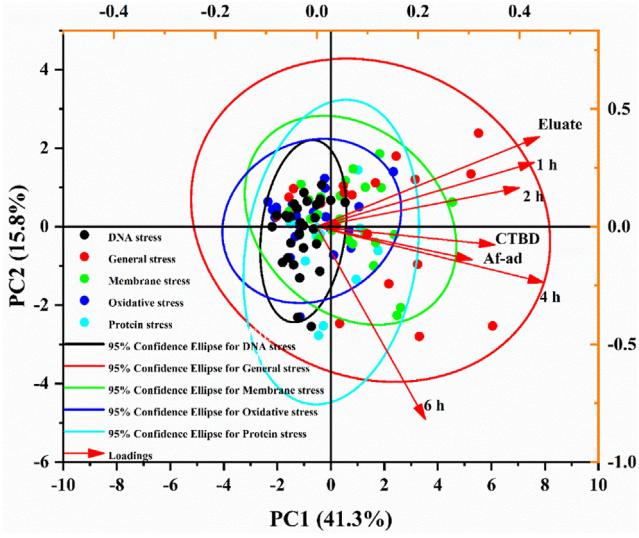


**Fig. 9.** Principal component analysis of TELI value of samples with 110 genes during adsorption- electrocatalytic oxidation.

$TiO_2$, chemical reagents, electric energy, etc. are referred to Alibaba.com and national industrial electricity charging standard of China. (detailed information in Table S6).

In order to calculate the operating cost of wastewater treatment, some necessary assumptions have been made as below: (1) the treatment capacity of the CTBD is 1000 $m^3$/d (Corresponding to a circulation capacity of the cooling system around 4000 $m^3$/h; (2) COD in the original CTBD is 65 mg/L and the treatment objective is 50 mg/L (Complying with the quality of discharged water in petroleum refining enterprise GB 31570-2015, China); (3) the maximum regeneration times for PANI/$TiO_2$ without obvious treatment efficiency decrease is 50 times; (4) COD of the desorption eluate is 12,000 mg/L and the objective is to decrease it to under 7000 mg/L (based on our finding that B/C could reach above 0.4); (5) Power consumption for the electrocatalytic oxidation treatment is 80 kW·h/(kg COD); (6) HCl or NaOH solution for pretreatments, desorption, and regeneration of PANI/$TiO_2$ are reusable for 10 times (based on our regeneration experimental results).

According to the calculation (Table 3), the costs for the treatment of CTBD using PANI/$TiO_2$ and electrocatalytic oxidation is 3.63–5.38 RMB/$m^3$, equivalent to about 0.52–0.78 \$/$m^3$, which was much lower than previously reported costs (reverse osmosis-evaporation crystallization process, 2.19 \$/$m^3$)[55]. In addition, compared with the previous technology, such as membrane distillation, electrocoagulation, etc. the process of adsorption-electrocatalytic oxidation in the work exhibited more advantages in environmental friendliness and investment cost. After the treatment, the COD of CTBD could be reduced to < 50 mg/L and $BOD_5$/COD of eluate could be increased to > 0.4, which meets the requirements of subsequent biochemical treatment. In addition, it was found from Fig. S13 that the proportion of the total cost in the whole CTBD treatment was Electricity (42.2%) > Adsorbent (31.1%) > HCl (20.5%) > NaOH (6.2%). This demonstrates that the operation cost mainly depends on the price of the adsorbent and electricity. Therefore, reducing the price of adsorbent and the power consumption in the electrocatalytic process will provide a greater possibility for the practical application of the combined process.

**Table 3**
Estimated operation costs of CTBD treatment in the adsorption-electrocatalytic oxidation process.

| Items | Price | Usage | Costs (1 × $10^3$ $m^3$) |
|---|---|---|---|
| Adsorbent | 50,000 RMB/t | 1.2–1.6 g/L CTBD | 1200–1600 RMB |
| HCl (31%, Liquor) | 600 RMB/t | 5.5 mL/g adsorbent | 792–1056 RMB |
| NaOH (99%, Solid) | 2500 RMB/t | 0.4 g/g adsorbent | 240–320 RMB |
| Electricity | 0.7–1.2 RMB/kW·h | 80 kW·h/kg COD | 1400–2400 RMB |
| Total costs: | | | 3632–5376 RMB |

## 4. Conclusions

In this work, a combined process of adsorption-electrocatalysis was used to treat cooling tower blowdown water (CTBD) and delivered an eco-friendly treatment loop. Meanwhile, the water toxicity during the whole treatment process was evaluated by TELI method which was a new detection technology at genes level. The specific conclusions are as follows:

(1) PANI/$TiO_2$ is an effective adsorbent for the treatment of CTBD, which could remove the COD and TP by around 55 and 90%, respectively. And after 30 cycles of regeneration, its adsorption capacity remains stable and its morphology and crystallinity didn't show obvious change.
(2) The adsorbent exhibits specific adsorption for macromolecule substances in CTBD, especially for biopolymers (molecular weight > 20 kDa). And the fluorescent intensity of three identified

substances (fulvic acid-like, humic acid-like and soluble microbial byproduct-like) decreased obviously after the adsorption.

(3) The refractory eluate with high-concentration pollutants was treated efficiently by electrocatalytic oxidation, with the COD removal around 50% after 6 h. In addition, the biodegradability of the eluate was greatly improved and the value of B/C could increase from 0.08 to 0.4 after 4.8 h of treatment.

(4) Toxicity evaluation results show that the toxicity of CTBD was mainly caused by oxidizing biocides of trichloroisocyanuric acid (TCCA) in the present work. The toxicity level of CTBD treated by adsorption decreases, while the toxicity of desorption eluate increases first and then decreases in the process of electrocatalytic oxidation. Gene stress analysis shows that the toxicity of wastewater mainly caused the destruction of cell membrane structure, hindrance of protein synthesis and the breakdown of intracellular metabolic balance.

(5) Through economic evaluation, the operating cost of the adsorption-electrocatalytic oxidation process for CTBD is 3.63–5.38 RMB/$m^3$, equivalent to about 0.52–0.78 \$/$m^3$, in which the electricity expenditure and adsorbents purchase could account for over 70% of the total cost.

## CRediT authorship contribution statement

**Xiaoliang Li:** Conceptualization, Methodology, Investigation, Writing - original draft. **Linjie Wu:** Validation, Investigation, Methodology, Data curation, Visualization. **Sijia Lu:** Validation, Formal analysis, Investigation. **Heyun Yang:** Resources, Supervision, Data curation. **Wenzhou Xie:** Resources, Supervision. **Huiyan Zhao:** Resources, Supervision. **Yaozhong Zhang:** Methodology, Investigation. **Xin Cao:** Formal analysis, Investigation. **Gang Tang:** Formal analysis, Writing - review & editing. **Hesheng Li:** Resources, Supervision. **Jiangtao Feng:** Resources. **Wei Yan:** Resources. **Xing Zheng:** Conceptualization, Writing - review & editing, Project administration, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2020.117484.

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