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Removal of trace organic pollutants (pharmaceuticals and pesticides) and reduction of biological effects from secondary effluent by typical granular activated carbon

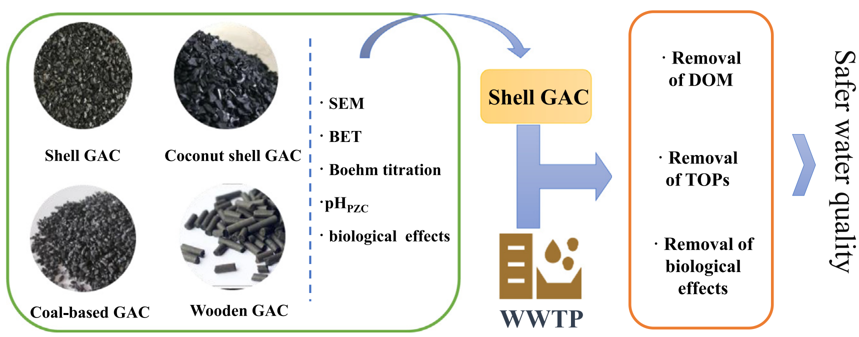
Lei Tang [a,b], Xiaoyan Y. Ma [a,b,*], Yongkun Wang [a,b], Shiying Zhang [a,b], Kai Zheng [c], Xiaochang C. Wang [a,b,*], Yu Lin [a,b]

[a] International Science & Technology Cooperation Center for Urban Alternative Water Resources Development, Key Lab of Northwest Water Resource, Environment and Ecology, MOE, Engineering Technology Research Center for Wastewater Treatment and Reuse, Shaanxi Province, China
[b] Shaanxi Key Laboratory of Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China
[c] PetroChina Changqing Oilfield Company, Xi'an 710021, China

HIGHLIGHTS

- Total amount of functional groups and S_{BET} had correlation with toxicity removal.
- Shell GAC showed a promising property of removing fluorescent DOM and TOPs.
- The process of GAC adsorbing chemicals should be described by multiple parameters.
- Shell GAC showed excellent properties of removing the three biological effects.

GRAPHICAL ABSTRACT



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ABSTRACT

Residual trace organic pollutants (TOPs) and associated biological effects from secondary effluent (SE) are attracting much attention because of their safety concerns. Granular activated carbon (GAC) adsorption, due to its low cost and high efficiency, is widely applied for further wastewater treatment, but its selective removals of TOPs and biological effects are poorly understood. In the present study, the surface physicochemical characteristics of four types of typical GACs were investigated, and their correlation with luminescent bacteria toxicity was discussed. Based on the biological effect control, shell GAC, with a great adsorption capacity and high functional group contents was selected for further study, including for the removal of fluorescent dissolved organic matter (DOM), 21 TOPs, and 3 biological effects. The shell GAC showed a promising property of removing fluorescent DOM and TOPs. The total concentration of 21 detected TOPs, including 12 pesticides and 9 pharmaceuticals, achieved 82% removal when 30 g/L shell GACs was added. Individual chemicals removal by GAC adsorption was not well described by an individual parameter (e.g., logD, molecular size, charge, functional groups), but rather by a variety of physical and chemical interactions among TOPs, DOM, and GAC. The biological effects from SE were mainly caused by TOPs and DOM. Hence, shell GACs also showed high removal efficiencies of luminescent bacteria toxicity, genotoxicity, and photosynthetic inhibition effect. The removal mechanisms of the three biological effects from SE were deeply discussed. Therefore, the GAC treatment is considered to be one of the most suitable options to ensure the ecological safety of discharged wastewater, because it can effectively control DOM, TOPs, and associated biological effects.

* Corresponding authors.
E-mail addresses: maxiaoyan@xauat.edu.cn (X.Y. Ma), xcwang@xauat.edu.cn (X.C. Wang).

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1. Introduction

In 2017, 3.5 million tons of pharmaceuticals and 2.9 million tons of pesticides were produced in China to meet people's living and production needs (Wang et al., 2020). From residential usage or industrial production, pharmaceuticals and pesticides would enter wastewater treatment plants (WWTPs). Due to the high frequency detection, residual pharmaceuticals and pesticides in discharged wastewater of WWTP are increasing much attention (Tan et al., 2020). It is one of the significant sources of chemical pollution to surface waters (Picó et al., 2019). In most cases, such as in domestic wastewater, reclaimed water, or surface water, pharmaceuticals and pesticides account for a great proportion of the total detected trace organic pollutants (TOPs). For example, researchers in Australia found that atrazine, diuron, metolachlor, simazine, and carbamazepine were dominant in Brisbane and Yarra River estuaries (Anim et al., 2020).

Actually, pharmaceuticals and pesticides as two types of chemicals affect biota they exposed to. The former is used by human and livestock breeding for disease control, and the latter acts on microorganisms, plants, and insects (via bactericides, herbicides, and insecticides, respectively) to improve crop yield. Despite the low levels of residual pharmaceuticals and pesticides in discharged secondary effluent (ng/L–μg/L), they would pose adverse effects to aquatic organisms. Especially pharmaceuticals, they are designed to be easily absorbed by living organisms and actively interact with them, but the adverse effects on the water environment are often not fully considered during their preparation and production. Galus et al. (2013) indicated that acetaminophen, carbamazepine, gemfibrozil, and venlafaxine caused reproductive problems in aquatic organisms. It has been shown that long-term exposure to a pervasive pharmaceutical can alter physiological and behavioral characteristics in fish (Tan et al., 2020). Pesticides alter the state of DNA, proteins, and lipids in the cells of fish (Yang et al., 2020a). Additionally, synergistic effects were observed when multiple pesticides were combined in wastewater (Fu et al., 2019). Therefore, it is important to control the discharge of pharmaceuticals and pesticides in WWTP effluent for ecological safety.

There are many ways to remove TOPs from wastewater, such as Fenton oxidation (Pliego et al., 2014), ozone oxidation (Yang et al., 2020b), biodegradation (Gao et al., 2014), photocatalytic degradation (Zheng et al., 2016) and adsorption (Guillossou et al., 2019; Li et al., 2020). Among them, activated carbon adsorption and ozone oxidation are two technologies currently advocated because of their strong applicability and high efficiency (Shanmuganathan et al., 2017). Through the strong oxidative properties of ozone and hydroxyl radicals produced spontaneously in its decomposition, ozonation processes efficiently degrade most TOPs in treated wastewater (Reungoat et al., 2012). But the potential disadvantage of this method is that it may produce unknown toxic oxidation by-products (Hollender et al., 2009). So, activated carbon adsorption is usually conducted after ozonation for removing undesirable by-products. Because of its large specific surface area and high content of functional groups, activated carbon can further efficiently remove TOPs and no by-products are generated. Various modified activated carbons were developed in previous studies, but they were seldom used in actual WWTP (Al-Kaabi et al., 2019; Lee et al., 2020). Meanwhile, previous studies only focus on the measures of removing TOPs from wastewater by activated carbon (Nguyen et al., 2012), but the selective removal efficiency of activated carbon adsorption on TOPs and associated biological effects still needs further study.

In the present study, textural characteristics, functional groups, pH_{PZC} and the biological effects removal efficiency of four types of granular activated carbons (GACs) were investigated. Main aims of this study were to: (1) analyze the relationship between biological effects removal and GACs physicochemical characteristics and select an optimizing GAC; (2) study the properties of selected GAC on the removal of fluorescent dissolved organic matter (DOM), TOPs, and biological effects (luminescent bacteria toxicity, genotoxicity, and photosynthesis inhibition effect); and (3) discuss the removal mechanisms of the three biological effects from SE.

2. Materials and methods

2.1. Water sampling and GAC adsorption

The secondary effluent was collected before chlorination from a local domestic WWTP in Xi'an, China, where anaerobic-anoxic-oxic biological treatment processes are applied. The treatment efficiency of the WWTP was stable. The water sample (30*L*) was collected into clean brown glass bottles and taken to the laboratory immediately and further in-depth processing was conducted within 24 h.

To select the GAC with the optimal properties of reducing biological effects, four commercial types of GAC were examined in this study, including wooden GAC, shell GAC, coconut shell GAC, and coal-based GAC. For GAC adsorption, a different dosage of commercial GAC (0–30 g/L) was added to SE. It was stirred at 200 rpm and allowed to settle up to 30 min. Then, each sample was filtered through a 0.7 μm glass microfiber filter (Φ 150 mm; Whatman™). UV_{254} and total organic carbon (TOC) of SE before and after the GAC adsorption process were detected, and three-dimensional excitation-emission matrix spectroscopy (EEM) of SE were scanned from 200 to 600 nm at 5 nm intervals using a Hitachi F-7000 Fluorescence Spectrophotometer (Japan).

2.2. Chemical analyses

To identify the pesticides and pharmaceuticals in the SE, a full scan was carried out using ACQUITY ultra-performance liquid chromatography – Xevo TQ mass spectrometer (UPLC/MS, Waters, USA). Twenty-one chemicals were selected and classified, including 12 pesticides (acetamiprid, atrazine, azoxystrobin, carbendazim, chlorpyrifos, difenoconazole, dimethomorph, dipterex, imidacloprid, prometryn prochloraz, and thiamethoxam) and 9 pharmaceuticals (carbamazepine, clarithromycin, diclofenac acid, diphenhydramine hydrochloride, ibuprofen, mefenamic acid, roxithromycin, sulfamethoxazole, and trimethoprim). Instrument conditions for analyzing different categories of pesticides and pharmaceuticals were described in detail in previously published studies (Ma et al., 2019).

2.3. Bioassays

Three bioassays, including acute luminescent bacteria toxicity test, SOS/umu test, and combined algae test (2 h-PSII) were conducted to evaluate the biological effects of SE. Acute luminescent bacteria toxicity test was conducted according to a modified ISO 11348 (2008) procedure using *Aliivibrio fischeri* (Ma et al., 2016). Phenol and the solution containing 1% DMSO and 2% NaCl were set as positive and negative control in the luminescent bacteria toxicity test, respectively. The genotoxicity of SE was assessed with the SOS/umu test using *Salmonella typhimurium* TA1535/pSK1002 without S9 activation according to ISO13829 (2000). 4-Nitroquinoline-N-oxide (4-NQO) and 1% DMSO were set as positive and negative control in the SOS/umu test, respectively. The combined algae test (2 h-PSII) was conducted using *Chlorella vulgaris* according to our previous studies (Ma et al., 2019). Diuron and 1% DMSO were set as positive and negative control in the combined algae test, respectively.

The dose metric of the water samples was expressed as the relative enrichment factor (REF), which is calculated as the volume of the original water sample ($V_{water\ sample}$) divided by the volume of its SPE extract ($V_{SPE\ extract}$), and then multiplied by the dilution factor used in the bioassay (Eq. (1)) (Macova et al., 2011).

$$\mathrm{REF} = \frac{V_{\text{water sample}}}{V_{\text{SPE extract}}} \times \text{dilution factor}_{\text{bioassay}} \quad (1)$$

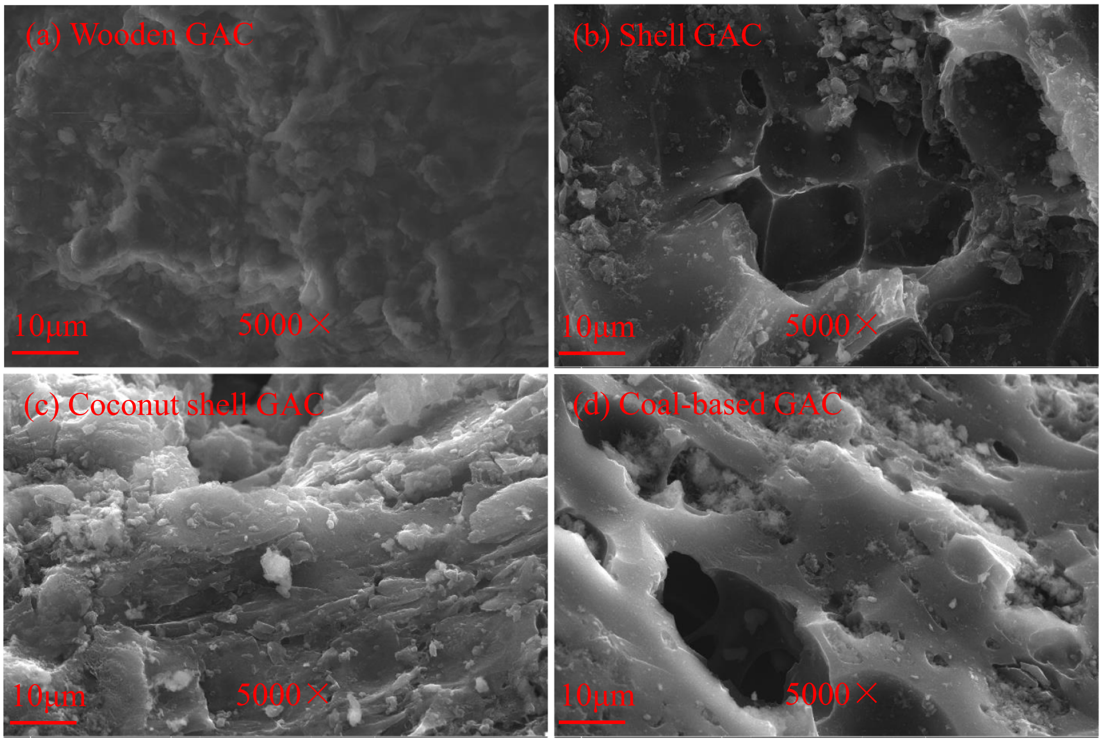

Fig. 1. SEM images of four types of GACs. (a) Wooden GAC; (b) Shell GAC; (c) Coconut shell GAC; (d) Coal-based GAC.

The effect concentration (EC) of each bioassay for the detected sample was derived from dose (REF) – effect curves. It was expressed as the EC_{50} for luminescent bacteria toxicity test and combined algae test (2 h-PSII), and the $IR_{1.5}$ for the SOS/umu test. To make the biological responses comparable, the biological effects of the water sample were standardized to the bioanalytical equivalent concentration (BEQ) using the positive control, as Eq. (2) shown (Macova et al., 2011).

$$\text{BEQ (mg/L or μg/L)} = \frac{EC_{50} \text{ or } IR_{1.5} \text{ of reference compound (mg/L or μg/L)}}{EC_{50} \text{ of water sample (REF)}} \tag{2}$$

2.4. Characterization of GACs

2.4.1. Textural characteristics

The surface texture and porosity of the four commercial GAC were analyzed using scanning electron microscopy (SEM, MLA650F, FEI, USA). Brunauer emmett teller (BET) surface areas of the GAC were determined by N_2 adsorption at 77 K using a surface area analyzer (V-Sorb2800P, China). The infrared spectrum of the GAC was obtained using a Fourier-transform infrared spectrophotometer (FTIR, IRPrestige-21) at room temperature over a 4000–400 cm^{-1}spectral range. Samples for FTIR analysis were finely ground and mixed with KBr in a mass ratio of 1:100 and pressed into a translucent pellet.

2.4.2. Boehm titration and pH_{PZC}

The surface functionality of GAC was assessed via a modified Boehm titration procedure (Satayeva et al., 2018). The Boehm method is a selective neutralization of surface acidic groups of varying strengths using bases that have conjugate acids with a wide range of acid dissociation constants (p*K*a). A sample of 0.5 g GAC was added to a series of flasks containing 50 mL of 0.05 M NaOH, Na_2CO_3, $NaHCO_3$, or HCl solutions. The flasks were then sealed and shaken for 24 h at room temperature. After that, the suspension was decanted and 10 mL of the remaining solution was titrated with 0.05 M HCl or NaOH. The number of acidic groups was calculated based on the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites was determined from the amount of HCl that reacted with the carbon. The surface functional groups were quantified as milliequivalents (meq) per gram of sample.

The pH_{PZC} (point of zero charge) of the GAC was obtained using the pH drift method (Strelko and Malik, 2002). The pH value was measured using a pH meter (PHS-3C, Sanxin, China). In brief, 50 mL of KNO_3 solution (0.1 M) was added in a flask containing 0.1 g of GAC. The initial pH is adjusted by addition of NaOH or HCl (0.1 M) to achieve a specific value (between 2 and 12). After a contact time of 48 h under magnetic agitation, the final pH was measured and plotted against the initial pH. The value at which pH (final) = pH (initial) was defined as pH_{PZC} and the surface charge of the GAC sample was neutral.

3. Results and discussion

3.1. Characterization and optimization of four types of GACs

3.1.1. Textural characteristics

The surface morphology of the four activated carbons was characterized by SEM as shown in Fig. 1. The surface of shell GAC and coconut shell GAC is relatively neat, with many delicate folds and protrusions, and a high degree of complexity (Fig. 1a-b). Their surface has edges and corners, and the pore structure is developed. However, the surface of wooden GAC and coal-based GAC is relatively rough and irregular. BET specific surface area (S_{BET}) of shell GAC and coconut shell GAC was 399.06 m^2/g and 271.58 m^2/g, respectively, but that of coal-based GAC and wooden GAC was 36.03 m^2/g and 20.68 m^2/g, respectively. The shell GAC and coconut shell GAC consist of a stacking multiple layers of thin sheets, and the interlayer forms large pores. The

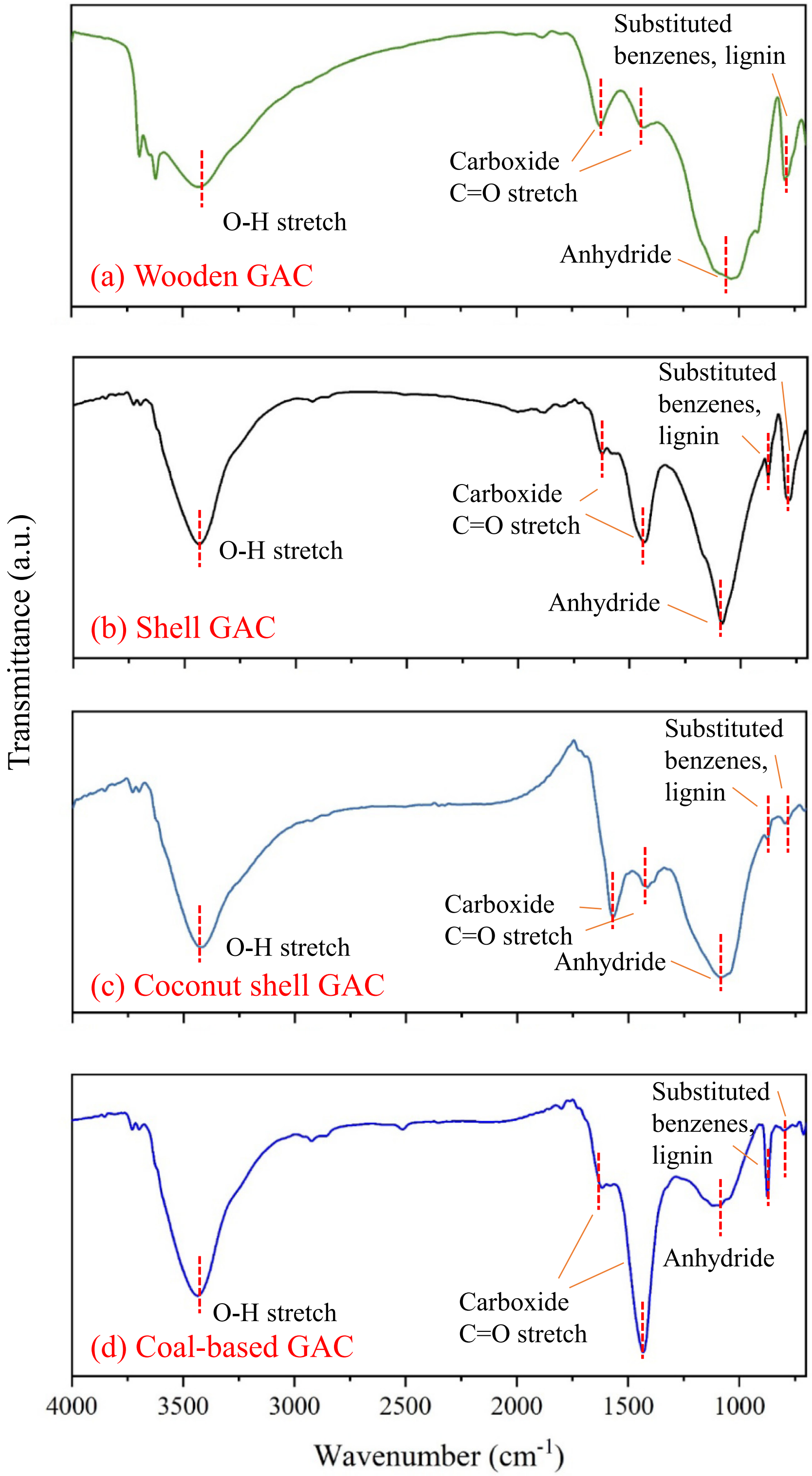

Fig. 2. FTIR spectra of four types of GACs. (a) Wooden GAC; (b) Shell GAC; (c) Coconut shell GAC; (d) Coal-based GAC.

structured large pores, that are the skeletons of micropores, mesoporous, and macropores, facilitate the diffusion of pollutants to the interior. Therefore, the S_{BET} of shell GAC and coconut shell GAC are greater than that of coal-based GAC and wooden GAC. There are many small particles accumulated on the surface of wooden GAC, making its surface rough and irregular (Fig. 1d). No micro-pores were formed on the surface area of wooden GAC. So, the S_{BET} of wooden GAC was the lowest.

3.1.2. Functional group characteristics and pH_{PZC}

The types of surface functional groups on GACs were determined by FTIR (Fig. 2). The FTIR spectra of the four types of GACs have the same trend. The characteristic peak at around 3428 cm^{-1} corresponds to the stretching vibration of hydrogen-bonded hydroxyl (-OH) groups, which support the presence of carboxyl, phenol or alcohol groups on the surface of GAC (Jawad et al., 2018). The characteristic peak at around

1750 cm^{-1} corresponds to the stretching vibration of carboxide C═O on the surface of the activated carbon (Sharma et al., 2019). The peak at 1086 cm^{-1} was mainly assigned to the vibration contraction of the carboxylic anhydride group. The stretching vibration intensity of the carboxylic anhydride group on the surface of coal-based GAC is lower than that of other activated carbons (Forouzesh et al., 2019). The absorption peaks of substituted benzenes and lignin were found in the four activated carbons

Boehm titration was used to quantify the content of acid-base functional groups on the surface of the activated carbon. As shown in Table 1, shell GAC has the largest total acidic functional group content, up to 900 μmol/g, followed by the coconut shell GAC with 755 μmol/g. For shell GAC, the content of lactone groups is the highest (325 μmol/g) of the three acidic functional groups. But, the content of the phenol hydroxyl group is the highest (330 μmol/g) of the three acidic functional groups on the surface of the coconut shell GAC. The shell GAC and coconut shell GAC also had a high content of basic functional groups. The high content of acidic/basic functional groups indicates that the surface of activated carbon has a high cation/anion exchange capacity and a strong adsorption capacity for cations/ anions (Forouzesh et al., 2019). Hence, it can be seen from the total amount of the acidic and basic functional groups that the ion exchange and adsorption capacity of shell and coconut shell GAC are stronger than that of coal-based and wooden GAC.

The pH_{PZC} is the pH where the net surface charge of the adsorbent reaches a zero-point value (Jawad et al., 2018). At $pH > pH_{PZC}$, the sorption of the cation species is favored where the charge of the adsorbent is negative, while the sorption of anionic species is favored on the positively charged adsorbent surface at $pH < pH_{PZC}$ (Abd-Elhamid et al., 2019). As is shown in Table 1, the pH_{PZC} of the shell GAC is acidic, which is related to the highest content of Boehm acidic functional groups, and the other three types of GACs are alkaline. The pH of secondary effluent discharged from the WWTP is about 8.0. Thus, the GACs have good property on the cation species adsorption.

3.1.3. Comparison of four types of GACs for the luminescent bacteria toxicity removal

In this study, the goal-oriented biological effects control was performed to select the GACs. The non-specific luminescent bacteria toxicity was used as the indictor, because it was defined as a priority biological effect from SE (Ma et al., 2019). Fig. 3 shows the removal efficiency of four types of GACs (10 g/L) on biological effect from SE. The shell GAC had the highest efficiency on the luminescent bacteria toxicity removal, followed by the coconut shell GAC, and the wood GAC had the lowest removal efficiency (Fig. 3a). The result of the luminescent bacteria toxicity test, reflecting the non-specific bacterial cytotoxicity, were posed by numerous non-specifically acting chemicals in the wastewater (Ma et al., 2019).

Among the four types of GACs, the shell GAC has a well-developed pore structure, the largest S_{BET}, and the largest amount of acidic and basic functional groups which could absorb electronegative and electropositive pollutants. In addition, the effluent of the WWTP is generally alkaline, while the surface charge of the shell GAC is acidic ($pH_{PZC} = 6.6$). Actually, the content of total acid-base functional groups and S_{BET} has been found to show a good positive correlation with bacterial cytotoxicity removal (Fig. 3b). The content of functional groups and S_{BET} of GACs are important factors affecting the adsorption of toxic substances. Hence, compared with the other three activated carbons, the shell GAC showed the promising property of reducing biological effect was selected for further study.

3.2. Removal of DOM by shell GAC

The responsible organic substances of biological effects from SE mainly consist of macro-molecule dissolved organic matter (DOM) and micro-molecule trace organic pollutants (TOPs). The property of shell GAC on DOM removal was investigated. When the dose of shell GAC increased from 0 to 30 g/L, the TOC decreased from 6.985 mg/L to

Table 1
Amount of acidic/basic groups on the surface of GACs and their pH_{PZC}.

Types of GAC	Boehm acidic groups (μmol/g)				Total Boehm basic groups (μmol/g)	Point of zero charge (PZC)
	Carboxyl groups	Lactones groups	phenolic hydroxyl groups	Total Boehm acidic groups		
Wooden GAC	150	300	150	600	473	7.8
Shell GAC	275	325	300	900	720	6.6
Coconut shell GAC	225	200	330	755	608	7.5
Coal-based GAC	200	150	175	525	630	7.3

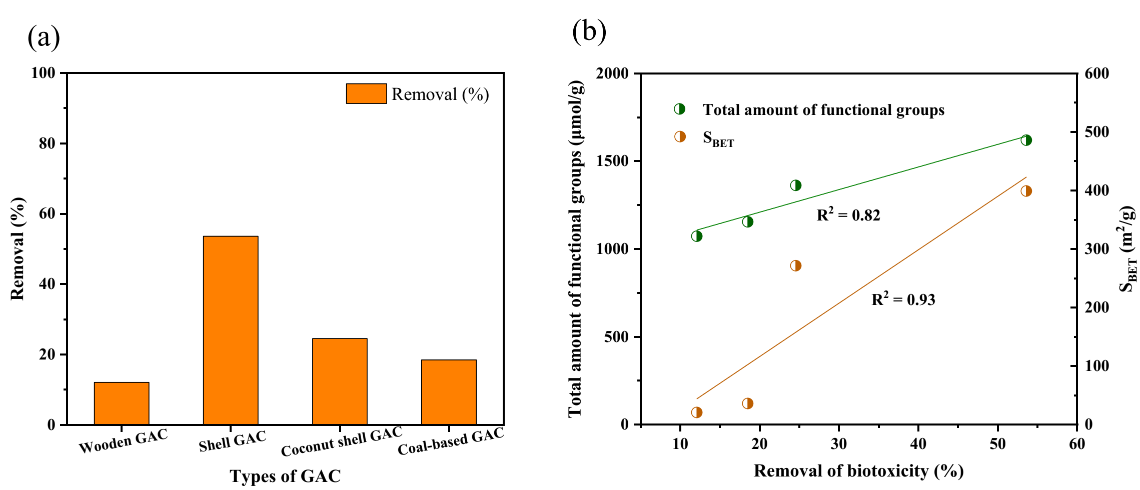

Fig. 3. The removal of the luminescent bacteria toxicity from SE using different GACs (a) and their relationship with the total amount of functional groups or S_{BET} (b).

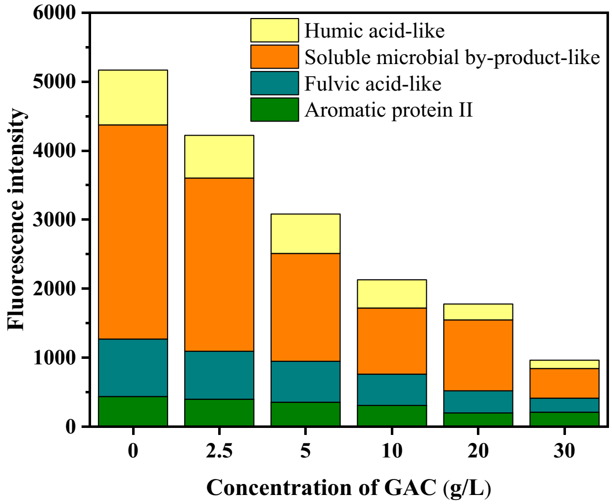

Fig. 4. Fluorescence intensity of four components in wastewater with different doses of shell GAC treatment.

4.792 mg/L (31.4% removal) and UV_{254} from 0.171 cm^{-1} to 0.054 cm^{-1} (68.4% removal) (SI Table S1). The EEM was divided into five regions (regions I—V) according to previous studies (Song et al., 2018; Chen et al., 2003). The five regions correspond to aromatic protein I, aromatic protein II, fulvic acid-like, soluble microbial by-product-like and humic acid-like materials (SI Table S2). There are four distinct fluorescence spectral peaks (peak A–D) in the EEM of SE (SI Fig. S1), observed at λex/λem = 260/520, λex/λem = 285/285, λex/λem = 240/380, and λex/λem = 240/480, corresponding to humic acid-like material, aromatic protein II, soluble microbial by-product-like material and fulvic acid-like material.

As can be seen from Fig. 4, the substances with the highest content in SE are soluble microbial metabolites, followed by humic acids and fulvic acids. It has been proved that most of the soluble organics in wastewater from biological processes were soluble microbial metabolites (Ly et al., 2018). The fluorescence intensity of each peak gradually decreases with the increase of the dose of shell GAC. When the dose of activated carbon reaches 30 g/L, the removal of humic acid-like material, soluble microbial by-product-like material, fulvic acid-like material, and aromatic protein II, was 85%, 86%, 76%, 52%, respectively. The soluble microbial products in the SE without the activated carbon treatment accounted for 60%. When the dose of GACs reached 30 g/L, the removal of soluble microbial metabolites reached 86%, yet still accounted for a large proportion of the total concentration after activated carbon adsorption. Adsorption of DOM on activated carbon was based on the multiple-functionalized interactions with the characteristics of (i) non-specific dispersive interplays, e.g., hydrophobic interactions, hydrogen bonds and van der Waals interactions (Han et al., 2015); (ii) complicated reactions that were multiply imposed by the composition of DOM, as well as functional groups and surface charges (Alvarez-Uriarte et al., 2010). This resulted in the GACs exhibiting excellent properties on DOM removal, especially soluble microbial by-product-like, humic acid-like, and fulvic acid-like materials.

3.3. Removal of TOPs by shell GAC

There were 12 pesticides (2 herbicides, 5 insecticides, 5 bactericides) and 9 pharmaceuticals detected in SE. The concentrations of the four

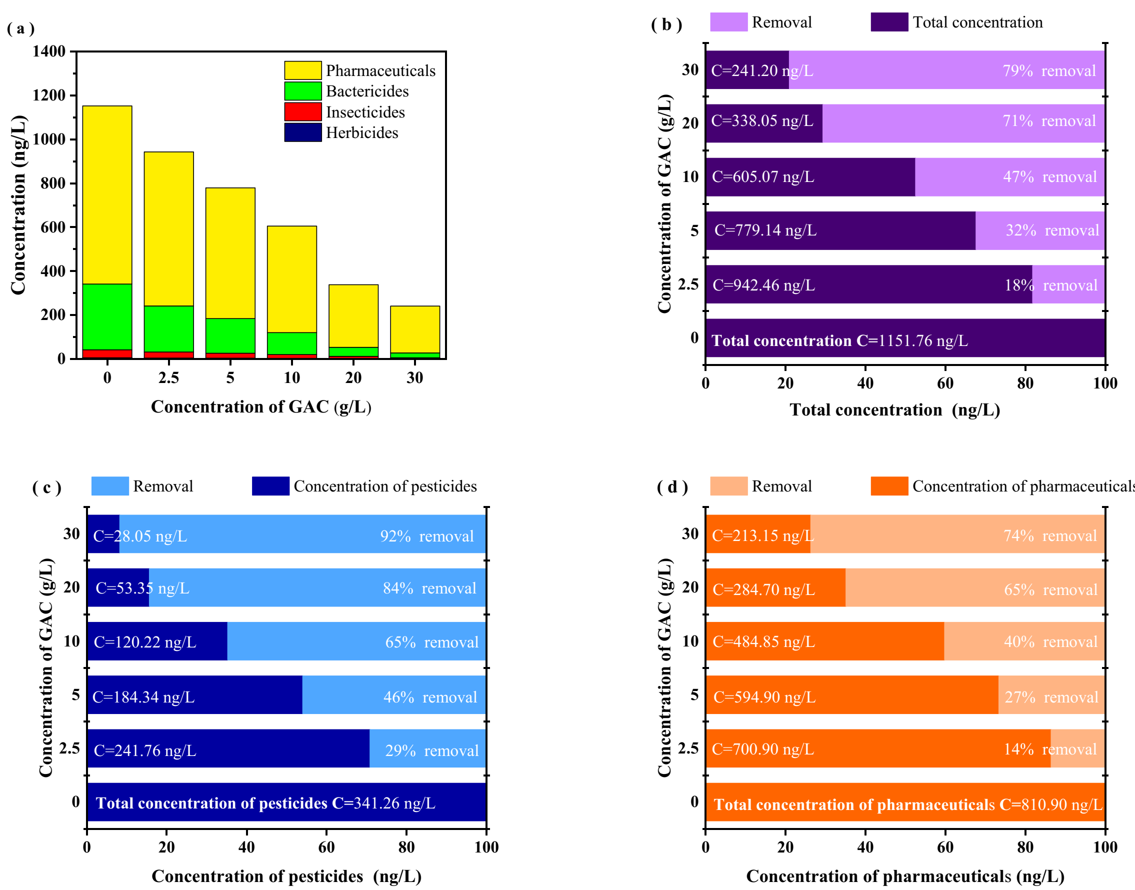

Fig. 5. Removal of TOPs by different doses of shell GACs.

categories of TOPs, including herbicides, insecticides, bactericides, and pharmaceuticals in SE were 5.95, 36.11, 299.2, and 810.7 ng/L, respectively (Fig. 5a). The main TOPs in SE without GAC treatment were pharmaceuticals and bactericides, accounting for 70% and 26% of all detected TOPs respectively. Previous studies have indicated the high content of pharmaceuticals and bactericides (especially carbendazim) in SE (Manoli et al., 2019). As shown in Fig. 5b, the total initial concentration of detected TOPs was 1152.16 ng/L. With the increase of shell GAC dosage from 0 to 30 g/L, the total concentration of TOPs decreased from 1152.16 ng/L to 241.20 ng/L, achieving 79% removal. After 30 g/L of shell GACs treated, most of the residual TOPs were anti-inflammatory drugs and antibiotics, accounting for 88% of total residual TOPs.

The removal of pesticides and pharmaceuticals increased with the shell GACs added. Comparing pesticides and pharmaceuticals, the removal of pesticides was as high as 92% under a dose of 30 g/L, while that of pharmaceuticals was only 74% (Fig. 5c and d). The removals of hydrophobic compounds which had logD (pH = 8) > 3.0, including chlorpyrifos, azoxystrobin, dimethomorph, difenoconazole, prochloraz, prometryn, and diphenhydramine hydrochloride, were above 80% at 30 g/L shell GAC dose (Table S3). Chemicals with high logD (pH = 8) showed high adsorption affinity to GACs (Westerhoff et al., 2005). For hydrophilic chemicals with log D (pH = 8) < 3.0, their removal efficiencies were inconsistent. These hydrophilic chemicals, including atrazine, acetamiprid, imidacloprid, carbendazim, trimethoprim, and carbamazepine, also could be effectively removed by 30 g/L of shell GACs; thiamethoxam, diclofenac acid, ibuprofen, clarithromycin, roxithromycin, sulfamethoxazole, were highly resistant to activated carbon treatment (< 80% removal).

The variation in the removal efficiency of TOPs during shell GACs adsorption was affected by their hydrophobicity, the presence of strong electron-withdrawing functional groups (e.g. chlorine, amide, and carboxylic) or strong electron-donating functional groups (such as hydroxyl and aliphatic) in their molecular structures, as well as aromaticity, charge, and size. (Tadkaew et al., 2011). The molecular structures of detected chemicals are shown in SI Table S3. The adsorption mechanisms related to these properties occur in parallel, and their respective dominance can vary from compound to compound (Nguyen et al., 2013). The removal of ibuprofen was only 62% at 30 g/L shell GAC doses, which may be due to the chemical's negative charge in a neutral environment (Ali et al., 2019). The surface charge of shell GAC (pHzpc = 6.6) is also negative in neutral solution, and the same electrical properties slow the adsorption of ibuprofen. Carbendazim which accounted for 83% of the total amount of pesticides, had a low logD (pH = 8) value, but its removal efficiency was significantly high. This may be attributed to intermolecular interactions, such as hydrogen bond, van der Waals force, and dipole-dipole (Prete et al., 2017). Giry et al. (2001) used activated carbon, clay, and coal as adsorbents to remove carbendazim in water, and found that activated carbon still had the best removal efficiency. Of the 12 pesticides, 5 insecticides were all effectively removed by shell GAC. Acetamiprid, imidacloprid, and thiamethoxam were the neonicotinoid insecticides, and chlorpyrifos and dipterex belong to the organophosphorus insecticides. Klarich et al. (2017) detected clothianidin, imidacloprid and thiamethoxam in SE with extremely high frequency, and found that all three neonicotinoids exhibited relatively rapid removal via GAC sorption. This may be attributed to specific binding actions between surface sites on GAC and specific functional groups in the neonicotinoids.

In addition, the DOM in SE also affects the adsorption of TOPs on GACs. It can not only compete for adsorption sites, but also affect the adsorption of chemicals by blocking the carbon pores of activated carbon (Zietzschmann et al., 2014). Guo et al. (2007) suggested that the adsorption of atrazine via five types of GACs was affected by DOM, and GACs with wider pore size distribution were more susceptible to DOM than those with microporous carbon (Li et al., 2003). It is shown in Fig. 4 that shell GAC has a significant removal effect on fulvic acid-like, soluble microbial by-product-like, and humic acid-like materials.

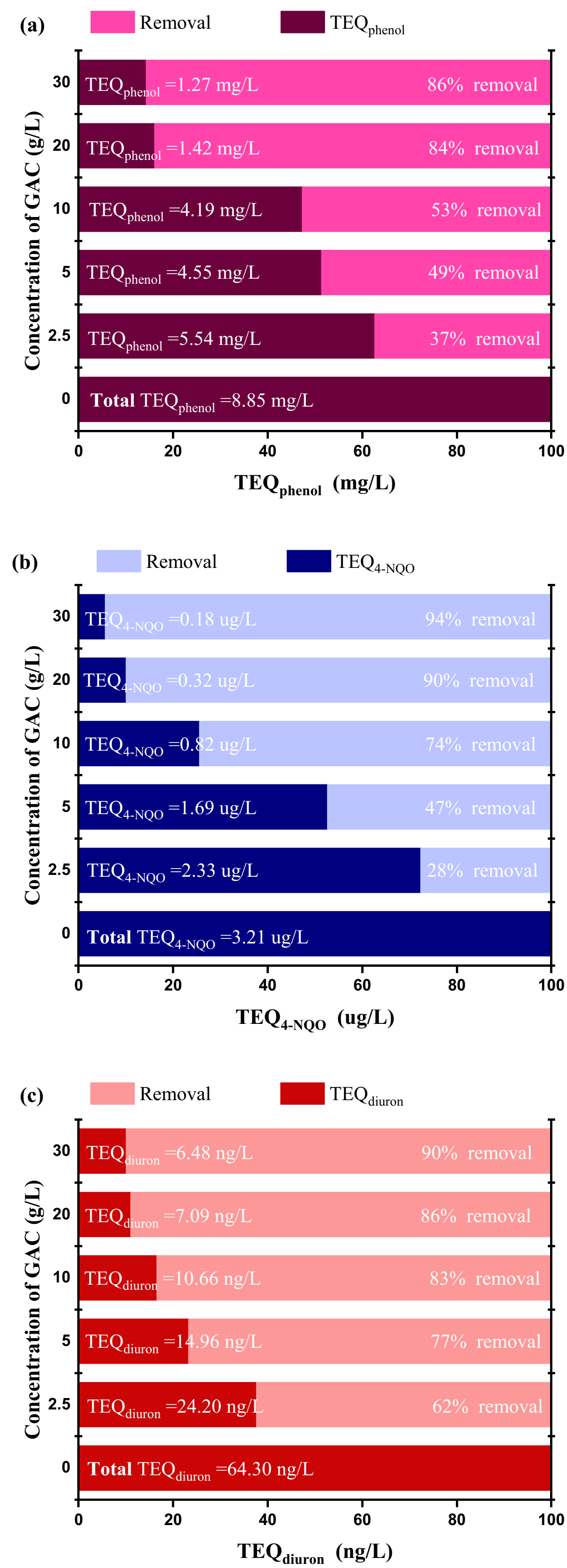

Fig. 6. Removal of three biological effects by different doses of shell GACs. (a) Luminescent bacteria toxicity; (b) genotoxicity; (c) photosynthetic inhibition effect.

These macromolecular substances will adsorb in the mesopores of activated carbon, and compete with TOPs for adsorption sites. The removal efficiency of TOPs can be improved by removing DOM before TOPs or by increasing the amount of GAC appropriately, but this will increase the treatment cost.

In general, the detected pesticides and pharmaceuticals were moderately or well removed via shell GACs adsorption, but no correlation was observed with the logD, indicating that the hydrophobicity alone was not sufficient to estimate TOP removal. This was affected by the physico-chemical properties of pollutants such as the molecular size, charge, polarizability and functional groups. The adsorption process cannot be described by a single parameter, but rather by a variety of physical and chemical interactions among TOPs, DOM, and GAC (Guillossou et al., 2018; Mailler et al., 2016).

3.4. Removal of biological effects by shell GAC

In the GAC adsorption process, the reduction of the three biological effects posed by SE, including luminescent bacteria toxicity, genotoxicity, and photosynthetic inhibition effect, improved with increasing shell GAC dose, and remained nearly stable after 20 g/L shell GAC addition (Fig. 6a-c). At 30 g/L of shell GAC dose, 86% of luminescent bacteria toxicity, 94% of genotoxicity, and 85% of photosynthesis inhibition effects from SE were eliminated. The shell GAC adsorption process showed promising performance in the reduction of the three biological effects.

As shown in Fig. 6a, when the dose of shell GACs was greater than 10 g/L, the removal efficiency on luminescent bacteria toxicity suddenly increased. This is consistent with the variation of UV_{254} removal. Wei et al. (2012) indicated that the genotoxicity and acute luminescent bacteria toxicity from WWTP wastewater were well correlated with the dissolved organic carbon (DOC) and UV_{254}. The results of luminescent bacteria toxicity tests, reflecting the non-specific bacterial cytotoxicity, were posed by the large number of non-specifically acting chemicals in the wastewater (Tang et al., 2014). The adsorption of shell GAC is also based on the non-specific dispersion interaction and the complex reaction between the pollutants and GACs (Han et al., 2015). Therefore, shell GAC has excellent property for luminescent bacteria toxicity reduction. It has been indicated that the detected TOPs could only explain less than 1% of measured luminescent bacteria toxicity (Tang et al., 2013). So, "toxic unknowns", which were not detected by instrumental analyses, were responsible for the luminescent bacteria toxicity, such as macromolecular DOM. It has been seen that DOM in WWTP effluent acts as a toxicity inducer of residual chemicals in the SE (Hara-Yamamura et al., 2020). In the present study, the removal of luminescent bacteria toxicity using shell GAC was positively correlated well with the removal of fluorescent DOM which were expressed from EEM (SI Fig. S2). Shell GAC has a large specific surface area and a well-developed pore structure, so that it has good adsorption properties for macromolecular organic compounds, resulting in the effective removal of luminescent bacteria toxicity.

TOPs in secondary effluent, as well as DOM, can cause genotoxic reactions (Khan et al., 2019). Ames test results of detected chemicals, which had a concordance of approximately 90% with the SOS/umu test used in this study are shown in SI Table S3 (Reifferscheid and Heil, 1996). The chemicals that obtained positive results are conservatively defined as direct-acting mutagens. During shell GAC adsorption, the removal of chemicals which showed positive results in the Ames test, including atrazine, acetamiprid, dipterex, roxithromycin, and carbamazepine, was the main reason for reduction of genotoxicity from SE. Additionally, UV_{254} as an indicator of DOM, which indicates the content of aromatic compounds, has a positive correlation with genotoxicity (Grandclement et al., 2017).

It has been revealed that herbicides play a leading role in the photosynthesis inhibition effect (Tang and Escher, 2014). In this study, only two herbicides, atrazine and prometryn, were detected in the SE (Table 2). Based on the combined algae test, the relative potencies (RPs) of atrazine and prometryn relative to diuron were 20.65 and 1.16. Using a concentration addition model to predict the photosynthesis inhibition effect following the previous studies (Ma et al., 2020), the detected pesticides in SE can explain 185%–255% of observed photosynthesis inhibition effect in the present study. Tang and Escher (2014) indicated that when there were only one or two herbicides detected in sewage, the prediction results may have a large deviation. Even so, due to the high detection concentration of atrazine and its high RP, the detected photosynthesis inhibition effect from SE was mainly caused by atrazine. The removal of atrazine by 30 g/L shell GACs reached 80% and the reduction of photosynthesis inhibition effect was as high as 90%. Many studies had also shown that atrazine has a high frequency of detection and was the main herbicide that produced photosynthetic inhibition effects in wastewater (Satayeva et al., 2018).

Table 2
Concentration of TOPs (ng/L) and the removal of TOPs at 30 g/L shell GAC dose.

Category	Chemicals	GAC dosage (g/L)						Removal (%)
		0	2.5	5	10	20	30	
Pesticides	Atrazine	5.8	4.6	3.7	2.9	1.7	1.2	80.00
	Prometryn	0.2	0.2	0.1	–	–	–	100.00
	Chlorpyrifos	3.5	2.8	1.7	1.8	1.7	–	100.00
	Dipterex	6	4	3.1	2.5	1.6	0.4	93.33
	Acetamiprid	18.6	14.5	11.7	9.1	4.9	2.8	84.95
	Imidacloprid	2.2	1.5	1.2	0.7	0.2	0	100.00
	Thiamethoxam	5.8	4.6	4.8	3.4	1.8	1.6	72.41
	Azoxystrobin	6.3	4.7	3.8	2.7	1.3	0.7	88.89
	Carbendazim	284.8	199.2	149.6	93.9	38.8	20.5	92.80
	Dimethomorph	5.4	4.1	3.5	2.7	1.4	0.9	83.33
	Difenoconazole	1.5	0.9	0.7	0.3	–	–	100.00
	Prochloraz	1.2	0.7	0.4	0.2	–	–	100.00
Pharmaceuticals	Diclofenac acid	521.1	476.5	405.4	342	209.1	160.1	69.28
	Ibuprofen	22.1	15.1	17.2	15.6	11.3	8.3	62.44
	Mefenamic Acid	112.5	93	80.6	61	28.5	22.7	79.82
	Clarithromycin	4.4	3.9	3.1	2.5	1.5	1.1	75.00
	Roxithromycin	28	24.5	20	15.4	9.2	6.3	77.50
	Sulfamethoxazole	16	12.6	10.9	9.2	6.2	3.95	75.31
	Trimethoprim	7.5	5.5	4.4	2.9	1.2	0.7	90.67
	Carbamazepine	27.5	21.6	16.8	12.5	7.6	4.3	84.36
	Diphenhydramine hydrochloride	71.6	48.2	36.5	23.8	10.1	5.7	92.04

4. Conclusions

Four types of typical GACs were compared comprehensively from the aspects of textural characteristics, functional groups, pH_{PZC} and the luminescent bacteria toxicity removal. Based on the goal-oriented biological effects control, the shell GAC, with a great adsorption capacity and a large number of functional groups, was preferably selected. The shell GAC showed a promising property of removing fluorescent DOM and TOPs. For DOM, soluble microbial metabolites and humic acid-like materials had a high removal efficiency. For TOPs, the total concentration of 21 detected TOPs achieved 82% removal when 30 g/L shell GACs was added. Regarding individual chemicals, its removal by GAC adsorption cannot be described by a single parameter (molecular size, charge, functional groups, etc.), but rather by a variety of physical and chemical interactions among TOPs, DOM, and GAC. Shell GAC showed excellent properties of removing the three biological effects. When the 30 g/L shell GAC was added, the removal of luminescent bacteria toxicity, genotoxicity, and photosynthesis inhibition effect could achieve 85.7%, 94.3%, and 89.9%, respectively. The reduction of luminescent bacteria toxicity from SE corresponded well with the removal of DOM. The effective removal of atrazine in the shell GAC adsorption process resulted in the reduction of photosynthesis inhibition effect from SE. The removal of genotoxicity from SE may be due to the adsorption of DOM, as well as TOPs, by shell GAC. The characteristics of shell GACs and the removal mechanisms of DOM, TOPs, and biological effects, could help managers of WWTP to improve discharged wastewater quality and ecological safety.

CRediT authorship contribution statement

Lei Tang: Writing- Original draft preparation, Formal analysis. **Xiaoyan Y. Ma:** Writing - Review & Editing, Supervision. **Yongkun Wang:** Methodology, Data Curation. **Shiying Zhang:** Data Curation. **Kai Zheng:** Methodology, Investigation. **Xiaochang C. Wang:** Conceptualization, Project administration. **Yu Lin:** Investigation.

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 data

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Corrigendum

Corrigendum to "Removal of trace organic pollutants (pharmaceuticals and pesticides) and reduction of biological effects from secondary effluent by typical granular activated carbon" [Sci. Total Environ. 749 (2020) 141611]

Lei Tang [a,b], Xiaoyan Y. Ma [a,b,*], Yongkun Wang [a,b], Shiying Zhang [a,b], Kai Zheng [c], Xiaochang C. Wang [a,b,*], Yu Lin [a,b]

[a] *Shaanxi Key Laboratory of Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China*
[b] *International Science & Technology Cooperation Center for Urban Alternative Water Resources Development, Key Lab of Northwest Water Resource, Environment and Ecology, MOE, Engineering Technology Research Center for Wastewater Treatment and Reuse, Shaanxi Province, China*
[c] *PetroChina Changqing Oilfield Company, Xi'an 710021, China*

The authors regret that the printed version of the above article contained an error. The correct and final version follows. The correct affiliation 'a' is:

[a]Shaanxi Key Laboratory of Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

The authors would like to apologise for any inconvenience caused.

Declaration of Competing Interest

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* Corresponding authors at: Shaanxi Key Laboratory of Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China.
URL's: maxiaoyan@xauat.edu.cn (X.Y. Ma), xcwang@xauat.edu.cn (X.C. Wang).

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