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Synthesis of an easily recyclable and safe adsorbent from sludge pyrochar for ciprofloxacin adsorption



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ABSTRACT

Utilization of sludge pyrochar (SP) is the terminal step to loop the entire harmless disposal process of sewage sludge with pyrolysis. A new, easily recyclable, and safe adsorbent with well-immobilized heavy metals (HMs) was prepared from SP for ciprofloxacin (CIP) adsorption. The operational conditions for the adsorbent preparation were systematically optimized based on recycling rate and adsorption performance. Additionally, the adsorption conditions, adsorption kinetics, isotherms, and regeneration of adsorbents were further investigated in the present study. The results showed that easily recyclable and safe adsorbents were successfully prepared at 1100 °C under N₂ atmospheric conditions (SPA-N-1100) with a maximum CIP adsorption capacity of 10.42 mg/g. SPA-N-1100 exhibited good CIP adsorption performance at an adsorption temperature of 45 °C and pH between 8.0 and 9.0. The adsorbents were regenerated by thermal desorption at 450 °C with a thorough decomposition of CIP. The adsorption mechanism was mainly dominated by its special porous microspheres-accumulation structure and surface species (e.g., FeP and graphite). Moreover, HMs in the adsorbents were well immobilized in SPA-N-1100 by the generation of new metal mineral phases and encapsulation of melting minerals, which had an ultralow potential for ecological risk during application.

1. Introduction

The large amount of sewage sludge with high moisture content produced from wastewater treatment plants is becoming a growing concern. Different hazardous matters, such as unpleasant odor (volatile sulfur and nitrogen compounds, e.g. H₂S and NH₃), pathogens, heavy metals, antibiotics, and microplastics, impede proper treatment of sewage sludge (Barbusinski et al., 2017; Li et al., 2018d; Xu et al., 2020). Over the past few decades, numerous efforts have been made to improve technologies for generating valuable resources and energy recovery from sewage sludge. Thermal conversion technologies, such as thermal pretreatment and subsequent pyrolysis or gasification, are emerging approaches for both sludge dewatering and valuable resource generation (Gong et al., 2016; Xia et al., 2020; Xu et al., 2019). Moreover, almost all organic contaminants within the sludge, including pathogens, antibiotics, and cacosmia, can be eliminated during the thermal conversion process. A pilot-scale verification equipped with hydrothermal treatment, anaerobic digestion, and pyrolysis for valuable products (e. g., biogas and pyrochar) generation from sludge has been reported in our previous work (Li et al., 2018d, 2017). These valuable products can be used as fossil fuel alternatives for offsetting energy consumption and reducing emissions. The volume of sludge can also be significantly minimized after pyrolysis with only a small amount of solid product, pyrochar, remaining.

Pyrochar is a multipurpose product that can be applied in many domains. For example, it can be used as adsorbents and soil conditioners owing to its porous structure, rich functional groups, nutrients, and mineral elements (e.g., C, N, P, K, Mg, and Ca) (Rehman et al., 2018; Yue et al., 2017). However, most of the heavy metals (HMs) in sludge are enriched in sludge pyrochar (SP) (Jin et al., 2016). Pyrochar with high

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Abbreviations: CIP, ciprofloxacin; SP, sludge pyrochar; KL, kaolin; SPA, adsorbent from sludge pyrochar; SPA-O-1025, SPA prepared at 1025 °C under air atmosphere; SPA-N-1025, SPA prepared at 1025 °C under N₂ atmosphere; SPA-N-1100, SPA prepared at 1100 °C under N₂ atmosphere; SPA-N-1100calc, a calculation value of HMs concentration according to the concentration of samples from individual KL and SP sintered at 1100 °C with N₂; HMs, heavy metals; F1, Acid soluble/ exchangeable fraction; F2, Reducible fraction; F3, Oxidizable fraction; F4, Residual fraction.

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HM contents is not permitted to be applied directly to the environment, although the HMs in pyrochar exist in a more stable form (Xie et al., 2020). Therefore, a new approach is needed to utilize these types of pyrochar, rather than to dispose them as hazardous waste. Our previous work found that the HMs in SP were further immobilized after sintering as high-strength construction ceramsite over 1000 °C under an air atmosphere (J. Li et al., 2018a, 2018c). Other studies reported that the generation of HM minerals with strong chemical bonds dominated the HM stabilization in the sludge-based ceramsite produced under high-temperature sintering (Xu et al., 2010, 2008). However, the aforementioned work primarily focused on the immobilization of HMs, instead of the application of products. Increased effort should be taken to prepare more valuable and advanced materials with HMs well trapped from SP. Previous studies have demonstrated that porous sludge-derived activated carbon with silicon carbide foam support could be synthesized as and an efficient odor gas adsorbent (Yang et al., 2018). A porosity waste gangue microsphere was prepared using a foaming approach to be utilized as a potential filtration material (Yan et al., 2019). The foaming modification of the pyrochar for the adsorbent preparation with a porous structure through sintering is probably to be a feasible approach to utilize SP with high added value. Our previous work verified that a heterogeneous Fenton-like catalyst could be sintered from SP (Li et al., 2019). However, the limitations of the Fenton-like catalyst include the requirement of additional H2O2 and catalyst deactivation. Therefore, synthesis of new adsorbents may be an alternative method to overcome these shortcomings and loop the final harmless disposal process of sewage sludge.

Ciprofloxacin (CIP) is among the most commonly used antibiotics in human and veterinary medicine (Pan et al., 2018). However, it is only partially metabolized by humans and animals due to its chemical stability, which results in CIP entering aquatic environments from excrement (Pan et al., 2018). Additionally, CIP can survive long durations in the environment because of its bacteria-inhibiting effects, which promotes the generation of antibiotic-resistant bacteria (P. Xie et al., 2020). CIP has been detected in hospital wastewater effluents with a concentration of 3–87 μ g/L and also in a high concentration (31 mg/L) from a drug production plant (Karthikeyan and Meyer, 2006; Larsson et al., 2007). Therefore, it is essential to be proactive to remove CIP from aquatic environments. Biodegradation (Yang et al., 2017), catalytic degradation (González-Labrada et al., 2020), and adsorption are three main strategies for CIP removal, with adsorption regarded as the simplest approach because of its easy design and operation (J. Li et al., 2018b). To date, only a few sludge-based materials have been applied for CIP removal and exhibited good performance (Li et al., 2019; Luo et al., 2019; Zhu et al., 2019), and much fewer of SP-based adsorbents for CIP adsorption. Our previous work verified that the sludge-based ceramsite possessed a weak ability for CIP adsorption (Li et al., 2017). Therefore, the preparation of a new adsorbent with foaming and sintering strategies for CIP adsorption could be an alternative approach.

In the present study, a novel easily recyclable and safe adsorbent with HMs well immobilized from SP was prepared for CIP removal by employing a foaming and sintering process. Various operational conditions, including additive species and ratio, mixing methods, foaming agent ratio, and time, were optimized, as well as the sintering temperature based on two different sintering atmospheres (air and N2), to improve the foaming porous structure and adsorption performance. Additionally, adsorbents prepared from the optimal parameters under air and N2 were chosen for further comparable investigation for CIP adsorption. The effects of adsorption conditions, including adsorption time, initial concentration of CIP, adsorbent dose, solution temperature, and pH value, on the CIP adsorption were explored. The adsorption kinetics, isotherm, desorption, and regeneration of the adsorbents were also investigated. Moreover, the HMs in adsorbents prepared from different atmospheres and temperatures were characterized and evaluated to ensure their safe application. The strategy for sludge-based pyrochar utilization in this study can increase knowledge for the

further immobilization of HMs and achieve a new easily recyclable adsorbent, which is beneficial for looping the resource utilization of sludge.

2. Materials and methods

2.1. Raw materials

Analytical standards for CIP were purchased from Aladdin Industrial Corporation in Shanghai, China. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All CIP solutions were prepared with ultrapure water. The SP was taken from a pilot-scale rotary pyrolysis furnace (30 t sewage sludge per day) in a wastewater treatment plant in Xiamen, Fujian Province, China. The details of the SP product line are illustrated in our previous work (Li et al., 2018d). Kaolin (KL), which has proven to be an effective additive for foaming improvement (Li et al., 2019), was produced in Longyan, Fujian Province, China. The chemical components of SP and kaolin are presented in Table S1.

2.2. Preparation of adsorbent

The preparation diagram of the adsorbent is illustrated in Fig. 1. To obtain a satisfied adsorbent from SP, additive types and mixed approaches were investigated in our preliminary experiments (Fig. 1a). Moreover, the solid content of wet ball-milling in step 1 (Fig. 1b) and the ratio of sodium dodecyl sulfate (SDS) in step 2 (Fig. 1b) were two important parameters to form the foaming slurry and make the adsorbent porous, penetrative, and were easily recyclable. Therefore, the two parameters were optimized in our preliminary experiments (supplementary materials). The results demonstrated that KL exhibited the best performance for improving the CIP adsorption ability. Solid content with 30 wt% in the wet ball-milling (230 r/min for 6 h) was suitable to make a sticky slurry which was beneficial for step 2 (magnetic stirring at a rate of 500 r/min for 10 min) and for foaming slurry preparation with an optimal SDS ratio of 1.0 wt%. When the foaming slurry was obtained, it was dried at 60 $^\circ \rm C$ for 12 h before sintering at a high temperature with a ramp rate of 5 °C/min in a tube furnace.

The sintering temperature and time were optimized under air (50 mL/min) as well as the temperature under N₂ (50 mL/min) based on preliminary experiments (Fig. 1a). After obtaining the adsorbents, both the CIP adsorption ability and the weight loss (*WL*) of the adsorbent after adsorption were taken into consideration to evaluate the adsorbents. *WL* indicated the strength and recycling potential of adsorbents from the adsorbent. Finally, the optimal adsorbents were prepared at 1025 °C under air (SPA-O-1025) and 1100 °C under N₂ (SPA-N-1100) atmospheric conditions, respectively. A higher sintering temperature under N₂ was needed to obtain a low *WL* (supplementary materials for additional information).

2.3. Characterization analysis

The morphology and surface composition of the optimal adsorbents were characterized by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS, S-4800, Hitachi, Japan). The adsorbent's porous structure was analyzed based on nitrogen adsorption/ desorption isotherms and the Brunauer–Emmett–Teller (BET) method under the relative pressure of 0.06–0.2. (Micromeritics ASAP, 2020 M + C, USA). The sample was dried and heated before the adsorption/ desorption isotherms determination. The pore volume was determined from the BJH adsorption cumulative surface area of pores between 1.70 nm and 300.00 nm. The pore size was achieved from BJH adsorption average pore diameter. The chemical components and the Fe species were employed with the aid of X-ray diffraction based on the existing database (XRD, X'Pert Pro, PANalytical B.V., The Netherlands, 20 from



Fig. 1. Main parameters optimization strategy (a) and steps (b) of adsorbent preparation (KL: Kaolin; SP: sludge pyrochar; SDS: sodium dodecyl sulfate).

 0° to $90^\circ)$ and X-ray photoelectron spectroscopy (XPS, ThermoFisher Scientific XLESCALAB250Xi, UK).

HM (Cu, Zn, Cr, Pb, Mn, Pb, and Cd) characteristics including total concentrations, speciation and risk assessments of HMs in the samples were investigated. The total concentrations of HMs in the samples were measured by digestion and attenuation. The speciation of HMs was extracted step-by-step based on a three-step sequential extraction procedure (BCR). The potential ecological risk index (RI) was employed to evaluate potential risk. The details of the HM analysis are given in the supplementary materials. To compare the impacts of both sintering temperature and atmosphere on HM migration, a sample was prepared at 1025 °C under air atmospheric conditions (SPA-O-1025) and was compared with SPA-N-1025 to investigate atmospheric impact. The sample from the condition of 1100 °C with N2 (SPA-N-1100) and a calculation value of HM concentration according to the concentration of samples from individual KL and SP sintered at 1100 °C with N2 (SPA-N-1100_{calc}) were analyzed to explore the synergistic effect of KL with SP on HM migration.

All samples obtained from digestion and sequential extraction were filtered through 0.45 μ m membrane filters and then diluted with a dilute HNO₃ solution (2 v.%) before detection. The total and different speciation concentrations of HMs were detected by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500cx, Agilent, USA). All experiments for HM analysis were conducted in triplicate, and average values were used for data analysis.

2.4. Experiments on CIP adsorption and adsorbent regeneration

2.4.1. CIP adsorption and detection

Batch adsorption experiments were conducted by adding 2.5 g of adsorbents prepared from different preparation parameters to 100 mL of the CIP solution with a concentration of 100 mg/L and a natural pH of approximately 6.75, respectively. The sealed conical flasks containing the CIP solution were placed in a dark rotary shaker (200 r/min) at 30 $^{\circ}$ C for 24 h.

Two optimal adsorbents prepared from air and N_2 (SPA-O-1025 and SPA-N-1100) were chosen to explore the impacts of adsorption time, CIP

concentration, adsorbent concentration, solution temperature, and pH in the adsorption process. All CIP solution samples taken from the adsorption experiments were filtered through a 0.45 μ m membrane prior to detection by high-performance liquid chromatography (HPLC, Hitachi L-2000, Japan). The detected approach was described in a previous study (Pan et al., 2018). All the adsorption experiments were conducted in triplicate to ensure data quality, and mean values with error bars are shown in the results.

The *WL* during the adsorption, its adsorption amount at the contact time (q_t) and equilibrium (q_e) , and the removal efficiency (*RE*) of CIP were calculated as follows:

$$WL = \frac{(M - M')}{m} \times 100 \tag{1}$$

$$q_t = (C_0 - C_t) \times \frac{V}{m} \tag{2}$$

$$q_{\ell} = (C_0 - C_{\ell}) \times \frac{V}{m}$$
⁽³⁾

$$RE = \frac{(C_0 - C_\ell)}{C_0} \times 100$$
 (4)

where *WL* (%) is the weight loss of the adsorbent during the adsorption, indicating the strength and recycling potential of adsorbent from the solution; q_t and q_e (mg/g) are the CIP amount adsorbed on the adsorbent at the contact time of t (h) and equilibrium; C_0 and C_e (mg/L) are the CIP concentrations at the beginning and at equilibrium, respectively, and V (L) is the solution volume; m and m' (g) represent the mass of the initial and recycled adsorbent from solution after adsorption; *RE* (%) is the removal efficiency of CIP by the adsorbent.

To better understand the adsorption process, adsorption kinetics and isotherms were investigated based on the adsorption data for different adsorption times and CIP concentrations. In terms of the adsorption kinetics, the pseudo-first-order model and pseudo-second-order model were employed (Ho and McKay, 1999). The Langmuir and Freundlich models were two commonly used models for adsorption isotherm investigation (Matsumoto, 1993). Details about the adsorption kinetics and isotherms are provided in the supplementary materials.

2.4.2. Adsorbent regeneration

Thermal desorption is a promising way to achieve adsorbent regeneration (Dutta et al., 2019), especially for the desorption of organic pollutants on the adsorbent prepared at high temperatures. In this study, the thermal decomposition characteristics of CIP were investigated using a thermal gravimetric analyzer to determine the temperature of thermal desorption. For the thermogravimetric analysis, the temperature was increased from room temperature to 900 °C at a ramp rate of 20 °C/min under an N₂ atmosphere. The temperature remained for 10 min at both 105 °C and then at 900 °C for water removal and complete decomposition, respectively. The temperature with a complete decomposition of CIP was chosen as the operational temperature for adsorbent regeneration in its own preparation atmosphere for 30 min. After thermal desorption, the adsorption ability of the regenerated adsorbents was evaluated by repeating the adsorption experiments.

3. Results and discussion

3.1. Characterization analysis

3.1.1. SEM-EDS and porous structure analysis

Fig. 2 shows the macro appearances and SEM micrographs of SPA-O-1025 and SPA-N-1100. For macro appearances, SPA-O-1025 was brown in color, while SPA-N-1100 appeared black. Both exhibited a honey-comb structure with many spherical sockets and small pores on the surface. For the microscopic structure, SPA-O-1025 possessed many stratified and hollowed-out structures with cross-vertical porous channels. The surface of SPA-O-1025 was rough and rugged owing to the accumulation of the lamellar structure. However, countless microspheres with different diameters were stacked on the surface of SPA-N-1100. The diameters of larger microspheres were near 2 μ m, while the

diameters of smaller ones were less than 0.2 μ m. In addition, many fine particles, or tiny balls, filled the gaps between the microspheres. The BET surface area of SPA-N-1100 was 18.95 m²/g. The surface area and pore volume of SPA-N-1100 were much higher than those of SPA-O-1025. Moreover, the average pore size of SPA-O-1025 was smaller than that of SPA-N-1100 due to its lamellar structure with thin slits.

The elemental compositions on the micro-surfaces of SPA-O-1025 and SPA-N-1100 were specifically analyzed by point scans and area scans with EDS (Fig. S6). They possessed roughly the same elemental composition with higher contents of Al, Si, Fe, O, and P (Table S6), while the contents of C and O were significantly different. C was not detected in SPA-O-1025, and the C content in SPA-N-1100 from the area scan was approximately 3.84%. Furthermore, the C content on the microspheres from points scan was higher than the area scan of the entire surface of SPA-N-1100. For the O and P elements of SPA-O-1025, the contents of the point and area scans were quite similar, which alludes to its even distribution, and the same was recorded for SPA-N-1100. However, the O content in SPA-O-1025 was much higher than that in SPA-N-1100 because of the presence of air in the sintering process. In addition, the contents of Al and Si on the sphere in SPA-N-1100 were higher than those on the whole surface, while the Fe content was much lower on the sphere surface. In terms of SPA-O-1025, the contents of Al and Si were lower in the bright region, while the Fe content was higher than that of the entire scanning surface of SPA-O-1025. The difference of contents with regards to the main elements on the surface of the two adsorbents suggests different compositions, especially the mineral compositions, which may cause the varying HM immobilization effects and CIP adsorption performance. Therefore, the XRD was continuously employed to investigate the detail mineral compositions in next section.

3.1.2. XRD and XPS analysis

The majority of compositions in the adsorbents were O, Si, Al, and Fe. To understand the detailed mineral compositions, XRD analysis was



Fig. 2. SEM micrograph of SPA-O-1025 (a) and SPA-N-1100 (b), and their pore structures (c and d).

conducted (Fig. 3a and b). SPA-O-1025 contained some typical minerals, including quartz (SiO₂) hematite (Fe₂O₃), and wagnerite (Mg₃(PO₄)₂), but also many types of special minerals with various types of embedded HMs (e.g., covelline (CuS), chrysocolla (CuSiO₃2·H₂O), braunite (Mn₇O₈(SiO₄)), and kehoite (Al₂H₁₂O₁₅P₂Zn)). Another remarkable result was that the HMs mainly combined with the oxides of Si, Al, and P. In SPA-N-1100, the variety of mineral compositions was much simpler than in SPA-O-1025. Its main mineral compositions also included quartz (SiO₂) and hematite (Fe₂O₃), and the different components were anorthite (CaAl₂Si₂O₈) and barringerite (Fe₂P). For the HMs in SPA-N-1100, only covelline (CuS) was detected, and other forms of HMs trapped in the SPA-N-1100 require further investigation in the future using other analytical instruments.

Fe was among the main elements in the adsorbent according to the EDS and XRD analyses. It has been confirmed as a crucial active metal in the adsorbent, which exhibits a positive effect on improving the performance of the adsorbent (Mao et al., 2016). Wang et al. (2020) demonstrated that chemical reactions occurred between the Fe elements $(Fe^{2+} and Fe^{3+})$ of biochar with the adsorbate. Therefore, the Fe species in SPA-O-1025 and SPA-N-1100 were further analyzed by XPS. As depicted in Fig. 3c and d, the peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ were detected, and the intensity of Fe $2p_{3/2}$ was much stronger than that of Fe $2p_{1/2}$ due to the spin-orbit (j-j) coupling of Fe $2p_{3/2}$ (Yamashita and Hayes, 2008). Many sub-peaks of Fe, indicating different valence states, were obtained by splitting and fitting the original peaks. When comparing the two adsorbents prepared from different atmospheres, the results showed that the satellite peak appeared at 718.8 eV for both adsorbents, while the positions of the other sub-peaks from Fe 2p_{3/2} were significantly different (Table 1). Three sub-peaks obtained from Fe 2p3/2 in SPA-O-1025 are located at positions 711.8, 711, and 710.0 eV (all represent Fe³⁺), respectively. For SPA-N-1100, four different sub-peaks were achieved, and two of them at 710.4 and 707.15 eV suggested that Fe²⁺ existed in SPA-N-1100. This may be due to the inert atmosphere during preparation (Li et al., 2019).

Table 1

The relative contents of peaks Fe 2p in SPA-O-1025 and SPA-N-1100 detected by XPS.

Position		SPA-O-1025	SPA-N-1100	Fe species	
Fe 2p1/2	724.6	29.3	39.46	Fe ³⁺	
Satellite	718.8	16.86	4.27	Fe ³⁺	
Fe 2p3/2	713.3	-	19.03	Fe ³⁺	
	711.8	7.45	30.31	Fe ³⁺	
	711.0	38.67	-	Fe ³⁺	
	710.4	-	6.44	Fe ²⁺	
	710.0	7.73		Fe ³⁺	
	707.15	-	0.49	Fe ²⁺	

3.2. Characterization of HMs

3.2.1. Total concentration of HMs

The EDS analysis revealed that various HMs, including Cr, Mn, Ni, Cu, Zn, Cd, and Pb, existed on the surface of the adsorbents. Hence, it was essential to determine the characteristics of HMs (i.e., their total concentrations and speciation distributions). The Cr, Mn, Ni, Cu, and Zn concentrations were high in the raw material, a mixture of SP and KL with a mass ratio of 8:2 (SP + KL (8:2)) (Table 2). Furthermore, the concentration of almost all HMs increased in SPA-O-1025 after sintering, indicating that the HMs were enriched during the sintering with air. However, the concentrations of Zn, Cd, and Pb decreased in SPA-N-1025 and further declined with a rise in sintering temperature to 1100 °C under the N₂ atmosphere (SPA-N-1100). This result suggested that the three HMs favored evaporation when heated under a N₂ atmosphere. Notably, the addition of KL in SP before sintering could mitigate the evaporation of all HMs because the concentration of HMs in SPA-N-1100 was much greater than in SPA-N-1100_{calc}.

3.2.2. Species evolution of HMs

The stability of HMs was further analyzed based on their speciation distributions from the BCR (Fig. 4 and Table S7). The fractions of Cr and Pd were almost 100% of F4 (residual fraction) in all samples. This indicated that the two HMs in all samples were quite stable and were difficult to migrate into the environment. A similar result was reported



Fig. 3. XRD analysis of SPA-O-1025 (a) and SPA-N-1100 (b), and Fe 2p XPS spectra of SPA-O-1025 (c) and SPA-N-1100 (d).

Table 2

Total heavy metals concentration (mg/kg) of samples prepared from different sintering temperature and atmospheres.

Items	Cr	Mn	Ni	Cu	Zn	Cd	Pb
SP + KL (8:2)	4444.02	3719.45	1032.18	6690.00	3225.87	0.46	13.27
SPA-O-1025	6954.47	6472.16	1595.11	6431.75	4453.29	0.60	34.65
SPA-N-1025	6920.19	6275.32	1529.01	6476.86	2987.12	0.31	16.33
SPA-N-1100	7542.32	6603.07	1695.73	6982.67	884.84	0.28	4.11
SPA-N-1100 _{calc}	6854.50	5595.10	1447.03	6858.97	576.31	0.17	0.40



Fig. 4. HMs speciation distributions of feedstock (SP + KL (8:2)), SPA-O-1025, SPA-N-1025, SPA-N-1100 and SPA-N-1100_{calc} (F1: Acid soluble/exchangeable fraction; F2: Reducible fraction; F3: Oxidizable fraction; F4: Residual fraction).

in our previous study for construction ceramsite production (J. Li et al., 2018c). The F4 of Mn, Zn, and Cd increased after sintering at 1025 °C with air and were further elevated with the N₂ as shielding gas instead of air. However, the F4 contents of Ni and Cu in SPA-N-1025 were lower than those in SPA-O-1025. Fortunately, the elevation of the sintering temperature with N₂ can further promote the F4 generation of Ni, Cu, and Mn. According to the area scan in EDS detection, the percentages of Ni and Cu on the surface of SPA-N-1100 were nearly three times higher than those of SPA-O-1025 (Table S6). This may explain the declination F4 of Ni and Cu in the SPA prepared under N₂. By comparing SPA-N-1100 and SPA-N-1100_{calc}, the KL addition in SP had a positive effect on the generation of F4 for Mn, Zn, and Cr. In general, the HMs in SP could be well immobilized after sintering at a high temperature (>1000 °C) with air as the shielding gas, and Mn, Zn, and Cd could be better immobilized in N₂.

Overall, the results demonstrated that the HMs in SPA-O-1025 and SPA-N-1100 were well immobilized. The mechanisms of HM immobilization can be speculated. XRD results showed that some HMs mainly combined with the other mineral elements to create new, stable, mineral phases (e.g., CuSiO₃2·H₂O, Mn₇O₈(SiO₄), and Al₂H₁₂O₁₅P₂Zn in SPA-O-1025). The above results indicated that the HMs tended to bond with Si, Al, and P during the sintering process. Although these mineral phases were not found in SPA-N-1100, the HMs may be trapped by the melting of normal minerals (SiO₂ and CaAl₂Si₂O₈). Mineral liquid generated at high temperatures probably swallowed the HM atoms and encapsulated them after cooling down. This is especially likely for the HMs with high vaporization points as the increase in temperature could promote the melting of mineral phases (J. Li et al., 2018c). This may explain why the F4 content of most HMs increased with sintering temperature. The encapsulation of HMs by the melting minerals is a typical mechanism of HM immobilization during high-temperature sintering. Better immobilization of Zn and Cd under N2 might be caused by a significant decrease in the total concentration of Zn and Cd under N2 due to their easier evaporation (Table 2).

3.2.3. Ecological risk of HMs

The ecological risk of HMs was evaluated based on the data of the

species fraction (supplementary materials). According to the potential ecological risk index (RI) in Table 3, the RI of the feedstock was 15.60, which significantly decreased in SPA-O-1025 (8.68) and SPA-N-1100 (7.82), while slightly reduction in SPA-N-1025 (15.33). The RI of SPA-N-1100 was lower than that of SPA-N-1100 calc, implying a positive effect of KL addition on ecological risk reduction. In detail, the highest risk HM in the feedstock was Cd due to its high Er (individual potential ecological index) and was still the highest in SPA-O-1025. Interestingly, the Er of Cr decreased to zero in SPA-N-1025 and SPA-N-1100 because of the reduction in total concentration (Table 2). The Er of Cu increased significantly compared to that of the feedstock and SPA-O-1025. In general, SPA preparation with KL under air or N2 at higher temperatures was beneficial for avoiding the ecological risk of HMs in SP. Compared to the ranks of ecological risk (Table S2) all the samples, especially the SPA-O-1025 and SPA-N-1100 exhibited ultralow ecological risk because their RI values were far lower than 50, indicating their safe application as adsorbents.

3.3. CIP adsorption on adsorbent

3.3.1. Effects of adsorption conditions

In terms of the impact of adsorbent dose on CIP adsorption, the *RE* of both adsorbents increased with increasing elevation and reached a plateau with a CIP *RE* of 97% (Fig. 5a and b). The CIP molecules could not be removed thoroughly by the adsorbents even with extreme amounts, due to the generation of the adsorption-desorption equilibrium. In addition, it was evident that the change in q_e of SPA-O-1025 and SPA-N-1100 exhibited an opposite trend to that of *RE*. It was reasonable that the mass of CIP absorbed on the catalyst was increasingly lower than the adsorbent mass, with a continuous increase in adsorbents mass, which in turn drastically reduced the q_e . Another important result was that the amount of SPA-O-1025 exceeded 25 g/L to ensure the adsorption of 97% of the CIP, which was five times higher than that of SPA-N-1100. This result suggested that SPA-N-1100 possessed a much higher CIP adsorption capacity than SPA-O-1025.

The effect of temperature on the CIP adsorption of SPA-N-1100 was more significant than that of SPA-O-1025. Both *RE* and q_e of SPA-O-1025

Table 3

Risk assessment code of heavy metal toxicity.

C_f	Cr	Mn	Ni	Cu	Zn	Cd	Pb	
SP + KL (8:2)	0.0022	1.1745	0.1132	0.7836	1.0264	0.2920	0.0067	
SPA-O-1025	0.0001	0.8006	0.0799	0.3085	0.1009	0.1919	0.0000	
SPA-N-1025	0.0001	0.5186	0.3066	2.5912	0.0102	0.0000	0.0000	
SPA-N-1100	0.0004	0.3136	0.0909	1.3815	0.0514	0.0000	0.0000	
SPA-N-1100 _{calc}	0.0021	0.6722	0.0586	1.2606	0.1519	0.0511	0.0000	
E_r	Cr	Mn	Ni	Cu	Zn	Cd	Pb	RI
SP + KL (8:2)	0.0044	1.1745	0.6790	3.9181	1.0264	8.7607	0.0333	15.5963
SPA-O-1025	0.0002	0.8006	0.4794	1.5426	0.1009	5.7575	0.0000	8.6812
SPA-N-1025	0.0003	0.5186	1.8396	12.9561	0.0102	0.0000	0.0000	15.3249
SPA-N-1100	0.0009	0.3136	0.5452	6.9075	0.0514	0.0000	0.0000	7.8187
SPA-N-1100 _{calc}	0.0042	0.6722	0.3514	6.3028	0.1519	1.5331	0.0000	9.0156



Fig. 5. Impacts of adsorbent amount (a and b), temperature I and pH (d) value of solution on CIP removal by SPA-O-1025 and SPA-N-1100 (CIP solution concentration: 10 mg/L; adsorption time: 24 h; solution pH in a, b, and c: 6.75; solution temperature in a, b, and d: 30 °C; adsorbent amount in c and d: 10 g/L for SPA-O-1025 and 5 g/L for SPA-N-1100).

showed a similar trend, with a slight initial increase and then a decrease as the solution temperature rose from 25 to 50 °C. The highest RE of SPA-O-1025 was obtained at 35 °C, while the RE of SPA-N-1100 continued to increase until 45 °C (Fig. 5c). Solution temperature is relevant to the thermal motion of molecules and the adsorption intensity on the adsorbents. A higher solution temperature enhanced the diffusion of CIP molecules to the internal pores of the adsorbents (Ghasemi and Asadpour, 2007), while excessive temperature would cause an escape of CIP molecules from the surface, owing to the faster thermal motion (Gupta et al., 2011). In this case, a higher temperature is preferred to achieve a better adsorption performance for SPA-N-1100 compared to SPA-O-1025. This result suggested that more CIP molecules could diffuse to the pore and the surface of the adsorbent, leading to a higher probability of CIP being captured by the adsorption sites. The higher temperature may also activate some new adsorption sites on the solid surface of SPA-N-1100 (Di Natale et al., 2015). The adsorption of CIP molecule on the surface of SPA-N-1100 was much stronger compared to SPA-O-1025, as a higher temperature led to a decrease of adsorption

capacity of SPA-O-1025 (Fig. 4c). The escape of CIP may occur on the surface of SPA-O-1025, but not on the SPA-N-1100 with the increase of the entropy of CIP action under a higher temperature.

The pH value of the CIP solution was another crucial factor that was significantly related to the adsorption performance (Fig. 5d). The *RE* and q_e of SPA-N-1100 increased with a rise in the pH of the CIP solution, and decreased when the pH was greater than 9.0. Previous studies have reported that the forms of CIP[±] and CIP⁰ (zwitterion) existed between pH values of 6.1 and 8.7 (Peng et al., 2015). Based on the form of CIP and the adsorption performance of SPA-N-1100 at different pH values, it can be inferred that the surface of SPA-N-1100 preferred to adsorb zwitterions of the CIP. When pH > 9.0, CIP⁻ was generated based on its intrinsic characteristics (Peng et al., 2015), and this led to a decrease of adsorption performance. This indicated that the surface of the adsorbents might be negatively charged with a pH over 9.0 because the same charge with CIP does not benefit adsorption due to the repulsive interaction between them (Li et al., 2011). For CIP adsorption onto SPA-O-1025, the *RE* and q_e tendencies were wavelike and slightly

increased with the increase in pH, implying a weakly charged surface with few active sites on the SPA-O-1025. This might be another explanation for the weak adsorption performance for CIP removal.

3.3.2. Kinetic studies of CIP adsorption

The impact of contact time on the CIP removal and kinetic studies with Pseudo-first order and Pseudo-second order models are depicted in Fig. 6a–b. The concentration of CIP in the solution decreased with increasing adsorption time. The time to the adsorption equilibrium of SPA-O-1025 was about 5 h, which was far shorter than SPA-N-1100 (12 h) (Fig. 6a). At the status of adsorption equilibrium, the adsorption capacity of SPA-N-1100 exceeded 1.0 mg/g, which was much greater than that (0.6 mg/g) of SPA-O-1025.

Based on the kinetic studies of CIP adsorption by the two adsorbents, both kinetic models fit the adsorption data well, with their R^2 values above 0.90. Furthermore, the adsorption processes of CIP by both adsorbents were more aligned with the Pseudo-second order model, owing to its higher R^2 value (0.97 and 0.98) and the accuracy of q_e calculation. According to the theory of the Pseudo-second order model, the adsorption ability was determined by the amount of free active sites on the surfaces of SPA-O-1025 and SPA-N-1100 (Li et al., 2015). Another insight could be obtained from the model, whereby the constant adsorption rate (k_2) of SPA-O-1025 was twice as high as that of SPA-N-1100, indicating a faster adsorption process on SPA-O-1025 (Ahmad et al., 2012). However, compared with values from literature, the k_2 (1.66) of SPA-N-1100 was competitive as the reported k_2 of sludge biochar, rectorite, and illite for CIP adsorption was 0.67, 0.2, and 0.3, respectively (Li et al., 2020; Wang et al., 2011). Combined with the textural properties of adsorbents, this study revealed that the pore size of adsorbents was not a significant factor leading to the difference of kinetic constant in both adsorbents as the main pores in both adsorbents were mesoporous. However, the higher surface area and pore volume might require more time to obtain an adsorption equilibrium as more adsorption sites exist, therefore it led to a smaller kinetic constant for SPA-N-1100.

3.3.3. Adsorption isotherm studies of CIP adsorption

Both the capacities at equilibrium (q_e) of SPA-O-1025 and SPA-N-1100 increased with an increase in the initial concentration of CIP, while the q_e of SPA-N-1100 increased more rapidly (Fig. 6c). The removal efficiency (*RE*) of SPA-N-1100 was much higher than that of SPA-O-1025. The highest *RE* of SPA-N-1100 was 95%, which was achieved at the initial CIP concentration of 10 mg/L. Furthermore, the increase in CIP concentration enhanced the concentration gradient, which was able to push the CIP molecules to occupy the unapproachable active sites on the surface of the adsorbents (Srivastava et al., 2006). Moreover, the *RE* values of both adsorbents drastically increased at first and then dropped with the increase in CIP concentration. The peak reached for the *RE* might be due to the sufficient number of active sites that the CIP molecules could reach when the CIP concentration was low, while the increasing CIP concentration resulted in insufficient active sites to trap all the molecules (Yang et al., 2010).

The adsorption isotherm of CIP adsorption was investigated based on the change in q_e with increasing CIP concentration at equilibrium (C_e) using the Langmuir and Freundlich models (Fig. 6d). The adsorption data (qe vs. Ce) of SPA-O-1025 and SPA-N-1100 were fit well by both models, with R^2 values greater than 0.96. In detail, the R^2 values from the Langmuir model were 0.98 and 0.99 for the CIP adsorbed on the SPA-O-1025 and SPA-N-1100, respectively. The maximum adsorption capacity (q_{max}) of SPA-N-1100 from the Langmuir model was 10.42 mg/ g, which was ten times higher than that of SPA-O-1025, and it was competitive among other similar studies (Table 4). Conversely, the R^2 of the Freundlich model's line of best fit was also high enough to obtain valuable insights. A higher K_F in SPA-N-1100 from the Freundlich model represents a higher adsorption capacity (Haghseresht and Lu, 1998). This might be corelated to its higher surface area, unique surface species, and a greater number of active sites, compared to SPA-O-1025. Moreover, SPA-N-1100 showed a high degree of surface heterogeneity, and the CIP adsorption intensity on its surface was stronger than that of SPA-O-1025 based on the value of *n* in the Freundlich model. This is an indicator of surface heterogeneity and adsorption intensity (Foo and Hameed, 2010; Haghseresht and Lu, 1998).



Fig. 6. Contact time impact (a), kinetic studies (b), initial concentration impact (c), and adsorption isotherm studies (b) for CIP adsorption by SPA-O-1025 and SPA-N-1100 (Adsorbent amount: 10 g/L; CIP solution concentration: 10 mg/L in a and b; solution pH: 6.75; solution temperature: 30 °C; adsorption time: 24 h in c and d).

Table 4

Literature summary for the maximum adsorption capacity of CIP by various adsorbents.

Adsorbents	Maximum adsorption capacity (mg/g)	R ² of Langmuir	Reference
Nonporous SiO ₂ Nonporous Al ₂ O ₃ Illite	2.17 18.72 33.13	0.96 0.92 -	Goyne et al. (2005) Wang et al. (2011)
Potato waste biochar	8.48	0.94	(R. Li et al., 2018)
Goethite	33.13	-	Zhang and Huang (2007)
Kaolinite	6.29	0.99	Li et al. (2011)
Water hyacinth biochar	2.72	0.99	Ngeno et al. (2016)
Hydrous aluminous oxides	13.59	0.98	Gu and Karthikeyan (2005)
Ferrihydrite and humic acid/ferrihydrite composite	35.12	0.84	Urdiales et al. (2020)
Pyrochar based adsorbent	10.42	0.99	This work

3.3.4. Thermal desorption for adsorbent regeneration

Thermogravimetry analysis was employed to determine the temperature for thermal desorption with a thorough CIP decomposition based on the decomposition characteristics of CIP. The TG and DTG curves are shown in Fig. 7a. When the temperature elevated to approximately 300 °C, the CIP molecules began to decompose and tended to complete the process when the temperature reached 470 °C. According to the DTG curve, two weightlessness peaks were generated at temperatures of 324 °C and 424 °C during the decomposition process. This result indicates that the main decomposition temperatures of the CIP molecules ranged from 324 to 424 °C. Therefore, 450 °C was identified as the thermal desorption temperature for regenerating the used adsorbents to guarantee the thorough CIP decomposition.

The adsorbents after CIP adsorption could be separated from the liquid directly by using a tweezer, with little weight loss. This process did not require any other operations due to the high strength of the adsorbents and nubbly structure. CIP adsorption validation was conducted to evaluate the regeneration ability of the recycled adsorbent. As seen in Fig. 7b, the concentration of CIP in the solution decreased sharply at the beginning of the adsorption process with the attendance of regenerated adsorbents, and it then plateaued after approximately 8 h. The q_e of regenerated SPA-O-1025 was as good as the fresh one, and the q_e of SPA-N-1100 slightly decreased while its *RE* was greater than 80%. Mao et al. (2016) regenerated magnetic carbon using NaOH and methanol, and the *RE* CIP of regenerated magnetic carbon declined by

approximately 10%. Wang et al. (2016) regenerated the used nanocomposite by methanol, and 92% of the adsorption ability remained. In summary, thermal desorption offers a feasible way to realize the desorption of SPA-O-1025 and SPA-N-1100, and the regenerated adsorbents still exhibited a good ability for CIP removal, which was beneficial for cyclic resource utilization.

3.3.5. Proposed adsorption mechanism

The above results revealed that the adsorption performance of SPA-N-1100 was much greater than SPA-O-1025. This was mainly due to their significantly different properties, including microtopography, microstructure, chemical composition, and active species on their surfaces. The ball-accumulated structure with higher BET surface area and prove volume, as well as the carbon and Fe^{2+} in the SPA-N-1100 were the main reasons for its higher adsorption performance based on our characterization. Furthermore, the microsphere stacking structure with the reductive species of SPA-N-1100 from the foaming and N₂ sintering processes dominated the CIP adsorption, as depicted in Fig. 8. Based on the XRD analysis, SiO₂ Fe₂O₃, CaAl₂Si₂O₈, and Fe₂P were the main components of SPA-N-1100. These components likely interacted with CIP molecules, especially for zwitterions of CIP (Fig. 7d). The protonated N4 in the piperazinyl group in CIP would be attracted by SiO₂ via a cation bridge that was possibly generated from the metal elements (K, Mg etc.) on the surface of SPA-N-1100 (Table 2) (Goyne et al., 2005; Li et al., 2011). In addition, a weak electrostatic interaction might occur between protonated N4 in the piperazinyl group and the SiO₂ (Goyne et al., 2005). For the metal oxide compositions, the complexation reaction or ligand exchange probably existed between the ketone, or carboxylate functional groups of zwitterions, CIP, and Fe₂O₃ or CaAl₂. Si₂O₈ (Li et al., 2011; Wang et al., 2011; Zhang and Huang, 2007). The O atom in the carboxylic group in the zwitterions of CIP has been reported with a stronger ligand to coordinate with Fe³⁺ (Zhang and Huang, 2007). The reductive Fe₂P was a unique composition in SPA-N-1100 and crucial for CIP adsorption. Many active sites existed because of the reduction state of Fe, which favored the attraction of CIP through intensive electrostatic attraction and complexation (Yanli et al., 2017). Moreover, C was detected on the surface of SPA-N-1100, implying the existence of graphite after sintering at a high temperature. The π - π interaction was triggered by the encounter of graphite and aromatic groups of CIP molecules. Prior studies have demonstrated that graphite combines with aromatic organic molecules via π - π stacking interactions (Zhang et al., 2007; Zhu et al., 2011).

4. Conclusions

Easy recycling and safe adsorbents with CIP adsorption capacities were successfully prepared from sludge-based pyrochar at 1025 and 1100 $^\circ\text{C}$, under air and N_2 based on systematical optimization. SPA-N-



Fig. 7. TG and DTG curves of CIP (a) and CIP adsorption (b) of regenerated adsorbents (TG: thermogravimetry; DTG, derivative of thermogravimetry. Adsorption conditions: adsorbent amount: 10 g/L; CIP solution concentration: 10 mg/L; solution pH: 6.75; solution temperature: 30 °C).



Fig. 8. Possible CIP adsorption mechanism of SPA-N-1100.

1100 possessed a maximum CIP adsorption capacity of 10.42 mg/g which was much higher than that of SPA-O-1025 (1.80 mg/g). The Freundlich model suggested that SPA-N-1100 had a higher degree of surface heterogeneity and CIP adsorption intensity than SPA-O-1025. The Pseudo-second-order model fitted the adsorption processes of CIP by both adsorbents well, with an R^2 as high as 0.97 and 0.98, indicating that the adsorption ability was determined by the amount of free active sites on their surface. The CIP molecules preferred to be captured by SPA-N-1100 at a higher adsorption temperature (45 °C) and pH value (8–9). The used adsorbents could be regenerated at 450 °C with a thorough decomposition of CIP. The cation bridge, complexation reaction, electrostatic attraction, and π – π stocking are the possible adsorption mechanisms of SPA-N-1100. Moreover, the HMs in the adsorbents were well immobilized with an ultralow potential ecological risk, indicating the safe application of the adsorbents.

Author contributions

Jie Li, Conceptualization, Methodology, Data curation, Investigation, Writing - original draft, Visualization. Lanjia Pan, Investigation, Data curation, Formal analysis, Writing - review & editing. Guangwei Yu, Supervision, Project administration, Funding acquisition, Resources, Writing - review & editing. Chunxing Li, Writing - review & editing. Shengyu Xie, Writing - review & editing. Yin Wang, Funding acquisition; Resources, Writing - review & editing.

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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2020.110258.

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