

Original Research

Sorption Behaviors and Mechanisms of Cadmium on Polypropylene, Bamboo Biochar, and Rice Husk Ash in Aqueous Solutions

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Abstract

This study investigated the adsorption behavior and mechanisms of cadmium ions (Cd^{2+}) from aqueous solutions on virgin polypropylene (PP_0), 1-to-3-week aged polypropylene (PP_1 , PP_2 , and PP_3), bamboo biochar (BBC), and rice husk ash (RHA). Adsorption kinetic and isotherm experiments were conducted to evaluate the performance of each material. Fourier-transform infrared spectroscopy and Brunauer–Emmett–Teller analyses revealed the presence of hydroxyl and carboxyl functional groups and microporous structures, respectively, on the adsorbent surfaces. The pH of the point of zero charge analysis indicated that the surfaces of PP_0 – PP_3 carried net negative charges at a pH solution of 7.0 ± 0.1 , whereas BBC and RHA exhibited net positive surface charges under the same conditions. The adsorption kinetics of Cd by PP_0 , PP_1 , PP_2 , PP_3 , and BBC followed the pseudo-second-order model ($R^2 = 0.951, 0.963, 0.997, 0.996$, and 0.999 , respectively), suggesting chemical adsorption as the dominant mechanism. In contrast, the adsorption by RHA was best described by the pseudo-first-order model ($R^2 = 0.990$), indicating a physical adsorption process. Isotherm analysis showed that the Freundlich model provided the best fit for PP_0 – PP_3 , indicating multilayer adsorption on the surfaces. For RHA, the Langmuir model was more suitable, with a maximum adsorption capacity of $815.02 \mu\text{g/g}$, implying monolayer adsorption on the surface. Overall, BBC and RHA demonstrated significantly higher cadmium adsorption capacities compared to PP_0 – PP_3 , likely due to their much greater surface areas, 42 to 56 times higher than that of the PP. Importantly, this study presents a comparative framework evaluating the sorption behavior of aged polypropylene microplastics in relation to biomass-based adsorbents, focusing on surface transformations during environmental aging and their interactions with heavy metals. These findings confirm the performance of agricultural waste-derived adsorbents and the emerging

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environmental risks posed by co-contamination from aged microplastics and heavy metals in aquatic systems.

Keywords: bamboo biochar, cadmium adsorption, microplastics, polypropylene, rice husk ash

Introduction

Cadmium (Cd^{2+}) is a highly toxic, non-biodegradable heavy metal, considered among the most hazardous due to its persistence in ecosystems and severe environmental and health risks [1]. Exposure to Cd^{2+} can lead to severe health problems such as kidney damage, bone fractures, and cancer [2]. Its contamination in water is a critical concern, as Cd^{2+} can be entered through various anthropogenic activities, including mining, industrial operations, and improper waste disposal. The contamination of Cd^{2+} has been reported in the Chao Phraya River Mouth Water, Thailand, with concentrations ranging from 0.029 to 0.193 $\mu\text{g/L}$ [3]. These concentrations of Cd^{2+} should not exceed 5 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$ at water hardness levels of <100 mg/L and >100 mg/L as CaCO_3 , respectively [4]. In addition, Cd^{2+} has been reported to accumulate in microplastics found in river sediments of the Beijiang River littoral, China, at concentrations of 2.1-17.6 $\mu\text{g/g}$ [5]. These findings highlight the widespread nature of cadmium pollution and provide important evidence that metals can interact with microplastics in the environment.

Microplastics are plastic debris waste with particle sizes smaller than 5 mm and are considered the most abundant in populated coastal and marine ecosystems [6]. They have been found in various environments, ranging from freshwater to seawater. In 2018, their global abundance in oceans was estimated at 268,940 tons, equivalent to about 5.25 trillion particles [7]. The quantity continues to rise alarmingly each year. They can pass through the wastewater treatment process, enter aquatic environments, and thus affect ecosystems [8]. Their relatively lower density than water allows them to float on the surface water or remain suspended in the water column. In addition, microplastics can release toxic additives or concentrate additional toxic chemicals in the environment, such as bacteria or microbial communities, persistent organic pollutants, carcinogens, endocrine-disrupting chemicals, and heavy metals [9-12]. This is due to the large specific surface area and strong hydrophobicity, which can ultimately affect the organisms in the food chain [13].

Recent *in situ* investigations confirmed the interactions between the microplastics and heavy metals in the aquatic environment. The microplastics were found to contain metals such as Pb, Cd, Cu, Cr, Mn, Hg, Ni, and Zn along the coastline in many localities in different parts of the world [14-15]. Moreover, in Thailand, it is found that Cd^{2+} was accumulated on microplastics in the Chao Phraya River, with a concentration of $2.81 \pm 2.05 \mu\text{g/g}$ [16]. This study affirmed that

the microplastics could transfer heavy metal pollution from one location to another [17], and thus these co-pollutants can be transported through the food chain to humans [18]. Therefore, the implementation of heavy metal treatment in polluted water containing microplastics in the environment is of importance. There are various technologies used to treat heavy metals, such as dissolved air flotation, membrane filtration, coagulation, and ultrafiltration. However, these techniques often have high operating costs. Adsorption, on the other hand, is a low-cost wastewater technology that has been widely applied for heavy metal removal from polluted water [19]. In Thailand, bamboo biochar (BBC) and rice husk ash (RHA), by-products of agricultural and biomass power plants, have emerged as promising adsorbents due to their porous structures, abundance, and low cost [20]. The present study aimed to explore the sorption mechanisms and adsorption capacities of cadmium on polypropylene (PP) microplastics, BBC, and RHA in aqueous solutions and possible transport behaviors of Cd^{2+} in the aquatic environment.

Materials and Methods

Polypropylene (PP) particles from Merck Limited, Klongtoey, Bangkok (Thailand) were used in this study. The particles were sieved using U.S. mesh standard sieve numbers 50, 270 to obtain a particle size range of 0.05-0.30 mm [16]. To remove metal contaminants on the PP surface, the particles were rinsed with 0.1 M HCl, followed by washing with tap water and then distilled water. Virgin polypropylene particles were subsequently aged for 0, 1, 2, and 3 weeks, and denoted as PP_0 , PP_1 , PP_2 , and PP_3 , respectively. The aging process was conducted at $30 \pm 2^\circ\text{C}$ to simulate the mechanical action of water flow. Ultraviolet A (UVA) lamps ($4 \times 18 \text{ W}$, with a wavelength range of 320-360 nm and a peak wavelength of 340 nm) were used to simulate sunlight UV irradiation. A shaker was operated at 200 rpm and $30 \pm 2^\circ\text{C}$ to mimic river currents. The aging experiments were performed under a 12/12 h light/dark photoperiod. After aging, all samples were rinsed with deionized water (DI), dried in an oven at 60°C for 24 h, and stored in desiccators for further use.

Bamboo biochar (BBC) used in this study was produced in a Japanese kiln (Iwate kiln) at $1,000^\circ\text{C}$ for 15 days from Bamboo D88, Nonthaburi (Thailand). Rice husk ash (RHA), a by-product obtained from a biomass power plant from Mungcharoen Green Power Co., Ltd., Surin (Thailand), was also used in this study. The power plant operates with high-pressure steam

at 65 bar and a combustion temperature of 480°C. Both BBC and RHA were sieved to obtain particle sizes from 0.25 to 1.0 mm using U.S. standard mesh sieve numbers 18 and 60. The samples were washed with DI until the pH value was equal to 7, dried at 60°C for 24 h in a hot air oven, and stored in desiccators for further use.

A solution of Cd^{2+} was prepared using cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) of analytical grade from SD Fine-Chemical Limited (India). A stock solution with a concentration of 100 mg/L Cd^{2+} was obtained by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in DI. Working solutions of Cd^{2+} with concentrations ranging from 1 to 10 mg/L were prepared by serial dilution of the stock solution with DI.

Characterization of BBC, RHA, and PP

The surface morphologies of BBC, RHA, and PP were analyzed using a scanning electron microscope and energy dispersive spectroscopy (SEM-EDS, Phenom ProX, Thermo Fisher Scientific, US). The surface area, pore volume and pore diameter were measured using the Brunauer–Emmett–Teller (BET, Autosorb iQ-C-AG, Quantachrome Instrument, USA). The elemental compositions were determined using an X-ray fluorescence spectrometer (XRF, XUV 773, Fischer, Germany). The surface functional groups were characterized using Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific, USA). The physicochemical properties of the samples were evaluated to establish correlations between these properties and to elucidate the possible sorption mechanisms between the adsorbents and adsorbates.

The pH of the point of zero charge (pH_{PZC}) of PP virgin (PP_0), 1-week aged PP (PP_1), 2-week aged PP (PP_2), 3-week aged PP (PP_3), BBC, and RHA was determined to investigate possible ion exchange properties of the adsorbents, which typically depend on the net surface charge. The method used for measuring the pH_{PZC} was the solid addition method by using 45 mL of 0.1 M KNO_3 , and adjusting the pH values of each solution to 2.0–12.0 by using 0.1 N HNO_3 and 0.1 N NaOH , and adjusting the solution volume to 50 mL. Next, 1 g of each sample was added to separate containers. The solutions were agitated at 120 rpm in an incubator shaker for 48 h, and the final pH values of all samples were measured after 48 h. The initial pH on the x-axis versus the final pH on the y-axis was plotted to obtain the pH_{PZC} of each adsorbent. The intersecting point between these two lines is the pH_{PZC} [21, 22].

Adsorption Kinetics and Isotherms

The adsorption kinetics of Cd^{2+} onto PP_0 , PP_1 , PP_2 , PP_3 , BBC, and RHA were performed in volumetric flasks. A 100 mg/L Cd^{2+} solution was diluted to a 1 mg/L stock solution. The total volume of each solution was 1000 mL. For the adsorption kinetic experiments, an initial Cd^{2+} concentration of 1 mg/L

in 1000 mL solution was mixed with an adsorbent dosage of 4 g/L. The sorption experiments were operated at an agitation rate of 150 rpm at $30 \pm 2^\circ\text{C}$ and an initial pH of 7.0 ± 0.1 . The experiments were performed in duplicate. After the sorption kinetics, the samples were collected at 0, 5, 15, 30, 60, 120, 240, 480, 1140, 1440, and 2880 min, and filtered with 0.2 μm cellulose acetate syringe filters. Adsorption isotherms were studied using Cd^{2+} solutions with initial concentrations ranging from 1 to 10 mg/L, each placed in a 50-mL bottle with 0.2 g of adsorbent added. The equilibrium time obtained from adsorption kinetics was used for adsorption isotherm studies. The oscillator speed was set to 150 rpm at $30 \pm 2^\circ\text{C}$ and an initial pH of 5.0. The Cd^{2+} concentrations were analyzed with atomic absorption spectroscopy (AAS) (AA-6300, Shimadzu Corporation, Japan).

Data Analysis

The adsorption kinetics of Cd^{2+} were fitted using the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models, while the Langmuir and the Freundlich isotherm models were applied to fit the adsorption isotherm data. The corresponding model equations are shown in equations 1–4 [23]. These models were used to describe the adsorption mechanisms of cadmium onto PP_0 , PP_1 , PP_2 , PP_3 , BBC, and RHA.

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (1)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (2)$$

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \left(\frac{1}{Q_m K_L} \right) \frac{1}{C_e} \quad (3)$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Results and Discussion

Material Characterization

Fig. 1(a, b) shows SEM images of the morphology of PP_0 and PP_3 . The results indicate predominantly irregular surface morphologies. Their surface after magnification was rough and bumpy. A more irregular surface is generally associated with higher adsorption capacity [24]. Fig. 1(c, d) reveals pore sizes ranging from micropores to mesopores in BBC and RHA, with a honeycomb-like morphology and cylindrically shaped pores [25]. This structure suggests their potential application as absorbent materials. Table 1 presents the physical and chemical properties of PP_0 , BBC, and RHA. PP_0 and BBC showed high C content with relatively low Au and Si contents, whereas RHA exhibited

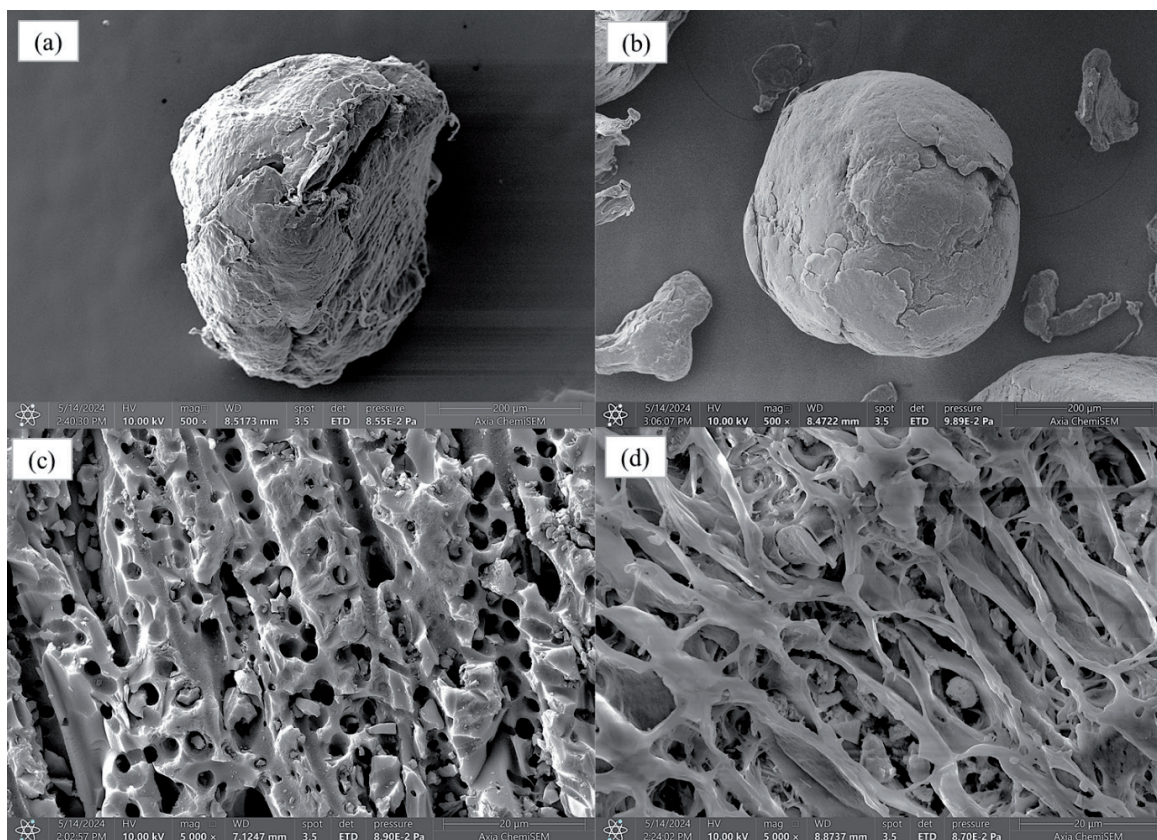


Fig. 1. SEM-EDS analysis of a) PP virgin, b) 3-week aged PP, c) BBC, and d) RHA.

a high Si content, appearing as mineral agglomerates on the fibers, along with a lower C content that reflects the structural characteristics typical of its biomass origin. In general, the presence of C, K, Mg, and Al is commonly observed in both biochar and microplastic [26, 27]. BET analysis revealed differences among PP₀, BBC, and RHA. PP₀ exhibited the lowest surface area (2.422 m²/g), negligible pore volume of 0.0005 cm³/g, and a microporous structure (0.7848 nm), indicating a limited ability to provide active sites for Cd²⁺ sorption. In contrast, BBC demonstrated the highest surface area (136.016 m²/g) and pore volume (0.0387 cm³/g), with a mesoporous structure (3.0105 nm), suggesting strong potential for ion diffusion and adsorption. RHA also exhibited a relatively high surface area (103.051 m²/g), with an average pore diameter of 2.7369 nm, reflecting its silica-rich and porous nature. Pore-size

distribution analysis revealed that both BBC and RHA are predominantly mesoporous (2-50 nm), while PP is largely microporous (<2 nm) [28]. These findings suggest that BBC, RHA, and PP can be considered effective adsorbents for pollutants, with BBC showing the highest performance [29].

XRF analysis revealed that PP₀ primarily contained P₂O₅ (10.7%) and Fe₂O₃ (10.6%), suggesting a considerable contribution of phosphate and iron-based mineral phases to the surface chemistry of the material. The high concentration of P₂O₅ implies that phosphate functionalities provide negatively charged site groups. These groups act as strong ligands capable of complexing with divalent and trivalent metal cations (Cd²⁺, Pb²⁺, Fe³⁺) via inner-sphere complexation mechanisms [30]. Moreover, Fe-oxide surfaces carry amphoteric Fe-OH group exhibit pH dependent charges

Table 1. Physical and chemical properties of PP₀, BBC, and RHA.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)	Elemental composition (% w/w)						
				C	Si	Au	O	K	Mg	Al
PP ₀	2.422	0.0005	0.7848	98.4	0.1	1.5	ND	ND	ND	ND
BBC	136.016	0.0387	3.0105	99.3	0.2	0.5	ND	ND	ND	ND
RHA	103.051	0.0373	2.7369	7.1	36.6	ND	53.6	4.4	0.3	0.3

ND: not detected

(PZC typically near neutral), enabling them to either attract Cd^{2+} electrostatically (as $\text{Fe}-\text{O}^-$ above the PZC) or competition with co-adsorbing anions [31], while BBC was dominated by K_2O (67.7%) along with CaO (8.33%), Na_2O (5.40%) and MgO (2.42%). This alkali (K, Na) and alkaline earth metals (Ca, Mg) tend to release positively charged cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) upon hydration, which can associate with surface oxygen-containing groups and shift the surface charge toward positive [32] and RHA by SiO_2 (83.5%) which would usually suggest a negative surface charge due to the presence of deprotonated silanol groups. However, the presence of K_2O (5.44%), CaO (3.46%), and MgO (0.86%), although at lower concentrations than in BBC, can still contribute positively charged species that may neutralize or overcome the negative charges from $\text{Si}-\text{OH}$, particularly in acidic to neutral pH conditions [33]. The presence of these chemical components is likely to influence the sorption of Cd^{2+} onto the adsorbents through surface chemical interactions.

The adsorption behavior is influenced by the chemical reactivity of the surface, especially in the form of chemisorbed oxygen in various forms of functional groups. FTIR shows results as Fig. 2, several peaks had disappeared at $3600\text{--}3200\text{ cm}^{-1}$ (O–H stretching vibrations of hydrogen-bonded hydroxyl groups and water). The peak at 3415 cm^{-1} was attributed to the presence of the O–H functional group (alcoholic and phenolic) and water. The surface complexation adsorption is great for $-\text{COOH}$ and $-\text{OH}$ functional groups, such as those in alcohols, phenols, or carboxyl. These groups are active sites for surface complexation with cations as Cd^{2+} [34]. However, RHA has the peak of Si–O–Si stretching at 1093.97 cm^{-1} , consistent with its high SiO_2 content. This may also affect the sorption mechanism by providing reactive oxygen-

containing sites [35]. These play a guiding role in the adsorption mechanism of Cd^{2+} by biochar in surface water [36].

The pH_{PZC} values obtained for PP_0 (6.4), PP_1 (5.2), PP_2 (4.9), PP_3 (4.7), BBC (8.0), and RHA (9.7). Given that the pH of the solution applied in this study was approximately 7.0 ± 0.1 , the surfaces of all adsorbents would be negatively charged, promoting electrostatic attraction toward cations such as Cd^{2+} . PP_0 and PP_1 , with pH_{PZC} slightly below the solution pH, likely generate moderate negative surface charges; PP_2 and PP_3 , with even lower pH_{PZC} values, would exhibit stronger negative charge, thus potentially enhancing their cation adsorption efficacy. The BBC and RHA have relatively high pH_{PZC} values, which might indicate that their surfaces would be positively charged at neutral pH. However, their surfaces often contain abundant oxygen-containing functional groups that can deprotonate and generate negative surface charges even below the pH_{PZC} [31]. This surface chemistry enables Cd^{2+} adsorption via surface complexation and ion exchange, which can override the purely electrostatic behavior predicted from pH_{PZC} alone. The relatively high pH_{PZC} values of BBC and RHA are attributed to their alkaline mineral composition, notably K_2O , CaO , and MgO , which contributes to basic surface sites [33].

Characterization confirmed the role of physicochemical properties in adsorption. SEM-EDS showed surface roughness and morphological changes, BET revealed differences in surface area and porosity linked to adsorption capacity, XRF identified residual minerals influencing surface charge, and FTIR detected oxygen-containing functional groups as active Cd^{2+} binding sites. Together, these analyses establish the mechanistic link between surface chemistry, porosity, and sorption performance [32].

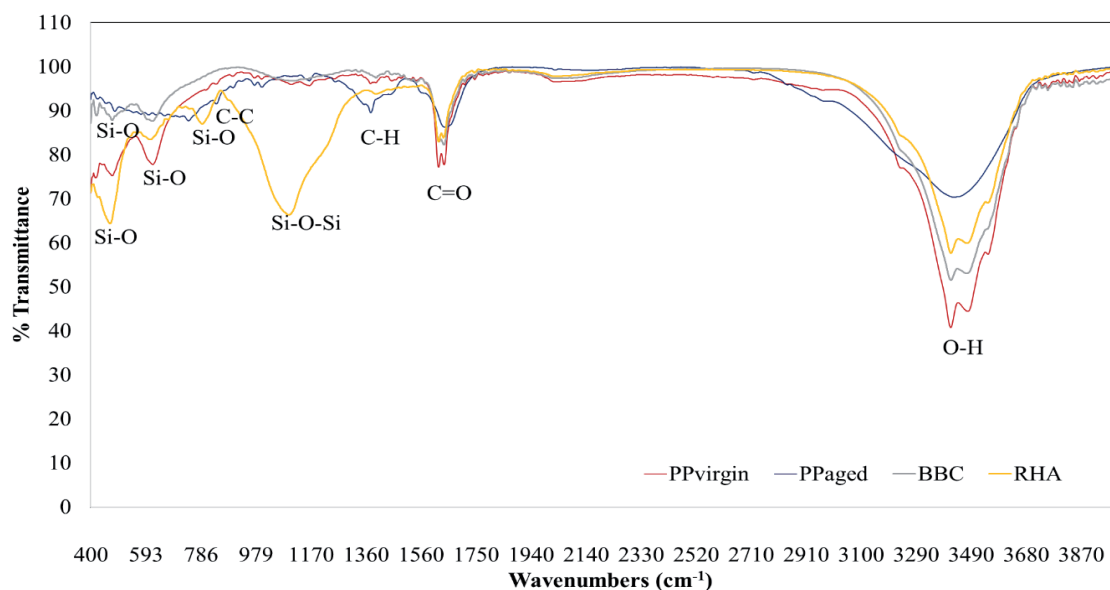


Fig. 2. FTIR analysis of virgin PP, 3-week aged PP, BBC, and RHA.

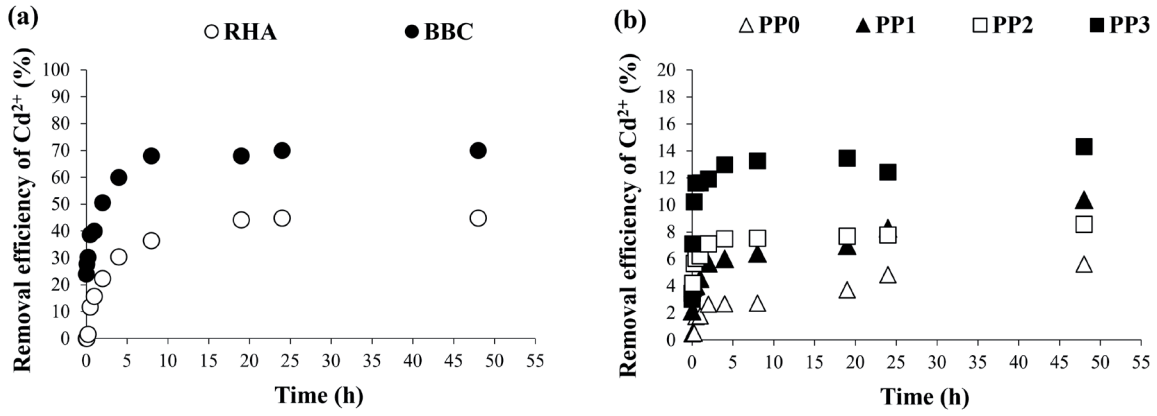


Fig. 3. Effect of contact time on the removal efficiencies of Cd²⁺ by a) BBC and RHA, and by b) PP₀-PP₃.

Adsorption Kinetics

The adsorption kinetics are performed to investigate the effect of contact time on the sorption capacity of Cd²⁺ onto the PP₀-PP₃, BBC, and RHA. The results are presented in Fig. 3. PP₀-PP₃ reached the equilibrium time at a similar period around 1140 min, and PP₃ had the highest removal efficiency for Cd²⁺. The aging of PP affected its ability to adsorb more Cd²⁺, with longer aging times resulting in higher Cd²⁺ binding capacity. The increased Cd²⁺ adsorption on PP aged can be attributed to the surface oxidation that occurs during the aging process. The oxygen-containing functional

groups that are produced provide sorption sites and thus enhance the adsorption capacity of metal ions [37]. The BBC and RHA reached equilibrium times at a similar time, around 1140 min, and the BBC had a higher removal efficiency for Cd²⁺ than RHA. This can be due to the smaller surface area and pore volume of BBC than RHA, which can attract more cations to adsorb on the surface.

Sorption model fitting by PFO and PSO is shown in Fig. 4 and Fig. 5, respectively. The adsorption kinetics are summarized in Table 2. The R² value could reflect the goodness of fit of each model. The R² values for PP₀-PP₃, BBC, and RHA using the PFO model were

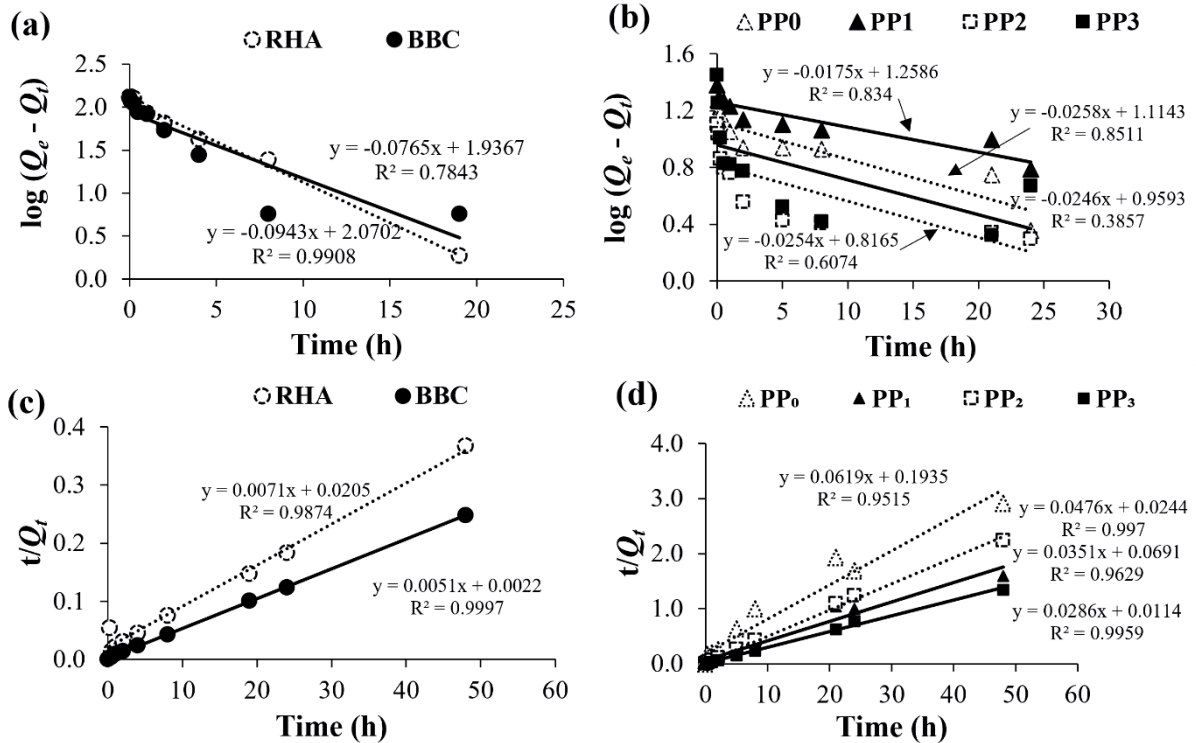


Fig. 4. Linear fittings of PFO kinetics for a) BBC and RHA and for b) PP (PP₀-PP₃), and PSO kinetics for c) BBC and RHA and for d) PP (PP₀-PP₃).

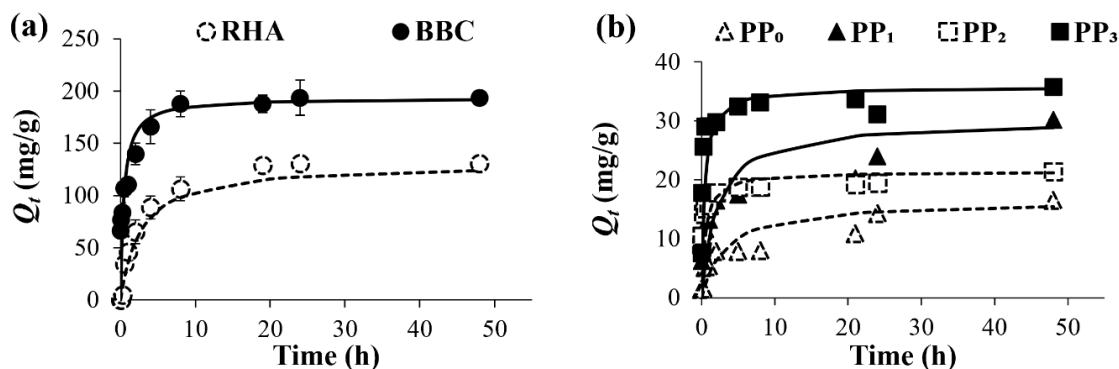


Fig. 5. Non-linear PSO model fittings for a) BBC and RHA, and for b) virgin PP (PP₀) and aged PP (PP₁-PP₃).

Table 2. Adsorption kinetic constants of PFO and PSO models, and adsorption isotherm constants of Langmuir and Freundlich models.

Sample	Kinetic models						Isotherm models					
	PFO			PSO			Langmuir			Freundlich		
	K_1 (1/min)	Q_e (mg/g)	R^2	K_2 (g/mg min)	Q_e (mg/g)	R^2	K_L (1/min)	Q_m (mg/g)	R^2	K_F (g/mg min)	n (mg/g)	R^2
PP ₀	0.059	13.01	0.851	0.019	16.16	0.951	0.267	345.26	0.972	67.639	1.51	0.987
PP ₁	0.040	18.14	0.834	0.016	28.50	0.963	0.237	400.99	0.974	71.276	1.44	0.987
PP ₂	0.059	6.55	0.607	0.090	21.00	0.997	0.162	550.17	0.827	74.573	1.41	0.997
PP ₃	0.057	9.11	0.385	0.069	34.97	0.996	0.146	633.89	0.770	78.866	1.38	0.996
BBC	0.176	86.45	0.784	0.012	195.28	0.999	0.635	779.47	0.831	291.163	2.58	0.884
RHA	0.217	117.54	0.990	0.003	141.40	0.987	0.805	815.02	0.959	320.778	2.57	0.903

0.851, 0.834, 0.607, 0.385, 0.784, and 0.990, respectively. In contrast, the PSO model provided higher R^2 values of 0.951, 0.963, 0.997, 0.996, 0.999, and 0.987, respectively. The Cd²⁺ sorption data conform better to the PSO model, with R^2 were limited to unity.

PP₀-PP₃ and BBC exhibited a better fit with the PSO model than the PFO model, implying that chemisorption, likely involving surface complexation with oxygen-containing functional groups, was the dominant mechanism. The sorption kinetics of Cd²⁺ on PP at different aging stages were best described by the PSO model, indicating chemisorption is the dominant mechanism. The increased R^2 values with extended aging suggest enhanced chemical interaction between Cd²⁺ and the PP surface, likely due to surface oxidation, enhanced roughness and porosity, and the generation of oxygen-containing functional groups (–COOH, –OH), which serve as active binding sites. These findings are in agreement with Wang et al. (2024) [38], who reported that the adsorption of Cd²⁺ onto UV-aged polystyrene microplastics and biochar also followed pseudo-second-order kinetics more closely ($R^2 = 0.8642$) than the pseudo-first-order model ($R^2 = 0.7711$), suggesting that chemical adsorption is a key process in Cd²⁺ retention on both synthetic and biomass-derived sorbents. Feng et al. (2025) [39] reported a 22-27%

increase in Cd²⁺ adsorption on aged microplastics due to greater surface area and functional group availability. The present study supports these mechanisms. Notably, the highest R^2 value (0.997) was observed for PP aged for 2 weeks, indicating optimal surface modification. In contrast, the comparable R^2 values observed at 3 weeks (0.996-0.999) may reflect a plateau effect, suggesting that beyond a certain aging duration, the adsorption performance stabilizes with minimal further improvement.

Conversely, RHA provided a better fit with the PFO model ($R^2 = 0.990$), suggesting that physical adsorption was the dominant mechanism. This observation aligns closely with findings by Nnaji et al. (2017), who demonstrated that RHA adsorption kinetics for Pb²⁺ were well described by PFO ($R^2 = 0.987$), with ion exchange being a dominant removal mechanism under acidic to neutral pH [40]. Collectively, the contrasting kinetic behaviors emphasize the role of surface chemistry and porosity characteristics in governing metal uptake: while biomass-derived adsorbents may follow chemisorption pathways, RHA appears to rely more on physisorption under certain conditions. Nevertheless, PP, BBC, and RHA have a good fitting effect, suggesting that partial complexation and chemical adsorption may control the whole adsorption process [41].

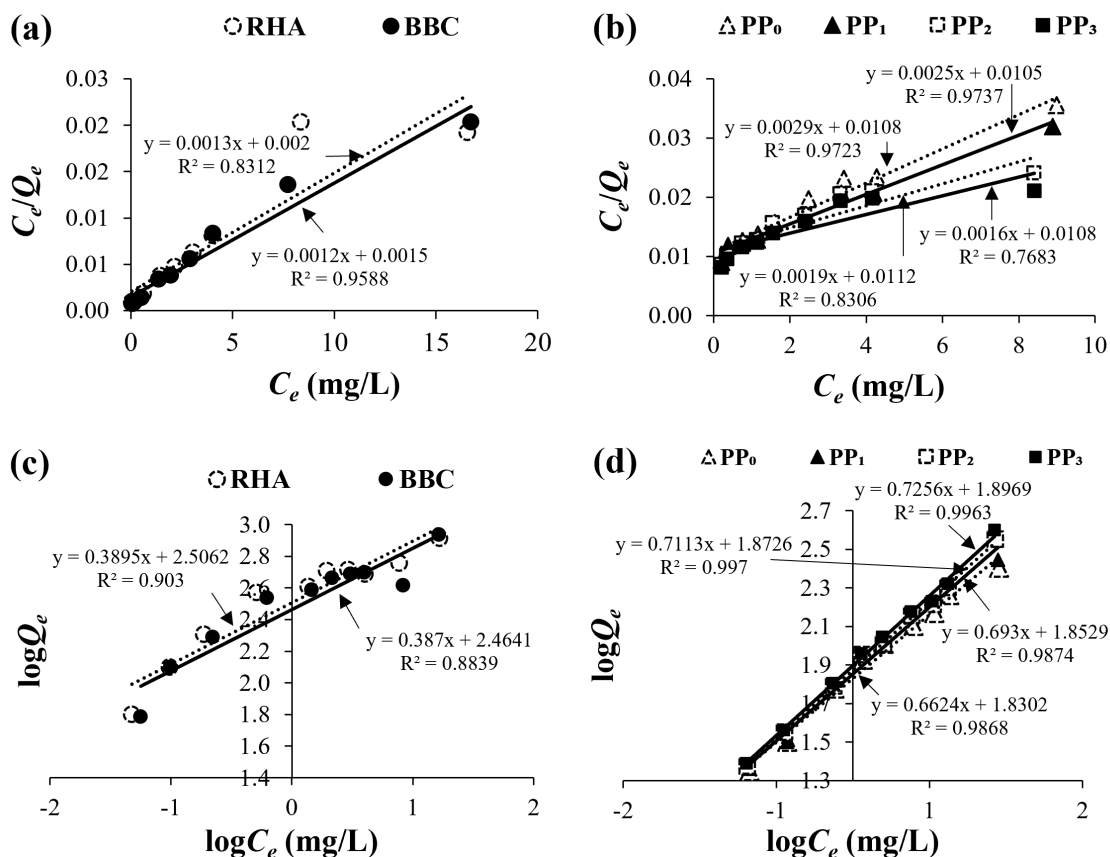


Fig. 6. Linear fittings of Langmuir isotherms for a) BBC and RHA and for b) PP (PP₀-PP₃), and Freundlich isotherms for c) BBC and RHA and for d) PP (PP₀-PP₃).

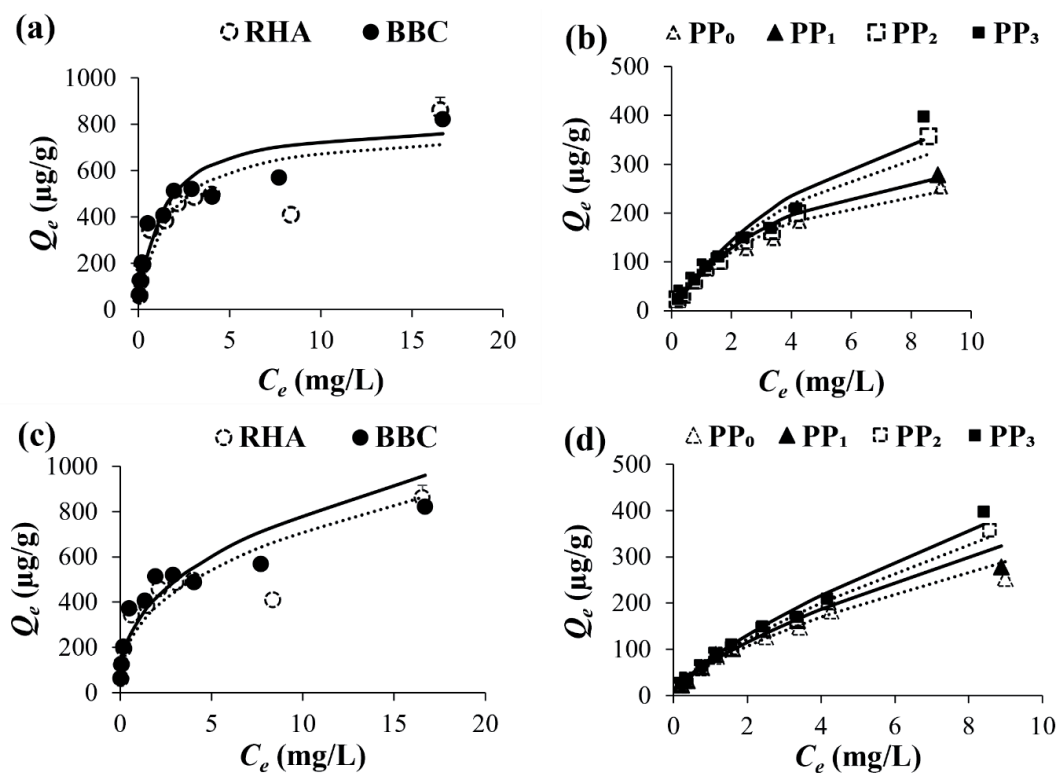


Fig. 7. Non-linear fittings of Langmuir isotherms for a) BBC and RHA and for b) PP (PP₀-PP₃), and Freundlich isotherms for c) BBC and RHA and for d) PP (PP₀-PP₃).

Adsorption Isotherms

The Freundlich model and the Langmuir model are capable of effectively fitting the adsorption behavior of PP₀-PP₃, BBC, and RHA to Cd²⁺. The correlation coefficients explaining the adsorption equilibrium mechanisms involved in each model are presented in Fig. 7. The PP₀-PP₃ and BBC samples were better fit with the Freundlich isotherm model, with R² values of 0.987, 0.987, 0.997, 0.996, and 0.884, respectively. This suggests that the adsorption process occurs on a heterogeneous surface with varying affinities for Cd²⁺ ions, indicating multilayer adsorption. In contrast, the RHA was a better fit with the Langmuir isotherm model, R² = 0.959, suggesting monolayer adsorption on a homogeneous surface [42].

The adsorption equilibrium was effectively described by both the Langmuir and the Freundlich isotherm models. However, the Freundlich model showed higher correlation coefficients, particularly for PP₀-PP₃ and BBC, indicating multilayer adsorption on heterogeneous surfaces [43]. This behavior is likely attributed to the presence of oxygen-containing functional groups and diverse sorption sites resulting from environmental aging and pyrolysis processes. These findings are consistent with Muthuraja et al. (2021) [44], who demonstrated that aged microplastics and biochar exhibited Freundlich-type Cd²⁺ adsorption due to their heterogeneous surface chemistry and mechanisms such as surface complexation and electrostatic attraction [45]. Similarly, Simón et al. (2024) [46] reported that biochar from agricultural waste follows the Freundlich model, influenced by microporous structures and functional group diversity. Alves et al. (2021) [47] also found that Freundlich isotherms better fit Cd²⁺ adsorption on modified biomass adsorbents, supporting the presence of multilayer chemisorption. In contrast, the Langmuir model provided a better fit for RHA, suggesting monolayer adsorption on a more homogeneous and silica-rich surface.

The overall isotherm parameters imply that Cd²⁺ adsorption across all tested materials is predominantly chemical in nature. This interpretation is further supported by Wang et al. (2024) [38], who demonstrated that multilayer adsorption coupled with pseudo-second-order kinetics is indicative of chemisorption involving ion exchange and specific interactions at the adsorbent surface.

The kinetic and isotherm model interpretations are consistent with the characterization results, providing clearer insights into the specific mechanisms driving Cd²⁺ adsorption on the different adsorbents.

Conclusions

This study investigated the sorption behaviors and mechanisms of Cd²⁺ on virgin and aged PP (PP₀, PP₁, PP₂, and PP₃), BBC, and RHA. Characterization

results revealed that differences in surface morphology, functional groups, and porosity directly influenced adsorption mechanisms, which suggests a good adsorption removal capacity.

The removal efficiencies of Cd²⁺, with initial Cd²⁺ concentration of 1 mg/L, by PP₀, PP₁, PP₂, PP₃, BBC and RHA were 5.62%, 10.39%, 8.56%, 14.31%, 70.03%, and 44.78%, respectively, under the optimum adsorption conditions at pH 7.0, temperature of 25°C, at adsorbent dosage of 4.0 g/L and in adsorption time of 1140 min. The PP₃ exhibited the highest removal efficiency for Cd²⁺. However, the aging of PP affected its ability to adsorb more Cd²⁺, with longer aging times resulting in a higher capacity to bind with Cd²⁺. The sorption models of kinetics and isotherms were used to fit the experimental results; PSO models fitted the data better than PFO for all of PP and BBC. Thus, the excellent PSO model fit across aged PP samples, especially from week 2 onward, confirms that chemical interactions dominate the sorption process, and this behavior is significantly promoted by aging-induced surface modifications. This suggested that the sorption of Cd²⁺ may imply chemical bond formation and ion exchange, consistent with Muthuraja et al. (2021) [44]. RHA is a better fit with the PFO model, suggesting that physisorption on its silica-rich surface, as also noted by Wang et al. (2024) [38]. The Freundlich isotherm model best fitted the results for PP and BBC, with maximum adsorption capacities of 396.7 µg/g and 862.6 µg/g, respectively. These imply a formed multilayer adsorption on heterogeneous surfaces. In contrast, for RHA, the fit of the Langmuir isotherm model was better, with a maximum adsorption capacity of 758.63 µg/g. It indicates that the monolayer sorption mechanism dominated the experiments. The characteristic analysis and modeling results suggested that multiple mechanisms might control the Cd²⁺ sorption, such as intraparticle diffusion and functional groups on the surface serving as sorption sites for the cations of toxic metals [34].

This study provides a comparative evaluation of aged polypropylene microplastics and biomass-derived adsorbents, demonstrating how environmental aging alters plastic surface properties and influences their interaction with heavy metals. The results confirm the superior performance of agricultural waste-based adsorbents in removing Cd²⁺ and highlight the emerging environmental risks associated with co-contamination by aged microplastics and heavy metals in aquatic systems. [48].

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Conflict of Interest

The authors declare no conflicts of interest.

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