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Adsorption Efficiency of Activated Carbon for Polystyrene Microplastics in Drinking Water Treatment

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Abstract

Microplastics have been found in various parts of the world and pose a threat to various environments, including the aquatic environment due to their ability to adsorb other pollutants and possible compound contamination. Therefore, it is necessary to evaluate the removal efficiency of techniques already used in water treatment plants. In this study, Granular Activated Carbon, CARBON BT (CBT), used in drinking water treatment processes, is evaluated for its ability to adsorb and remove polystyrene microplastics (MPS) after undergoing a washing process to remove impurities. Characterization analyzes such as scanning electron microscopy and zero charge potential of MPS and CBT were performed. Equilibrium and kinetic studies were performed to understand the adsorption mechanisms and limiting factors. It was found that the adsorption capacity increased with decreasing CBT concentration, with a maximum capacity of 0.774 mg/g using 2.5 g/L of CBT. The adsorption kinetics followed the pseudo-second order model and the Freundlich isotherm best represented the system. The results showed that the MPS removal efficiency was 26.35% at 2.5 g/L increasing to 37.72% at 10 g/L in 72h.

Keywords: Microplastics; Polystyrene; treatment processes; removal efficiency; adsorption capacity.

1. Introduction

The use of plastic materials increases every year, in parallel with this, a significant amount of plastic is improperly discarded [1]. Once in the environment, plastic waste undergoes physical, mechanical, photocatalytic, and biodegradation, breaking down into small particles called microplastics (MPs) and nanoplastics (NPs), classified as secondary. Additionally, we have primary ones that are manufactured in micro and nano sizes, used as abrasives and exfoliants in personal care products [1]. Microplastics are plastic particles within a size range of 1μm to 5mm [2], nanoplastics are plastic particles smaller than 100 nm [3].

MPs and NPs have been found in various parts of the world, including oceans [4], rivers [5], tap water [5], and even in the human placenta [6]. The ingestion and accumulation of MPs and NPs in organisms can have harmful and toxic effects at the molecular level [7]. Additionally, these particles can adsorb heavy metals [8], pesticides [9] and various toxic pollutants, forming compound pollution that can be passed to humans through the food chain [10]. Therefore, it is necessary to study technologies for removing MPs and NPs in water.

Several methods are being evaluated for the remediation of MPs and NPs, among them adsorption stands out, as it presents high efficiency, simple operation and reusability, and it has been widely used in water treatment [4].

In this study, monodisperse polystyrene (PS) microplastic was used as adsorbate as it is found in abundance in the aquatic environment [4], and granular carbon (CARBON BT) as an adsorbent, which is commonly applied in water treatment processes, as it is produced from renewable sources (coconut shells), and can present a sustainable solution for removing microplastics from the aquatic environment.

2. Materials and methods

Materials

Poly(styrene) microparticles (MPS) of 500 nm, purchased from Sigma Aldrich, density of 1.05 g/cm³ at 25 ºC. The granular activated carbon from coconut shell (CARBON BT) from Madecarbo, supplied by Canpack Group, is used in water treatment.

Methods

The carbon was standardized granulometrically (0.5 – 1 mm), 1 gram of the standardized material was washed with 100 mL of 0.1 M HCl to remove ash, rinsed with 500 mL of deionized water until constant pH, the water resulting from the washing process was filtered for the proper disposal of ash, after that the carbon was dried in an oven (De Leo, DL SE 42L) at 110 ºC for 48 hours.

The zero charge potential (PCZ) of CARBON BT (CBT) was determined according to [11,12] using 0.1 M NaCl solution, adjusting the pH with 0.1 M HCl and 0.1 M NaOH. The PCZ of microplastic solution (8 mg/L) was measured with Zetasizer Nano ZS90 (Malvern Instruments Ltd) in a pH range of 2 to 10.

Scanning electron microscopy was performed with a Quanta FEG 450 FEI. The concentration of microplastics before and after adsorption was quantified with a HANNA turbidimeter (HI98703) according to [13,1].

The experiments used deionized water, a reaction volume of 10 mL, an initial MPS concentration of 8 mg/L, pH = 4.0 ± 0.1, and a CBT concentration of 2.5 to 10 g/L. The solutions were stirred at 25 ºC, without light, for 3, 16, 24, 30, 48, 54, and 72 h at 150 RPM [14]. After the contact time, the turbidity of the supernatant was measured. Controls with deionized water and CBT were used to evaluate the interference of carbon particles with turbidity measurements.

The MPS removal efficiency (%R) and adsorption capacity (qt (mg/g)) of CBT were calculated following the following equations:

$$\%R = \frac{(C_i - C_f)}{C_i} 100 \quad (1)$$

$$q_t = \frac{(C_i - C_f)}{m} V \quad (2)$$

To determine the pseudo-first and pseudo-second order kinetic models, the following equations were used [4,15]:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

To determine the Langmuir and Freundlich adsorption isotherm models, the following equations [4,15] were used:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

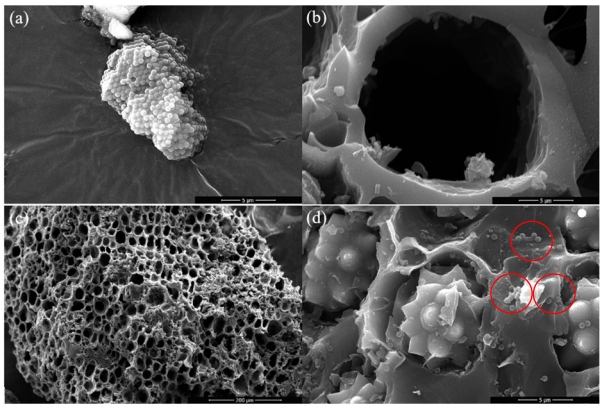
$$logq_e = logK_F + \frac{1}{n} logC_e \quad (6)$$

2. Results and discussion

PS microplastics and activated carbon characterization

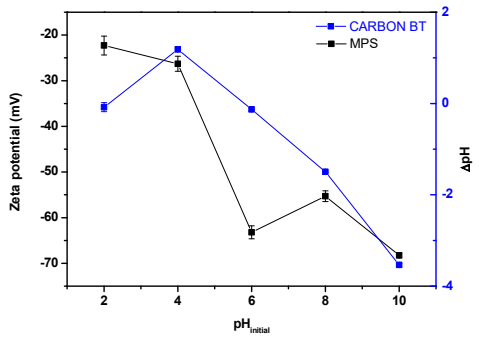
The SEM image (Fig. 1(a)) shows spherical and regular MPS, with an average diameter of 500 nm. Fig. 1(c) reveals many pores of varying sizes and shapes. The pores of CBT, with an average diameter of 17 µm, are larger than MPS (Fig. 1(b)), offering an additional surface for deposition and adsorption of MPS particles. The presence of adsorbed MPS was confirmed in SEM analyzes (Fig. 1(d)).

Fig.1. (a) SEM of MPS (8 mg/L) in deionized water, magnification 15,000x; (b) SEM of CBT, magnification 15,000x; (c) CBT SEM, 500x magnification; (d) SEM of CBT with adsorbed MPS, magnification 15,000x.



MPS are negatively charged across the pH range (Fig. 2) [1]. CBT has a positive charge at pH 2.13, approaching zero charge at pH 5.77. Above this value, CBT becomes negatively charged. Thus, pH 4 used in the experiments favors electrostatic attraction due to the opposite charges of the materials.

Fig.2. Zero charge potential (MPS and CBT).



Effect of adsorbent concentration

Fig. 3 shows that MPS adsorption is rapid at the beginning (3-24h), but does not reach high efficiency, even with more adsorbent. The adsorption capacity increases (Fig. 4) with lower adsorbent concentration, being maximum at 2.5 g/L of CBT. The maximum adsorption capacity was lower than that found in [13] which also used coconut shell-based carbon; however, the study used polystyrene nanoplastics with modified surface charge, facilitating the adsorption process.

Fig. 3. Effect of CBT concentration on removal efficiency.

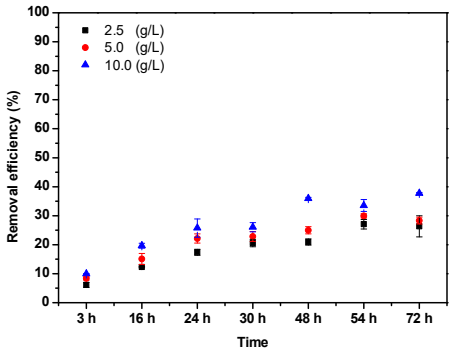
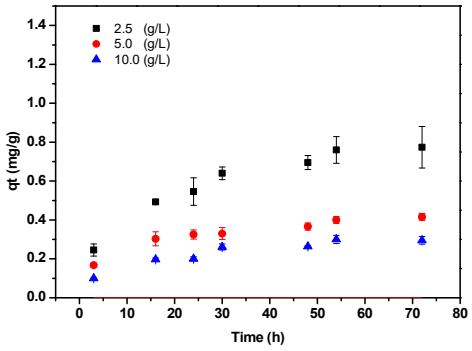


Fig.4. Effect of CBT concentration on adsorption capacity.



Equilibrium adsorption studies and kinetic adsorption rates

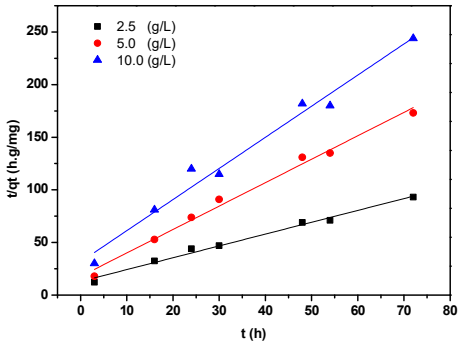
The results obtained for the pseudo-first and pseudo-second order kinetic model are presented in the Table. 1. They indicate that the pseudo-second order kinetic model fits the experimental data better, thus, we have that chemical sorption is the decisive step that affects the adsorption process [4, 16].

Table 1. Values of pseudo-first-order and pseudo-second-order parameters for MPS adsorption.

Models	Parameter	2.5 g/L	5.0 g/L	10.0 g/L
Pseudo-first order kinetic	$k_1(h^{-1})$	0.062	0.045	0.062
	R^2	0.872	0.896	0.840
	q_e (mg/g)	0.791	0.279	0.278
Pseudo-second order kinetic	$k_2((g/mg)/min)$	0.097	0.279	0.277
	R^2	0.989	0.990	0.979
	q_e (mg/g)	0.889	0.449	0.338

The q_e obtained by the pseudo-second order kinetic fitting was closer to the real value than by the pseudo-first order fitting. Furthermore, calculations showed $q_{e2,5g/L} > q_{e5g/L} > q_{e10g/L}$, consistent with experimental data.

Fig.5. Pseudo-second order kinetic model for the adsorption of MPS at different concentrations of CBT.



The results of the adjustment of the Langmuir and Freundlich models at 25 ºC are shown in Table 2. The correlation coefficient of the Freundlich model (R^2 = 0.979) was greater than that of the Langmuir model, indicating that the Freundlich model is more suitable for the adsorption process.

Table 2. The parameters of adsorption isotherms.

Equations	Parameter	25 ºC
Langmuir isotherms	$k_L(L.mg^{-1})$	0.062
	R^2	0.809
	q_m (mg/g)	3.248
Freundlich isotherms	$k_F[(mg.g^{-1})/(mg.L^{-1})^{-1/n}]$	0.210
	R^2	0.979
	1/n	0.795

Conclusion

The work evaluated the MPS removal performance using an industrial carbon. The system showed a maximum removal efficiency of 37.72% at 10 g/L of CBT. The adsorption kinetics follow the pseudo-second order model and the Freundlich isotherm best represented the system.

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