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Study of a polymer for removing Hg^{2+} from water by adsorption and its ecotoxicological effect on *Girardia tigrina*

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Abstract

The prevalence of water pollution is on the rise, attributable to a multitude of factors including population growth, industrial development, and mineral exploitation. This phenomenon has the potential to impact the accessibility of this vital resource for human survival. Among the array of environmental contaminants, mercury stands out as one of the top ten most detrimental pollutants, affecting not only human health but also the integrity of entire ecosystems. Consequently, the advancement of efficacious methodologies for the removal of the Hg^{2+} ion from aqueous solutions can prove invaluable in the remediation of contaminated water bodies and effluents. This study employed an experimental design comprising four variables (acrylamide, N-N-methylene-bisacrylamide, acrylic acid, and benzoyl peroxide) to assess the adsorption capacity (Q_e) of nine polymer samples. The results were subjected to statistical analysis using the Minitab program to identify the optimal combination of variables for the synthesis of an ideal polymer with the highest adsorption capacity for Hg^{2+} ions. The resulting value for Q_e was 82.22 ± 0.0132 $mg.g^{-1}$. A kinetic and isothermal model were developed to investigate the polymeric material. The pseudo-second order model and the Temkin model were obtained, respectively. The disinfection potential of the material was evaluated and an inactivation of 2.3 and 2.5 logs, respectively, was observed for *Escherichia coli* and total coliforms using a dose of 5 $g.L^{-1}$. Finally, the material was evaluated for its ecotoxicity against *Giardia tigrina*, in which the locomotion capacity was affected at a concentration of 100 $\mu g.mg^{-1}$.

Keywords: isothermal; kinetic; acrylic acid; acrylamide; disinfection

1. Introduction

The contamination of the environment by toxic metals, particularly mercury, represents a significant concern due to the adverse effects on human health and wildlife [1,2]. Mercury is naturally present in geological formations as a trace element. It can also be released into the environment by anthropogenic activities, including those related to chlorine industries, illegal gold mining, and the burning of fossil fuels, among others [3-5]. Mercury contamination of drinking water is a significant cause of mortality, resulting in approximately 2 million deaths per year [6].

The removal of mercury from water the conventional treatments may not be totally efficient, necessitating the use of complementary advanced treatments, such as solid phase chromatography columns, stabilization/containment, membrane separation, precipitation, ion exchange, microalgae-assisted methods, reduction/volatilization, solvent extraction, and adsorption [7-9].

Adsorption is an effective and economical method for treating water contaminated with toxic metals. The choice of the most suitable adsorbent for the contaminant is made possible by this method. In addition to the production of high-quality treated effluent, in certain instances it is feasible to regenerate the adsorbent for subsequent reuse [10].

Considering the challenges posed by the presence of Hg^{2+} ions in water and the need for effective treatments for such contamination, this study aimed to develop a polymeric material through the copolymerization of acrylic acid, acrylamide, and N-N-methylene-bisacrylamide. To study the kinetics and isotherms of adsorption in the removal of Hg^{2+}, the disinfection potential and ecotoxicological effects of the material were also examined.

2. Materials and methods

2.1 Synthesis of the samples

The samples were synthesized by the addition of acrylamide (AC), N-N-methylene-bisacrylamide (N'N'), and acrylic acid (AC) to vials in quantities corresponding to those utilized in each experimental procedure, as detailed in Table 1. The systems were subjected to ultrasound until dissolution in acetonitrile was achieved. Subsequently, the systems were heated to 65°C, stirred, degassed using a vacuum pump, and the benzoyl peroxide (BP) was added in accordance with the specifications outlined in Table 1. The systems were then stirred for a period of five hours, after which the samples were filtered, washed with distilled water, and subsequently dried in an oven at 100°C.

Table 1. Experimental planning.

Experiment	AA/ mmol	AC/ mmol	N'N'/ mmol	BP/ mmol
A	1.5	1.5	4.5	1.0
B	1.5	3.0	6.0	2,5
C	1.5	4.5	7.5	4.0
D	3.0	1.5	6.0	4.0
E	3.0	3.0	7.5	1.0
F	3.0	4.5	4.5	2.5
G	4,5	1.5	7.5	2.5
H	4.5	3.0	4,5	4.0
I	4.5	4.5	6.0	1.0

2.2 Adsorption kinetics

To determine the adsorption kinetics, 70 mg of the sample was weighed into 14 vials and 50 mL of $HgCl_2$ solution (0.1643 gL^{-1}) was added. The systems were agitated at 120 rpm and removed from the shaker at specified times, 30, 60, 120, 180, 240, 300, 360, 420, 1440, 1560, 1800, 1920, 2160, and 2400 minutes. The Pseudo first order, Pseudo second order, Elovich, and Weber and Morris intraparticle diffusion models were employed to investigate the adsorption kinetics.

2.3 Adsorption kinetics

The adsorption isotherms were obtained by weighing 70 mg of the sample into 9 flasks, to which 50 mL of $HgCl_2$ solution was added at different concentrations for each flask (414.3; 368.3; 322.2; 276.2; 230.2; 184.1; 138.1; 92.08 and 46.04 mgL^{-1}). The systems were agitated for a period of 24 hours at a speed of 120 rpm and 25°C. The isotherms were studied using the Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin models.

2.4 Disinfection capacity

The disinfectant capacity of the sample was evaluated by assessing the inactivation of the contamination indicators total coliforms and *Escherichia coli* in a sewage sample. The microorganisms were identified using the filter membrane technique, which was applied to a selective and differential chromogenic culture medium for total coliforms and *E. coli*.

2.5 Toxicological effects on G. tigrina

Toxicological effects on *G. tigrina* were evaluated using the parameters of locomotion, regeneration of blastema and photoreceptors, locomotion, fertility and fecundity.

Analysis of variance (ANOVA) was performed, followed by Dunnet's post hoc test for comparison with the control. Before performing the ANOVA, its assumptions were met, namely: homogeneity of the analysis of variance, Bartlett's test; and normality of the data, Kolmogorov-Smirnov test. For all statistical tests. The significance level was set at $p < 0.05$ for all statistical tests.

3. Result and discussion

Nine samples of polymeric materials (A-I) were obtained from the experimental design. All the samples showed good adsorption capacity, and the

sample with the best adsorption capacity was sample "I" with Qe = 80.96 ± 0.2088 mg.g^{-1} and the sample with the worst result was 'B' with Qe = 66.57 ± 0.8388 mg.g^{-1}. However, the statistical treatment provided the best combination of factors to synthesize the sample with the best adsorption capacity (4.5 mmol AA, 4.5 mmol AC, 4.5 mmol N'N' and 4.0 mmol BP). The value predicted by the statistical treatment of the adsorption capacity of this sample was 81.95 ± 0.8909 mg.g^{-1} (Hg^{2+}), which is close to the experimental value, sample "J" (82.22 ± 0.0132 mg.g^{-1}).

The adsorption kinetics of Hg^{2+} ions by the 'J' polymer sample was evaluated and the kinetic model that best fits the polymer material is the pseudo-second-order model, since the R^2 was closest to 1.0. This means that the adsorption rate depends on the adsorption capacity of the material and not on the concentration of the adsorbate. From this model it was possible to obtain the value of the adsorption capacity at equilibrium (89.50 mg.g^{-1}) and the equilibrium constant (k = 1.799x10^{-4} g.mg-1.min^{-1}). The kinetic model of Weber and Morris, which considers intraparticle diffusion as the determining factor for the adsorption rate, showed the lowest coefficient of determination, so it can be said that it is not relevant for the adsorption kinetics of this system.

Table 2 presents the values of the coefficients of determination (R^2), chi-squared (χ^2), and the parameters extracted from each isotherm studied. The R2 values indicate that the Temkin model best fits the experimental data. This model assumes that the heat of adsorption of all molecules decreases linearly with the increase in coverage of the adsorbent surface and is characterized by a uniform energy distribution, up to a maximum value.

The Langmuir isotherm postulates that the adsorption sites are identical in terms of their energetic characteristics, that the adsorbent surface is uniform, and that adsorption occurs in a single layer. From this model, we can obtain a Q_{max} of 247.1 ± 0.2259 mg.g^{-1}, a K_L of 0.0987 ± 0.0001 L.mol^{-1}, and an R_L of 0.2119. This parameter indicates that the adsorption process is favorable.

The Dubinin-Radushkevich isotherm is a model commonly employed to elucidate adsorption mechanisms with a Gaussian energy distribution on heterogeneous surfaces. This model allows for the differentiation between physical, ion exchange, and chemical adsorption based on the average adsorption energy. The system under investigation exhibited an average adsorption energy of 5983 J mol^{-1}, which is indicative of a physical adsorption process.

Table 2. Parameters of the isotherms.

Isotherms	Parameters	
Langmuir	R^2	0,9349
	χ^2	2,720x10^4
	$Q_{máx}$	247,1 ± 0,2259 mg g^{-1}
	K_L	0,0987 ± 0,0001 L mg^{-1}
	R_L	0,2119
Freundlich	R^2	0,8266
	χ^2	7,526x10^{-4}
	K_F	28,56 ± 0,0198 mg$^{1-1/n}$ g^{-1}L$^{1/n}$
	N	1,731 ± 0,0009
	1/n	0,5777
Dubinin-Radushkevich	R^2	0,8988
	χ^2	2,980x10^4
	$Q_{máx}$	0,0013 ± 1,065x10^{-6} mol.g^{-1}
	Energia (E)	5983 J.mol^{-1}
Temkin	R^2	0,96234
	χ^2	1,110x10^4
	K_T	234,3 ± 0,2008 L.mol^{-1}
	B	9,703x10^6 ± 6457 J.g.mol^{-2}

The ecotoxicity tests demonstrated that the sample from experiment "J" did not affect the physiological response of *G. Tigrina* in relation to the parameters of auricle regeneration, blastema regeneration, fertility, and fecundity. However, the test with a concentration of 10 µg.mL^{-1} indicated a negative effect on the locomotion criterion. This result is a significant, given that locomotion speed is an important factor in feeding and escaping predators.

In terms of disinfection capacity, sample "J" demonstrated favorable results, reducing the colony-forming units of *E. coli* and total Coliforms by 2.3 and 2.5 logs, respectively (Figure 1).

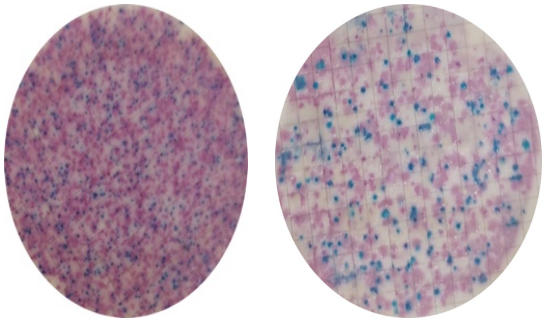

Fig. 1. (a) Colony formation in the raw effluent; (b) Colony formation following disinfection with experiment J.

4. Conclusion

The experimental results demonstrated the potential of the 'J' polymeric material for application in the decontamination treatment of solutions containing Hg^{2+}, with an adsorption efficiency of 82.22 ± 0.0132 $mg.g^{-1}$. In the study of adsorption kinetics, the pseudo-second order model was identified as the optimal fit for the adsorption kinetics of sample 'J', with an R^2 value of 0.9994. In the study of adsorption isotherms, the Temkin model exhibited the highest linear correlation, with a value of 0.9623, indicating that the experimental data were best fit by this isothermal model. In addition to its adsorption capacity, the material demonstrated efficacy in disinfecting *E. coli* and total coliforms. Finally, the ecotoxicity tests demonstrated that the material affects the locomotion parameter of *Giardia tigrina*.

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