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Adsorption of Reactive Red 120 Dye by Polyamide Nylon 6 Microplastics: Isotherm, Kinetic, and Thermodynamic Analysis

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Abstract: In this work, we investigated the effect of various adsorption parameters (solution pH, temperature, contact time, and the presence of phosphate and nitrate ions) on the adsorption of Reactive Red 120 (RR120) dye by Polyamide Nylon 6 (PN6) microplastics (MPs). Maximum uptake was achieved at pH 2.0, and the temperature rise from 295 to 313 K resulted in the decrease of the RR120 sorption by PN6. Equilibrium was achieved after 7 h, and the adsorption kinetic data obeyed the pseudo-second-order kinetic model. The experimental adsorption data were better fitted by the Langmuir isotherm model, and the q_m was found to be 3.96 mg/g at pH 2.0 and 295 K. Thermodynamic studies pointed out that the adsorption was spontaneous and exothermic, with decreasing entropy at the solution/solid interface. Future work will focus on the effect of aging on the adsorptive properties of PN6 toward RR120 dye.

Keywords: adsorption; Polyamide Nylon 6; microplastics; Reactive Red 120; dyes

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1. Introduction

The presence of microplastics (MPs) in the environment has become a global issue due to their persistence and long-term presence in the ecosystem [1]. According to recent studies, MPs can act as carriers for toxic pollutants, since they can adsorb considerable amounts of pollutants and transport them into environmental compartments, including the biosphere [2,3]. Polyamides (also known as nylons), which are a group of synthetic polymers, have found applications in various fields due to their unique properties, such as mechanical strength, flexibility, toughness and resistance [4]. Nylon 6 (PN6) is one of the most manufactured nylons and is formed from caprolactam via ring-opening polymerization, leading to six-carbon chain units with amide and carbonyl functional groups [5]. Due to its excellent mechanical and thermal properties, as well as good adhesion and attractive visual characteristics [6], the polymer has many applications, such as in the textile, plastic, electronic and food industries [5].

Reactive Red 120 (RR120) is one of the dyes that is frequently used in the textile industry, due to its high level of chemical, biological, and photocatalytic stability [7]. RR120 is a dye that reacts directly with textile molecules, making the dye a part of the fabric. However, the dyeing processes produce enormous amounts of wastewater containing unreacted dyes. Untreated effluent discharges may interfere with the aquatic ecosystem, resulting in serious hazard. Treatment of RR120 is difficult because it is not effectively removed by conventional water-treatment technologies [8].

Preliminary work indicated that Reactive Red 120 (RR120) has a high affinity for various MPs, such as polyethylene (PE), polyvinyl chloride (PVC), and particularly PN6 [9].

Our previous study highlighted that the presence of the electronegative N and O in the PN6 polymeric structure may form H bonds and electrostatically interact with negatively charged moieties present in RR120. RR120 that has been adsorbed by PN6 can be further dispersed in the environment and enter the biosphere, thereby affecting living organisms. Hence, a comprehensive analysis based on isotherm, kinetic and thermodynamic analysis is required to provide more information on the adsorption mechanism.

Therefore, to have an in-depth understanding of the sorption behavior of RR120 onto PN6 microplastics, a batch equilibrium approach was performed. The effects of different adsorption parameters, such as solution pH, temperature, contact time, and the presence of other ions (e.g., phosphate and nitrate ions), were investigated. In addition, kinetic and thermodynamic modeling was also applied and discussed.

2. Materials and Methods

Polyamide nylon 6 powder (5–50 µm) was obtained from M/S Goodfellow. Reactive Red 120 ($C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$, MW: 1469.98, called RR120) was obtained from M/S Merck (Europe). The amount of RR120 adsorbed at time t (Equation (1)) or the equilibrium state (Equation (2)) was determined using the following equations:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where C_i (mg/L) represents the starting RR120 concentration in the aqueous phase, C_t (mg/L) and C_e (mg/L) are the RR120 concentrations in the liquid phase at a given time (t) and at equilibrium, respectively, V (L) is the liquid phase volume, and m (g) is the mass of PN6 added.

The parameters of the experimental setup are summarized in Table 1. The parameter under investigation was varied, whereas the others were kept constant. Generally, in the experiments, the MPs' mass (0.4 g), the volume (0.05 L), and the agitation rate (A.R. = 125 rpm) were kept constant. The residual RR120 concentration in the supernatant liquid was analyzed using a UV/VIS spectrophotometer (model) at λ_{max} = 515 nm.

Table 1. The experimental setup for the RR120 adsorption by PN6 microplastics (read from left to right on each line for the different factors).

	Starting Concentration (mg/L)	pH	Time of Contact (h)	T (K)	Presence of NO_3^- or PO_4^{-3}
Initial concentration (mg/L)	10–60	2	24	295 K	-
pH	40	2–7.8	24	295 K	-
Contact time (min or h)	35	2	0.5–48	295 K	-
Temperature (K)	10–60	2	24	295 K and 313 K	-
Presence of NO_3^- or PO_4^{-3}	40	2	24	295 K	10–100

Table 2 presents the isotherms, kinetics and thermodynamic equations used for this study.

For isotherms and kinetics studies, C_e (mg/L) and q_e (mg/g) are the equilibrium liquid-phase concentrations and amount of solute adsorbed at equilibrium, respectively.

The ΔH^0 (enthalpy change) and ΔS^0 (entropy change) were estimated using the following equations [15]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

$$\Delta H^0 = R\left(\frac{T_2 \times T_1}{T_2 - T_1}\right) \ln\left(\frac{K_{T2}}{K_{T1}}\right) \quad (4)$$

where T_2 and T_1 are the two operational temperatures ($T_2 > T_1$); and K_{T1} and K_{T2} are the equilibrium constant K_e^0 at T_2 and T_1, respectively.

Table 2. Isotherms, kinetics and thermodynamic equations.

Expression	Equation	Constants
Langmuir (*L*) [10]	$q_e = q_m \frac{K_L C_e}{1+K_L C_e}$	q_m (mg/g): maximum monolayer adsorption capacity K_L (L/mg): constant related to the energy of sorption and equilibrium constant
Freundlich (*F*) [11]	$q_e = K_F \mathrm{C_e}^{1/\mathrm{n}}$	K_F (mg/g)(L/mg)$^{1/\mathrm{n}}$: Freundlich constant 1/n (dimensionless): adsorption intensity parameter
Pseudo-first-order kinetic (PS1) [12]	$q_t = q_e(1 - \exp^{-k_1 t})$	q_t (mg/g): the amount adsorbed at time t (min) k_1 (min^{-1}): PS1 rate constant
Pseudo-second-order kinetic (PS2) [13]	$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}$	q_t (mg/g): the amount adsorbed at time t (min) k_2 (g/mg min): PS2 rate constant
Gibbs [14]	$\Delta G^0 = -RT \ln K_e^0$	Free energy change

3. Results and Discussion

3.1. Effect of Adsorption Parameters (pH, Contact Time, Temperature, and Co-Existing Anions)

The adsorption of RR120 and PN6 is mainly attributed to H-bonding and electrostatic interactions between the positively charged microplastic surface and the negatively charged dye molecule. Figure 1 shows the chemical structure of PN6 and the RR120 dye in aqueous solutions.

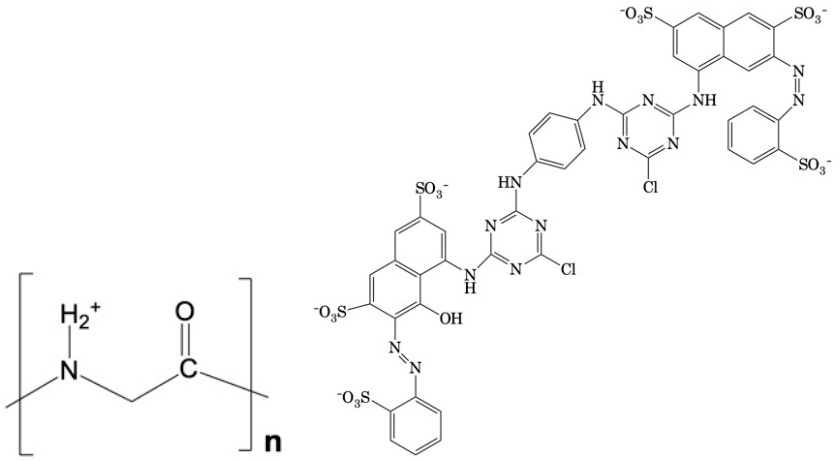

Figure 1. Chemical structures of PN6 and the RR120 dye.

The effect of pH on the RR120 removal by PN6 microplastics was investigated in a pH range of 2 to 8 (Figure 2). It was observed that the uptake of RR120 by PN6 microplastics decreased from 3.7 to 1.93 mg/g as the pH increased from 2.0 to 7.8. RR120 has six sulfonate (R-SO_3^-) groups that are easily deprotonated in aqueous solution and that, following the RR120 molecules (D-SO_3H), are converted to anionic dye species (D–SO_3^-) [16]. PN6 microplastic contains amide and amino groups, which are protonated under acidic conditions [17]. Thus, the maximum adsorption obtained under acidic conditions may be due to the electrostatic attraction that takes place between the dye's sulfonate groups and the cationic functional groups on the surface [18]. Similar results have been reported by Munagapati et al. [16] who investigated the removal of RR120 by quaternary amine-modified orange-peel powder.

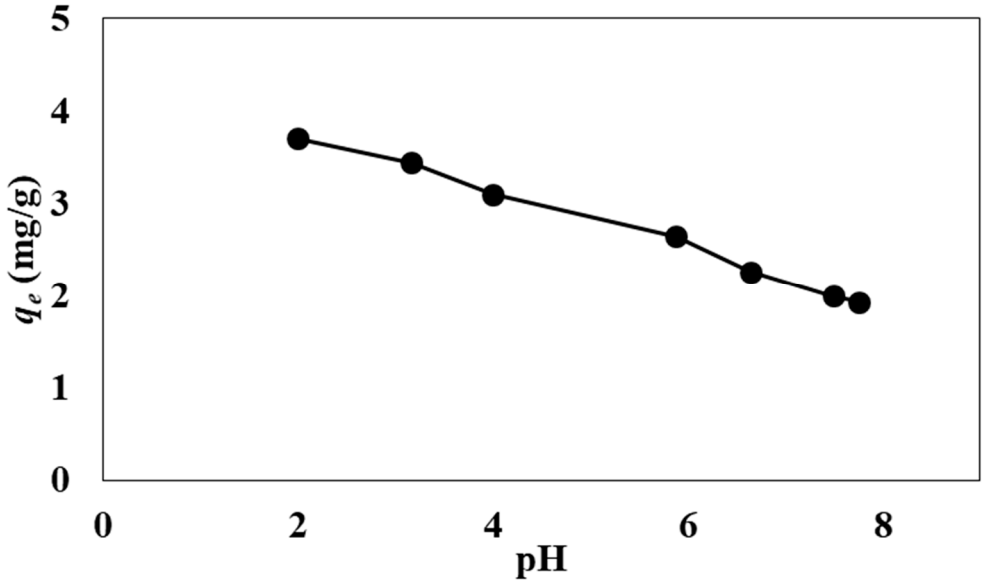

Figure 2. Effect of pH in a range of 2.0–8.0 on the adsorption of RR120 by PN6 microplastics. Experimental conditions: C_i = 40 mg/L, t = 24 h, pH = 2, A.G. = 125 rpm, solid/liquid ratio = 0.4 g/0.05 L, T = 295 K (n = 2).

The effect of the contact time on the removal of RR120 by PN6 microplastics is illustrated in Figure 3. The uptake was found to rise with time, and equilibrium was reached after 7 h. Ay and Sarpaşar [19] found that the removal equilibrium of RR130 when using zeolite and Fe_3O_4@zeolite composites was attained between 30 and 50 min.

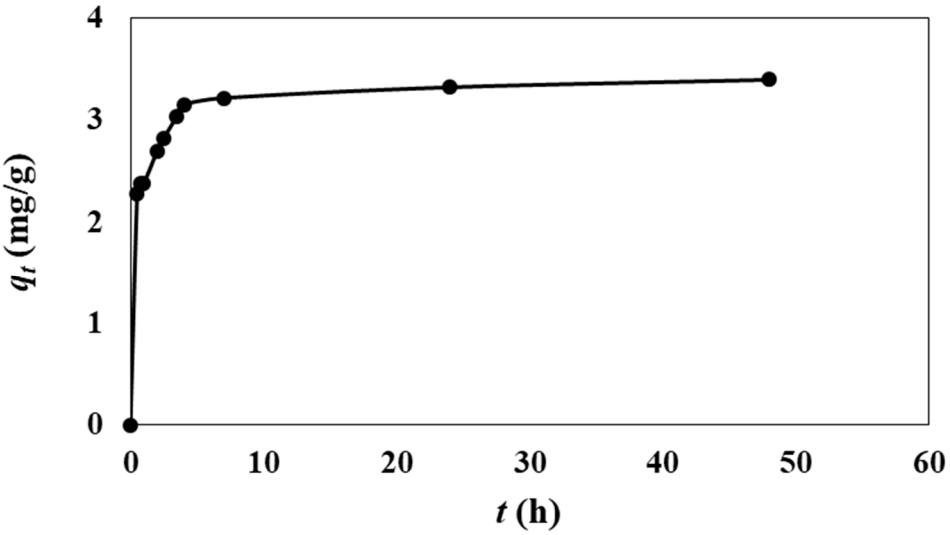

Figure 3. Effect of contact time on the adsorption of RR120 onto PN6 microplastics in the time range between 0.5 and 48 h. Experimental conditions: C_i = 35 mg/L, pH = 2, A.R. = 125 rpm, solid/liquid ratio 0.4 g/0.05 L, T = 295 K (n = 2).

Figure 4 presents the effect of temperature (295 K and 313 K) on the adsorption of RR120 by PN6 microplastics. The increase of the initial concentration from 10 to 60 mg/L was found to enhance the adsorption capacity (the experimental q_e values increased from 1.25 to 3.92 mg/g and from 1.18 to 3.39 mg/g at 295 K and 313 K, respectively). Similar results have also been observed by Jawad et al. [20], who investigated the adsorption of RR120 by cross-linked chitosan-epichlorohydrin biobeads. This is ascribed to higher initial concentrations, which provide an increased driving force to overcome mass transfer resistance of RR120 dye molecules between the aqueous and solid phases [21]. Regarding

the temperature effect, the temperature rise from 295 K to 313 K led to a reduction of the adsorption capacity, indicating the exothermicity of the adsorption process. For example, at a concentration of 60 mg/L, the adsorption capacity was reduced from 3.92 to 3.39 mg/g. A similar trend has been noticed by Çelekli et al. [22], who investigated the removal of RR120 by *Moringa oleifera* seeds.

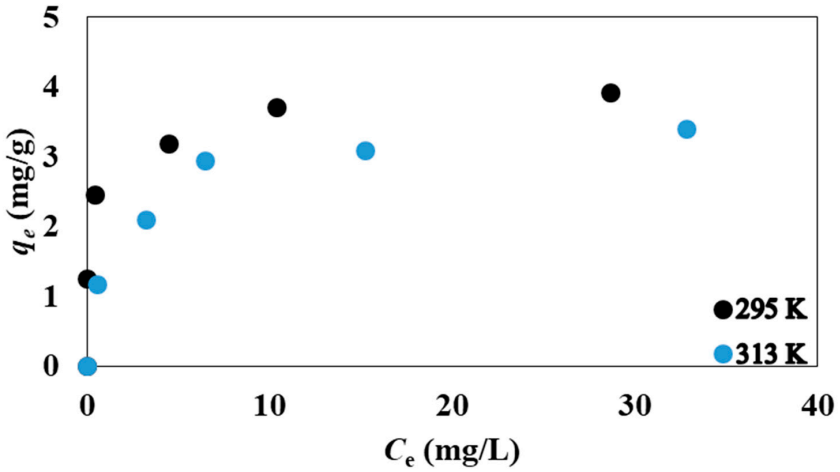

Figure 4. Isotherms of the adsorption of RR120 onto PN6 microplastics at 295 K and 313 K. Experimental setup: t = 24 h, pH = 2, A.R. = 125 rpm, solid/liquid ratio 0.4 g/0.05 L, C_i range: 10–60 mg/L (n = 2).

The effect of phosphate or nitrate ions on the adsorption of RR120 by PN6 is shown in Figure 5. According to the associated data, the presence of co-ions has a negligible effect on dye sorption, suggesting no antagonism effect between the dye and competing anions. This is in good agreement with our earlier study, which attributed the RR120 adsorption on PN6 both to Coulomb interactions between the anionic dye and the positively charged surface moieties and to the formation of hydrogen bonds between the hydroxy groups of RR120 and the carbonyl moieties of the PN6 surface [9]. This multisite interaction favors the adsorption of RR120 by PN6 compared to other simple anionic competitors such as phosphate and nitrate anions.

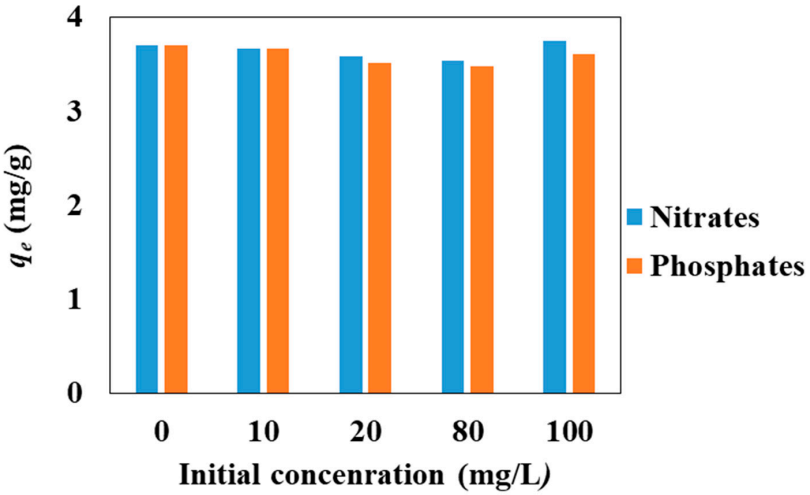

Figure 5. The effect of NO_3^- or PO_4^{-3} ions at various concentrations (10, 20, 80 and 100 mg/L) on the adsorption of RR120 by PN6 microplastics. Experimental conditions: C_i = 40 mg/L, t = 24 h, pH = 2, A.R. = 125 rpm, solid/liquid ratio = 0.4 g/0.05 L, and T = 295 K (n = 2) (y-axis presents the adsorption of dye in the presence of nitrates (blue) or phosphates (orange) at various concentrations (x-axis)).

3.2. Isotherm, Kinetic and Thermodynamic Modeling

The adsorption experimental data were fitted to the L and F isotherm models, and the corresponding results are summarized in Table 3. Based on the regression coefficients R^2, it was observed that for both temperatures the experimental data were better fitted to the Langmuir isotherm (R^2 = 1 at 295 K and 313 K) model compared to the Freundlich isotherm model (R^2 = 0.89 at 295 K and R^2 = 0.93 at 313 K). Tabak et al. [23], who studied the uptake of RR120 by cetylpyridinium-modified bentonite, also found that the Langmuir isotherm model fitted the adsorption experimental data better. In another work, Cardoso et al. [18] investigated the removal of RR120 by *Spirulina platensis* microalgae and commercial activated carbon and found that the equilibrium data had the best fit with the Liu isotherm model.

Table 3. Equilibrium isotherm parameters for RR120 onto PN6 at 295 K and 313 K.

T (K)	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2
295	3.96	2.148	1	2.32	5.34	0.89
313	3.54	0.607	1	1.50	3.75	0.93

The experimental kinetic data were fitted to the PS1 and PS2 kinetic models. The kinetic constants, which have been evaluated by PS1 and PS2 models, are k_1 = 0.416 min^{-1} ($q_{e,cal1}$ = 1.49 mg/g and R^2 = 0.98) and k_2 = 0.690 g/mg min ($q_{e,cal2}$ = 3.40 mg/g and R^2 = 1), respectively. Based on the results, the PS2 fits the associated experimental data pointed out by the corresponding R^2 values better. Moreover, the calculated adsorption capacity value ($q_{e,cal2}$ = 3.40) is similar to the corresponding experimental value ($q_{e,exp}$ = 3.40 mg/g). Ay and Sarpaşar [19], who investigated the removal of RR120 using natural zeolite and iron oxide-zeolite (Fe_3O_4@Z), have also found that the PS2 kinetic model fitted the experimental kinetic data better.

Regarding the thermodynamic parameters, the ΔG^0 values were estimated to be −36.70 and −35.65 kJ/mol at 295 and 313 K, respectively, suggesting a spontaneity adsorption of RR120 onto PN6. The ΔH^0 was found to be −53.92 kJ/mol, indicating the exothermicity of the adsorption of RR120 onto PN6 MPs. The ΔS^0 was estimated at −0.058 kJ/mol K, implying a decreasing randomness in the solid/solution system interface during the adsorption process. A similar observation was also reported by Al Rubai et al. [24], who explored the adsorption of RR120 by bentonite modified with cetyltrimethylammonium bromide.

4. Conclusions and Future Works

The results of this work showed that PN6 MPs are capable of adsorbing and acting as carriers of RR120 dye. Dye uptake was strongly affected by the solution pH, contact time, and temperature, whereas the presence of nitrates or phosphates did not alter the adsorptive properties of PN6 MPs towards RR120 dye. The experimental data fitted better with the Langmuir and PS2 kinetic models. The thermodynamic studies indicated the spontaneity and exothermicity of the adsorption process. Future studies will focus on the exploration of the adsorption properties of PN6 MPs for RR120 dye uptake from real wastewater samples and column studies. Desorption studies in various water matrices will also be of particular interest. The effect of aging on the physicochemical characteristics of PN6 MPs and their effect on the adsorption of RR120 will also be investigated.

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References

1. Kumari, A.; Rajput, V.D.; Mandzhieva, S.S.; Rajput, S.; Minkina, T.; Kaur, R.; Sushkova, S.; Kumari, P.; Ranjan, A.; Kalinitchenko, V.P. Microplastic Pollution: An Emerging Threat to Terrestrial Plants and Insights into Its Remediation Strategies. *Plants* **2022**, *11*, 340. [CrossRef] [PubMed]
2. Kinigopoulou, V.; Pashalidis, I.; Kalderis, D.; Anastopoulos, I. Microplastics as carriers of inorganic and organic contaminants in the environment: A review of recent progress. *J. Mol. Liq.* **2022**, *350*, 118580. [CrossRef]
3. Zhao, M.; Huang, L.; Arulmani, S.R.B.; Yan, J.; Wu, L.; Wu, T.; Zhang, H.; Xiao, T. Adsorption of different pollutants by using microplastic with different influencing factors and mechanisms in wastewater: A review. *Nanomaterials* **2022**, *12*, 2256. [CrossRef] [PubMed]
4. Winnacker, M. Polyamides and their functionalization: Recent concepts for their applications as biomaterials. *Biomater. Sci.* **2017**, *5*, 1230–1235. [CrossRef]
5. Didovets, Y.; Brela, M.Z. Theoretical Study on the Thermal Degradation Process of Nylon 6 and Polyhydroxybutyrate. *Physchem* **2022**, *2*, 334–346. [CrossRef]
6. Völtz, L.R.; Geng, S.; Teleman, A.; Oksman, K. Influence of Dispersion and Orientation on Polyamide-6 Cellulose Nanocomposites Manufactured through Liquid-Assisted Extrusion. *Nanomaterials* **2022**, *12*, 818. [CrossRef] [PubMed]
7. Manogaran, M.; Yasid, N.A.; Othman, A.R.; Gunasekaran, B.; Halmi, M.I.E.; Shukor, M.Y.A. Biodecolourisation of Reactive Red 120 as a sole carbon source by a bacterial consortium—Toxicity assessment and statistical optimisation. *Int. J. Environ. Res. Public Health* **2021**, *18*, 2424. [CrossRef] [PubMed]
8. Aliasghar Navaeia, M.; Alidadid, H.; Dankooba, M.; Bonyadid, Z.; Dehghand, A.; Hosseinie, A. Biosorption of Reactive Red 120 dye from aqueous solution using Saccharomyces cerevisiae: RSM analysis, isotherms and kinetic studies. *Desalination Water Treat.* **2019**, *171*, 418–427. [CrossRef]
9. Anastopoulos, I.; Pashalidis, I.; Kayan, B.; Kalderis, D. Microplastics as carriers of hydrophilic pollutants in an aqueous environment. *J. Mol. Liq.* **2021**, *350*, 118182. [CrossRef]
10. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. [CrossRef]
11. Freundlich, H. Over the adsorption in solution. *J. Phys. Chem.* **1906**, *57*, 1100–1107.
12. Lagergren, S. About the theory of so-called adsorption of soluble substances. *Sven. Vetenskapsakad. Handingarl* **1898**, *24*, 1–39.
13. Blanchard, G.; Maunaye, M.; Martin, G. Removal of heavy metals from waters by means of natural zeolites. *Water Res.* **1984**, *18*, 1501–1507. [CrossRef]
14. Lima, E.C.; Hosseini-Bandegharaei, A.; Moreno-Piraján, J.C.; Anastopoulos, I. A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoof equation for calculation of thermodynamic parameters of adsorption. *J. Mol. Liq.* **2019**, *273*, 425–434. [CrossRef]
15. Giannakoudakis, D.A.; Anastopoulos, I.; Barczak, M.; Antoniou, E.; Terpiłowski, K.; Mohammadi, E.; Shams, M.; Coy, E.; Bakandritsos, A.; Katsoyiannis, I.A.; et al. Enhanced uranium removal from acidic wastewater by phosphonate-functionalized ordered mesoporous silica: Surface chemistry matters the most. *J. Hazard. Mater.* **2021**, *413*, 125279. [CrossRef] [PubMed]
16. Munagapati, V.S.; Wen, J.-C.; Pan, C.-L.; Gutha, Y.; Wen, J.-H. Enhanced adsorption performance of Reactive Red 120 azo dye from aqueous solution using quaternary amine modified orange peel powder. *J. Mol. Liq.* **2019**, *285*, 375–385. [CrossRef]
17. Ioannidis, I.; Xenofontos, A.; Anastopoulos, I.; Pashalidis, I. Americium Sorption by Microplastics in Aqueous Solutions. *Coatings* **2022**, *12*, 1452. [CrossRef]
18. Cardoso, N.F.; Lima, E.C.; Royer, B.; Bach, M.V.; Dotto, G.L.; Pinto, L.A.; Calvete, T. Comparison of Spirulina platensis microalgae and commercial activated carbon as adsorbents for the removal of Reactive Red 120 dye from aqueous effluents. *J. Hazard. Mater.* **2012**, *241*, 146–153. [CrossRef]
19. Ay, Ç.; Sarpaşar, Z. Using zeolite and Fe3O4@ zeolite composites in removal of Reactive Red 120 from wastewater: Isotherm, kinetic, thermodynamic and adsorption behaviors. *J. Dispers. Sci. Technol.* **2022**, *44*, 370–381. [CrossRef]
20. Jawad, A.H.; Shazwani, N.; Mubarak, A.; Sabar, S. Adsorption and mechanism study for reactive red 120 dye removal by cross-linked chitosan-epichlorohydrin biobeads. *Compos. Part B Eng* **2019**, *75*, 415–418. [CrossRef]

21. Bazrafshan, E.; Mostafapour, F.K.; Hosseini, A.R.; Raksh Khorshid, A.; Mahvi, A.H. Decolorisation of reactive red 120 dye by using single-walled carbon nanotubes in aqueous solutions. *J. Chem.* **2013**, *2013*, 938374. [CrossRef]
22. Çelekli, A.; Al-Nuaimi, A.I.; Bozkurt, H. Adsorption kinetic and isotherms of Reactive Red 120 on Moringa oleifera seed as an eco-friendly process. *J. Mol. Struct.* **2019**, *1195*, 168–178. [CrossRef]
23. Tabak, A.; Baltas, N.; Afsin, B.; Emirik, M.; Caglar, B.; Eren, E. Adsorption of Reactive Red 120 from aqueous solutions by cetylpyridinium-bentonite. *J. Chem. Technol. Biotechnol.* **2010**, *85*, 1199–1207. [CrossRef]
24. Al Rubai, H.F.; Hassan, A.K.; Sultan, M.S.; Abood, W.M. Kinetics of Adsorption of Reactive Red 120 Using Bentonite Modified by CTAB and Study the Effect of Salts. *Nat. Environ. Pollut. Technol.* **2021**, *20*, 281–289. [CrossRef]