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Sorption kinetics of heavy metals from aqueous solution using *Spirogyra* sp.: a microcosm study

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Abstract: Understanding the mechanisms by which algae communities respond to disturbances in the lotic aquatic environment that is polluted by heavy metals is important, considering that algae is a biotic component of waters that acts as a producer in the aquatic food chain which has the potential to bio-magnify. This study examines the influence of time, biomass weight, heavy metal concentration, sorption capacity, and efficient removal on epilithic periphyton as a bio-accumulator of Cr, Pb, and Ni. The experiment was conducted on a laboratory scale using a canal system with a length and width of 1.2 and 1.0 meters, respectively. The canal system contains 132 L of water, has a 1.2 m^2 substrate and periphyton area, a depth of 0.09 – 0.10 m, and a current flow rate of 0.04 – 0.06 m/s. The dissolved Cr^{6+} initial concentration in the medium was 1.64 mg/L, Pb^{2+} and Ni^{2+} concentrations were 1.4 mg/L, and the adsorption process was studied for 24 hours. Based on microscope observations and functional group interpretation utilizing infrared spectra (FTIR), the periphyton community is dominated by *Spirogyra* sp., which has hydroxyl (O-H), carboxyl (C-H), and carbonyl (C-C and C=O) functional groups with the ability to binding heavy metals. The remaining quantities of Cr, Pb, and Ni in water were 0.43 mg/L (removal 69.29%), 0.05 mg/L (96.43% removal), and 0.03 mg/L (97.86% removal). Periphyton has a maximal sorption capacity of 1.019 mg Cr/g, 1.97 mg Pb/g, and 1.92 mg Ni/g. The sorption kinetics of Cr, Pb, and Ni follow a pseudo-second-order model with k_2 = 1.686 x 10^{-2} g/mg.min for Cr, 4.516 x 10^{-3} g/mg.min for Pb, and 2.259 x 10^{-2} g/mg.min for Ni, with R^2 of 0.965 for Cr and 0.971 for Pb and 0.972 for Ni. Periphyton can potentially play a role as a bio-accumulator in lotic habitats, adsorbing Cr, Pb, and Ni ions, according to this study.

Keywords: sorption capacity, sorption kinetics, Spirogyra, Cr, Pb, Ni

1. Introduction

Heavy metals are considered to be among the most serious ecological issues, as well as one of the most difficult to address. Heavy metals such as mercury, lead, arsenic, chromium, copper, cadmium, and nickel are frequently employed in the industrial sector, particularly in metal polishing and plating, as well as in products such as batteries and electronic equipment (Ali *et al.* 2021). Heavy metal-containing wastewater has been a serious cause of concern due to its toxicity, environmental persistence, bio-accumulative nature, and carcinogenic effects (Vertinsky, 2021). Even a trace amount may cause severe physiological and neurological consequences (Jaishankar *et al.* 2014; Ali et al. 2021). As a consequence, several attempts have been made to prevent or reduce this type of possible health threat.

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As a result, algae might serve a significant part in removing heavy metals from aquatic ecosystems and can contribute to environmental sustainability (Goswani *et al.* 2022). Algae are an enormous and diversified grouping of simple plant-like organisms that occur in freshwater, maritime, and wetlands areas, that vary from single-cellular to multi-cellular species. This bio-sorbent has received substantial research because of its widespread presence in nature. Algae has found uses as a compost, energy source, pollution reduction tool, stability substance, and nourishment, among other things. Recently, the metal adsorption capabilities of untreated and treated algae have been investigated. A lightweight, stiff cell membrane encloses the algal cells, with pores 3 – 5 nm wide that allow molecular-weight components such as water, ions, gases, and other elements to move freely across for growth and metabolism. Cell walls, on the other hand, appear to be impervious to bigger particles or macromolecules (Shamshad *et al.* 2014; Shamshad *et al.* 2016).

Algae in freshwater can acquire heavy metals via the sorption process, which comprises either physical as well as chemical sorption. The distinctive cell wall component structures in algal biomass, particularly through the cellular surfaces and cell wall spatial structure, determine the nature of metal bioaccumulation by algae (Znad *et al.* 2022). Through physical interactions and van der Walls forces, algae bind heavy metals to the surface of algae cells through physical adsorption (Yogeshwaran & Priya, 2022; Zeng *et al.* 2022). Algae cells' negatively charged surfaces can bind positively charged metal ions like chromium (Cr^{6+}), lead (Pb^{2+}), and nickel (Ni^{2+}). Chemical adsorption involves chemical bonding such as complexation, chelation, and exchange of ions between the outer layer of algae cells and metallic ions. Various functional groups in algal cell wall polysaccharides, such as carboxyl, hydroxyl, sulfate, sulfhydryl (thiol), phosphate, amino, amide, imine, thioether, phenol, carbonyl (ketone), imidazole, phosphonate, and phosphodiester, have the attributes to be associated with metal bonding (Omar, 2013; Ahmad *et al.* 2019; Spain *et al.* 2021). Some algae are capable of heavy metal absorption into specific organelles or intracellularly. High heavy metal concentrations, on the other hand, can harm the integrity of the algal cells (Ge *et al.* 2022).

Research using dried Spirogyra biomass as a biosorbent against heavy metals Pb, Cu (Lee et al. 2011), Cr (Onyancha et al., 2008), Ni (Guler & Sarioglu, 2013), Fe and Pb in fixed bed column (Yahya et al., 2020), Mn, Zn, Cd (Rajfur et al., 2010), and textiles dyes (Khataee et al., 2013) has been widely carried out, however, the sorption mechanism for the bioaccumulation of natural Spirogyra biomass in lotic waters and its potential for biomagnification in the food chain is still not well-informed. The purpose of this research was to assess the ability of the species of freshwater algae *Spirogyra* sp. to accumulate heavy metals Cr, Pb, and Ni ions. The effects of contact time, biomass weight, and initial level of heavy metals on capacity and biosorption efficiency were investigated and assessed. As a result, this work contributes to a better understanding of heavy metal pollution at compartment levels such as water and algae in lotic waters.

2. Materials and Methods

The experimental study was conducted at the Research Centre for Limnology and Water Resources, BRIN – Indonesia. This research includes several stages, (i) canal system development, (ii) colonization of periphyton, (iii) preparation of ion Cr^{6+}, Pb^{2+}, and Ni^{2+} solution, (iv) metals bioaccumulation test using periphyton.

The materials used were algae of *Spirogyra sp*, HNO_3 65%, standard solution of Cr, Pb, and Ni 1000 mg/L, NPK solution in 2 mg/L, and deionized water. Instruments used were Spectrophotometer UV-Vis 1800 Shimazu, GF-AAS Hitachi Z2000, Infrared Spectrophotometer Transformation Fourier (FTIR) Shimadzu IRPrestige-21, microscope Nikon Diaphot 300, analytical balance Ohaus, vacuum filters Eyela A-3S, oven Memmert, hotplate magnetic stirred Ika C-Mag HS-7, and glassware in the laboratory.

(i) The canal system was designed to simulate the stable condition of lotic water. The canal system was manufactured of acrylic and had

dimensions of a length and width of 1.2 and 1.0 meters, respectively. It was filled with 132 L of water and had a periphyton area of 1.20 m^2. The water depth ranges from 0.09 to 0.10 m, with a current flow rate of 0.04 – 0.06 m/s.

(ii) The periphyton was grown in a canal system by spreading *Spirogyra* sp. seeds and adding a 2 mg/L NPK solution. The attached periphyton grew to the substrate for two weeks, assuming that periods are sufficient to determine the homogeneity of periphyton that grow in the lotic layer. To determine the prevalent periphyton algae species, samples of growing periphyton were taken during the acclimatization period, at the beginning and end of the observation, and examined under a microscope.

(iii) Ion Cr^{6+} solution was obtained at 1.64 mg/L, Pb^{2+} dan Ni^{2+} at 1.40 mg/L using a standard solution of ion Cr, Pb dan Ni 1000 mg/L. The concentrations used are ion Cr, Pb, and Ni effective concentration of 50% (EC50) (Yap *et al.* 2004).

(iv) The preparation of 1000 mL of 50 mg/L Cr^{6+} stock solution from $K_2Cr_2O_7$ was established by weighing 0.14144 grams of dry $K_2Cr_2O_7$, which was then weighed and dissolved in a 1000 mL volumetric flask with demineralized water. A 1.64 mg/L Cr solution was pipetting 3.28 mL of 50 mg/L Cr (VI) stock solution into a 100 mL volumetric flask and adding demineralized water to exactly 100 ml.

(v) A 50 mg/L Pb and Ni standard solution was made by pipetting 5 mL of a 1000 mg/L Pb and Ni standard solution and diluted in 100 mL of demineralized water using a volumetric flask. A 1.4 mg/L Pb solution was prepared by pipetting 2.8 mL of a 50 mg/L Pb and Ni solution into a volumetric flask and adding demineralized water to exactly 100 ml.

(vi) Cr^{6+} measurements were carried out by pipetting 3 mL of water samples and adding 0.15 mL of 50% H_2SO_4, 0.5 mL of 0.5% diphenyl carbazide, and 9 mL of demineralized water. Then the sample was left for 5 minutes and its absorbance was measured at 540 nm using a UV-Vis spectrophotometer.

(vii) Periphyton structures were analyzed before and after the bioaccumulation process. Periphyton samples were dried and mixed with KBr. The mixture was crushed until it became a fine particle and then pressed to form pellets. The pellets obtained were inserted into the sample holder and the infrared absorption spectrum was observed between 400 and 4000 cm^{-1} wavelengths. Bioaccumulation of metal ions using periphyton was observed for time periods of 0, 15, 30, 60, 120, 240, 480, and 1140 minutes after metal exposure to determine the sorption rate. Periphyton biomass and water samples were taken randomly. Water samples were digested with 65% HNO_3 according to standard methods (APHA, 2012). Periphyton biomass attached to the substrate was brushed and then dried at 40°C, weighed for its dry weight, and then digested with 65% HNO_3 according to standard methods (APHA, 2012). The solution was measured using AAS at a wavelength of 540 nm for Cr, 261 nm for Pb, and 232 nm for Ni. The heavy metal content in periphyton biomass was analyzed based on total Cr, Pb, and Ni.

The sorption capacity can be calculated by the formula in Equation 1:

$$Q = \frac{V(C_0 - C_t)}{m} \quad \text{....Eq. 1}$$

The sorption efficiency can be calculated using the formula in Equation 2:

$$\text{Efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad \text{....Eq. 2}$$

where:
Q = adsorption capacity per biomass weight (µg/g biomass)
V = volume of solution (mL)
C_0 = metal level at t 0 (mg/L)
C_t = metal level at t (mg/L)
m = periphyton biomass (g)

Kinetics of biosorption. The rate of pseudo-first-order (PFO) biosorption kinetics rate equation was proposed by Lagergren (1989) for the adsorption of a liquid-solid system derived from solid adsorption capacity. A PFO kinetic model's linearized equation is expressed as Equation 3 follows (Satya *et al.* 2020):

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \quad \text{....Eq. 3}$$

to get the k_1 and q constants, the equation above can be derived from Equation 4:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad \text{....Eq. 4}$$

where:
k_1 = the constant of PFO (min^{-1})
q_e = the number of metallic ions adsorbed at equilibrium
q_t = the number of metallic ions adsorbed at t (mg/g)

The rate of pseudo-second-order (PSO) kinetics was evaluated from Equation 5 which may be written below (Satya *et al.* 2020):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \text{....Eq. 5}$$

where:
k_2 = the constant of PSO ($g/mg.min^{-1}$)
q_e = the number of metallic ions absorbed at t (mg/g).

The formula can be modified into the passage that follows linear by separating the variables in the formula and fostering the equation under the constraints of t = 0 to t and qt = 0 to t:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad \text{....Eq. 6}$$

where:
h = the $k_2 q_e^2$ constant (mg/g.hr). The constant of PSO (k_2) was obtained through experiment by graphing t/qt against t.

3. Results and Discussion

3.1. The dominant type of algae community

Periphyton colonies formed on the rock substrate for two weeks (Figure 1a) until green filamentous algal periphyton were obtained (Figure 1b). Filamentous algal periphyton grows longitudinally and covers practically the entire rock surface, reaching a biomass density acceptable for bioaccumulation testing. The canal system's water temperature ranges from 25 to 35^0C, while the pH ranges from 7 to 9. The dissolved oxygen content measured ranged from 5 to 15 mg/L. This condition meets the parameters for periphyton growth, with temperatures ranging from 20 to 36^0C and pH ranging from 7.5 to 8.4 (Nybakken, 1993).

The periphyton colonies were dominated by filamentous algae from Chlorophyta, *Spirogyra* sp., unicellular algae *Cosmarium* sp., and diatoms. Spirogyra is a genus that is commonly found in freshwater environments. Microscope images demonstrate Spirogyra's unbranched form and spiral-shaped bands of *Spirogyra's* chloroplast (Lee & Chang, 2011).

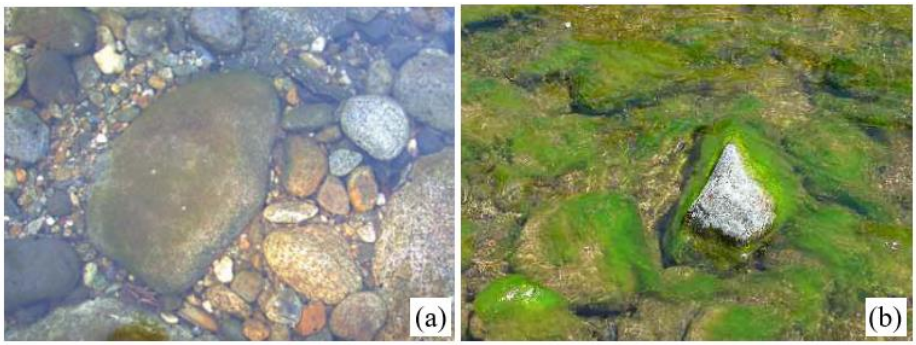

Figure 1. (a)Rock substrate used for periphyton growth, (b) periphyton colonies obtained after two weeks

3.2. FTIR Spectrum

Algal cells are comprised of polysaccharides with ion exchange properties such as cellulose, acid alginic, and sulfate (Loukidou *et al.* 2004; Turker & Baytak, 2004). This polymer has several groups with functions that can act as metallic ion binding regions. During or following the adsorption of the Cr, Pb, and Ni processes, the periphyton was analyzed using FTIR to observe changes in the functional group contained in the periphyton. The FTIR spectrum before the adsorption process shows similarities to the FTIR spectrum of Spirogyra (Table 1). The FTIR spectrum of Spirogyra displays hydroxyl (O-H) and amine (N-H), carboxyl (C-H), and carbonyl (C-C and C=O) functional groups (Onyancha *et al.* 2008).

Interaction of Spirogyra with heavy metals, carbonyl, and carboxyl groups in molecules such as proteins, amino acids, lipids, or carbohydrates can all play a part in heavy metal binding. Pb, Cr, and Ni may react with complexity with these groups, influencing the structure and function of algal molecules. The hydroxyl group contains oxygen, which can act as an electron pair donor in coordination bonds with heavy metals. Pb, Cr, and Ni ions can form bonds with hydroxyl oxygen, which is found on the surface of algae in molecules such as alcohol, phenol, or sugar. Lignin molecules in algal cell walls include phenol groups. Carboxylate groups also include oxygen, which can link to heavy metals. Heavy metals can make complicated interactions with oxygen carboxylates in fatty acids or amino acids in algae. This is often accomplished through coordination bonding, in which oxygen carboxylate functions as an electron donor to create bonds with metal cations. Algae amine groups can form coordination connections with heavy metals. Heavy metals can form strong coordination bonds with electron pairs on amine nitrogen. Although these interactions are often weaker than those via hydroxyl or carboxylates, amines can nonetheless contribute to heavy metal binding.

Table 1. Periphyton spectrum IR comparison before and after Cr, Pb, and Ni adsorption

Adsorption wave number (cm^{-1})			Chemical bounds
Periphyton before adsorption	Periphyton after adsorption	*Spirogyra* (Onyancha *et al.* 2008)	
–	–	3622	N–H
3339	3420	3341	O–H
2926	–	2925	C–H
–	–	2360	–CC–
1654	1653	1656	C=O and COOH
1425	1425	–	C–H
1037	1038	1038	C–O
876	–	–	C–N–S

Pb, Cd, Hg, and Zn have a great affinity for sulfide groups. Sulfide-heavy metal interaction can result in less solubility precipitation of heavy metal sulfides. Sulfide groups found in algal components such as cysteine and glutathione can help heavy metals bind via coordination interactions. A carbon atom is doubly linked to an oxygen atom to form the carbonyl group (C=O). Because of the difference in electronegativity between carbon and oxygen, this group displays substantial polarity. Coordination bonds, in which the oxygen atom functions as an electron pair donor to create bonds with metal cations, allow the carbonyl group to interact with heavy metals. Interactions between carbonyl groups in protein or carbohydrate molecules and heavy metals occur in Spirogyra. A carboxyl group is a complex structure made up of the group carbonyl (C=O) and hydroxyl (OH) which are both connected to one single carbon atom. This group offers organic compounds acidic properties along is capable of creating coordination bonds with metallic substances. In bonding with heavy metal cations, an oxygen atom that is part of the carboxyl acts as an

electron pair. The carboxyl group is more polar in general and can interact with heavy metals in a variety of chemical compounds found in *Spirogyra* sp.

3.3. Bioaccumulation of Cr, Pb, and Ni using periphyton

The ideal biosorbent has to be one that can speedily adsorb large quantities of metals from wastewater and desorb them using chemical substances (Singh *et al.* 2007). The relationship of dissolved Cr, Pb, and Ni metal ion concentration in waters with time is presented in Figure 2.

Rapid bioaccumulation of Cr and Pb occurred in the first 480 minutes, and Ni occurred until 1440 minutes. At the adsorption time of 480 minutes, the remaining Cr and Pb concentrations in the water were 0.96 mg/L and 0.14 mg/L and at the adsorption time of 1440 minutes, the water's residual Ni content was 0.03 mg/L. During this time, ion exchange and physical adsorption rapidly that occurred are suspected on the periphyton surface cell wall. The adsorption rate of metals was very high during the first 8 hours, reaching about 85% of the total adsorption with Cr, Pb, and Ni concentrations remaining in water at 0.96 mg/L, 0.14 mg/L, and 0.09 mg/L, respectively. Then the adsorption rate starts to remain constant towards the equilibrium state. Ion Pb was adsorbed faster at the beginning because Pb's radius (0.175 nm) is bigger than Cr (0.139 nm) and Ni (0.072 nm), so the active site on the adsorbent surface saturates faster. The subsequent slow phase of adsorption may involve other mechanisms, such as saturation of the active site, complexation, or micro-precipitation (Lee & Chang, 2011; Onyancha *et al.* 2008). The concentration of Cr in the water at twenty-four hours of adsorption was 0.43 mg/L, Pb was 0.05 mg/L, and Ni was 0.03 mg/L. The value of Cd and Pb are still higher than the quality standard for Class C according to The Ministry of Environmental Decree No. 115/2003 amounting to 0.03 mg/L while for Ni there is no certain standard value for standard quality.

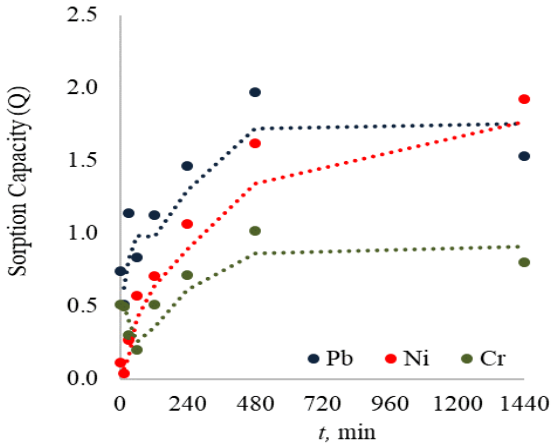

Figure 2. The sorption capacity of periphyton on Cr, Pb, and Ni

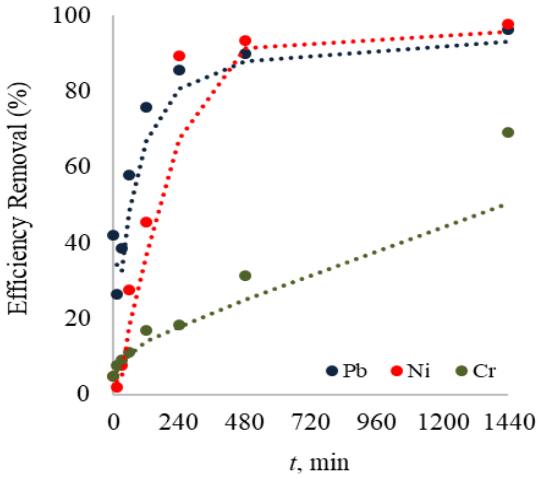

Figure 3. The sorption efficiency of periphyton on Cr, Pb, and Ni

Metal ion concentrations in periphyton biomass generally increase with time, but there is an inflection point on the Pb adsorption curve at 60 to 240 minutes. This decrease may occur depending on the circumstances or the process (Hill & Boston, 1991). In this study, the decrease could be caused by the presence of biological processes in periphyton which are living organisms. In addition, the random sampling process allows the extraction of stones of non-uniform thickness for each time of collection. The difference in nutrient consumption between periphyton colonies can also be the cause of the uneven metal adsorption process in the canal.

The composition of the type of periphyton growing in the canal system greatly affects the metal's capacity to bind in the waters. The differences in metal adsorption by various kinds of algae are mostly owing to variances in cell surface properties, particularly within the cell membrane. The outer layer of a cell is the main target of attaching metals in algae, and metal trapped on the surface frequently outnumbers metal accumulated in the internal compartment. (Andrade *et al.* 2005; Mehta & Gaur, 2005).

The biosorption capacity value was directly proportional to the biomass concentration. Biosorption was carried out at a media pH of 7 – 8, which is the optimum pH in the sorption process for Pb and Ni (Sing & Yu, 1998). Cr has a lower sorption capacity than Pb and Ni because Cr is more easily absorbed at pH which tends to be acidic (Imyim *et al.* 2016; Ding *et al.* 2022; Nafisyah *et al.* 2023). Pb, Ni, and Cr have the highest adsorption potential (Q_{max}) of 1.973 mg/g, 1.922 mg/g, and 1.019 mg/g, with the biosorption efficiency reduction Pb by 96.43%, Ni 97.86% and Cr 69.29% (Figure 3).

3.4. Sorption Kinetic

The bioaccumulation kinetics of Cr, Pb, and Ni were determined using the Lagergren equation. The Lagergren equation can be applied as pseudo-first-order (PFO) kinetics, assuming the number of metallic ions exceeds the percentage of active sites along the outer layer of the adsorbent. This formula becomes successfully utilized for modeling sorption kinetics data that occur in living microorganisms when concentrations are high and the process is constant (Loukidou *et al.* 2004; Gupta & Rastogi, 2008; Onyancha *et al.* 2008). Linear regression by passing log (*qe* – *qt*) against t will produce a PFO kinetics model with a constant value of k_1 (Figure 4).

The findings revealed the validity of the Cr, Pb, and Ni biosorption kinetics followed the PSO equation, indicated by a degree of determination coefficient (R^2) of 0.971, 0.972, and 0.965. According to Eq. 4, if the path is linear, the sorption mechanism is known as chemisorption. The PSO adsorption rate constants (k_2) for Cr, Pb, and Ni were 1.686 x 10^{-2}, 4.516 x 10^{-3}, and 2.259 x 10^{-2} g/mg. min, respectively (Figure 5).

The biosorption of metal ions in periphyton Spirogyra follows two phases. The first phase is rapid metabolism with adsorption on the outermost layer and cellular wall, the second phase is slow metabolism depending on transport across the cell membrane.

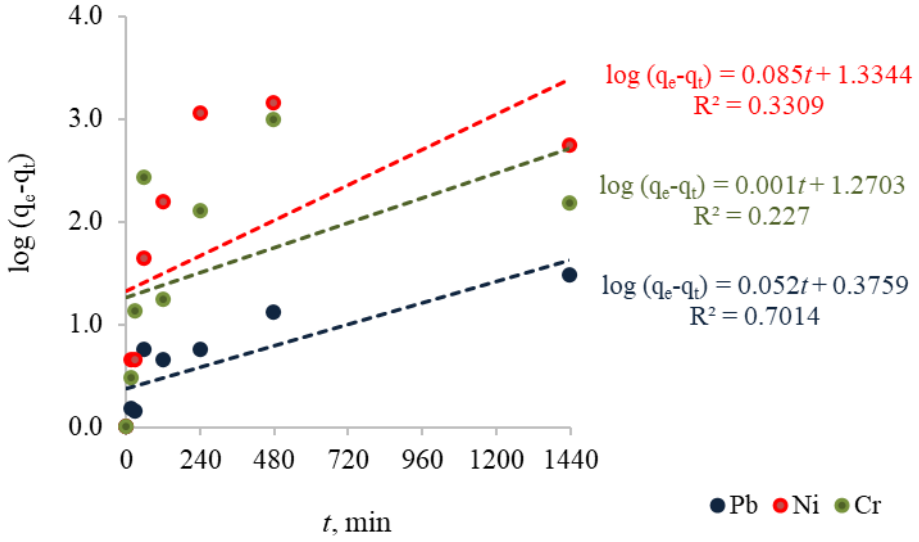

Figure 4. PFO sorption model of Pb, Ni, and Cr in periphyton biomass

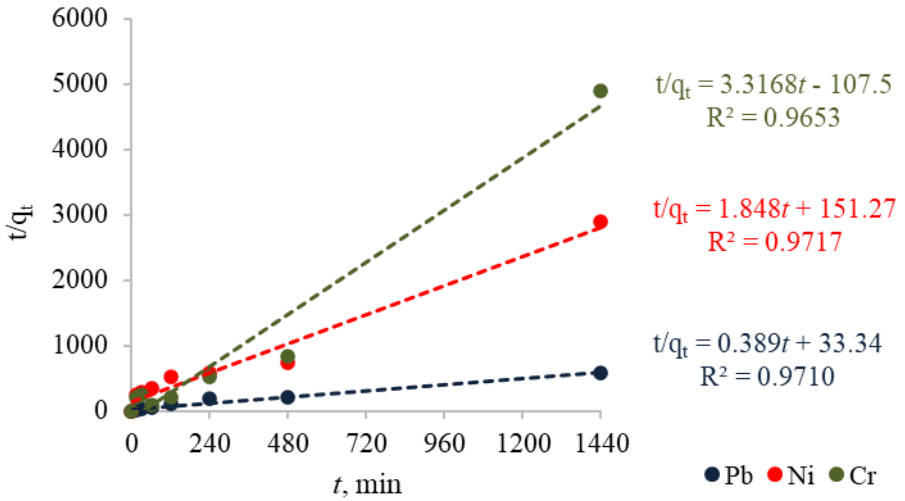

Figure 5. PSO sorption model of ion Pb, Ni, and Cr in periphyton biomass

4. Conclusion

Periphyton dominated by Spirogyra has the potential as a bio-accumulator for Cr, Pb, and Ni. The maximum biosorption capacity for Cr was 1.019 mg/g, Pb was 1.973 mg/g and Ni was 1.923 mg/g. The biosorption kinetics of Pb and Ni follow a pseudo-second-order reaction equation with a value of k_2 = 1.686×10^{-2} g.mg^{-1}.min^{-1} for Cr, k_2 = 4.516×10^{-3} g.mg^{-1}.min^{-1} for Pb and k_2 = 2.259×10^{-2} g.mg^{-1}.min^{-1} for Ni. The coefficient of determination (R^2) was 0.965 for Cr 0.971, for Pb, and 0.972 for Ni. The findings of this study can be used to characterize the bioaccumulation mechanisms of Cr, Pb, and Ni by periphyton Spirogyra in lotic waters.

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Author Contributions

ES and **FSL** as the main contributors conceptualized the study and data analysis, and wrote the original article. **RK**, **MRW**, **DO**, **EN**, and **NM** carried out the canal system construction, sampling, and analysis processes in the laboratory.

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