Adsorption of Cu(II) Ions on Adsorbent Materials Obtained from Marine Red Algae *Callithamnion corymbosum sp.*

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Abstract: In recent years, studies on the more efficient use of natural materials in adsorption processes have increased significantly. Thus, obtaining new adsorbents from marine algae biomass with higher adsorptive performance will ensure a better use of these renewable resources. In this study, the adsorption of Cu(II) ions from aqueous solution was done using three types of adsorbent materials obtained from marine red algae biomass (*Callithamnion corymbosum sp.*), namely: alginate (Alg), algae waste biomass resulted after alginate extraction (AWB) and iron nanoparticles functionalized with alginate (Fe-NPs-Alg), compared to raw marine red algae biomass (RAB). FTIR spectra and SEM images recorded for each type of adsorbent indicate a porous structure and the presence of various superficial functional groups who may be involved in the retention of Cu(II) ions. The biosorption experiments were performed in a batch system, at different initial Cu(II) ion concentrations and contact times, maintaining a constant initial solution pH (4.4), adsorbent dose (2.0 g/L), and temperature (25 ± 1 °C). The obtained results indicate that the retention of Cu(II) ions requires a maximum of 60 min to reach equilibrium, and the maximum adsorption capacity increases in order: RAB (47.62 mg/g) < Fe-NPs-Alg (52.63 mg/g) < AWB (83.33 mg/g) < Alg (166.66 mg/g). The quantitative removal of Cu(II) ions from aqueous effluents can be done in two successive adsorption stages, using AWB (in the first stage) and Fe-NPs-Alg (in the second stage), when the treated solution has a Cu(II) ions concentration below the maximum permissible limit. The quantitative recovery of retained Cu(II) ions (over 97%) can be done by treating these exhausted adsorbent materials with 0.1 N HNO_3 solution. Therefore, the extraction of alginate from marine red algae biomass could be a viable solution to obtain efficient adsorbent materials for Cu(II) ions removal from aqueous media, and allow for a better valorisation of marine red algae biomass.

Keywords: adsorption; Cu(II) ions; marine red algae biomass; aqueous media; valorisation

1. Introduction

One of the major environmental issues around the world is heavy metal pollution. The presence of heavy metal ions in water resources has become an important factor in degrading the quality of ecosystems globally, especially as they are toxic, persistent, and have a strong tendency to accumulate [1]. Industrial activities are considered the main sources of environmental pollution with heavy metal

ions. Thus, different industrial sectors, such as metallurgy, mining, electroplating, coating, fertilizers manufacturing, etc., [2–4] generate an important amount of effluents that contain huge amounts of heavy metals ions, and whose discharge without proper treatment is a threat to the quality of the environment. Therefore, it is necessary to find suitable methods that are environmentally friendly and remove heavy metal ions more efficiently and cheaply [5].

Traditional methods used for heavy metal ion removal from aqueous effluents, such as: chemical precipitation [6], electrochemical methods [7,8], membrane processes [9,10], solvent extraction [11], ion exchange [12,13] are costly, require high energy consumption, and in some cases can cause serious secondary pollution. Compared to these, adsorption is considered a favourable alternative for removing heavy metal ions from aqueous effluents, which involves the retention of heavy metal ions on the surface of solid materials [14]. The main advantages of this method are high efficiency even at low concentrations of heavy metals, recycling of adsorbent material, low energy consumption, and ease of operation [14–16].

Various materials, natural or agricultural and industrial wastes of biological origin, have been shown to have a high efficiency in retaining heavy metal ions from aqueous environments, under various working conditions [17,18]. Such materials used as adsorbents have in their composition numerous functional groups (hydroxyl, carboxyl, amino, phosphate, phenol, amide, sulphate, etc.) which can bind heavy metal ions from synthetic or industrial wastewater during removal processes [19,20]. This is the main reason why adsorption is considered a promising and flexible alternative method, which in addition to being readily adaptable on a large scale, also has a high selectivity and high efficiency to remove such pollutants [19].

One of the most used natural materials as an adsorbent for the removal of heavy metal ions from aqueous environments is marine algae. The marine algae are found in large quantities in many regions of the world, their preparation requires a small number of simple steps, and are of great interest to environmental engineering, as they have the ability to solve various environmental problems, such as wastewater decontamination, soil decontamination, soil quality improvement, etc. [21–23]. However, the removal of heavy metal ions from contaminated wastewater is the most known use of marine algae biomass in environmental engineering.

Numerous studies from literature have been presented the ability of different types of marine algae biomass to retain various heavy metals ions (Pb(II), Cd(II), Cu(II), Cr(VI), etc.) from aqueous media [24–26], and the encouraging results have indicate the potential applicability of this renewable resource in the adsorption processes. Unfortunately, their moderate adsorption capacities have drastically limited the use of such biomass in industrial-scale decontamination processes, for economic reasons. Therefore, viable technical solutions still need to be sought, so that the adsorption efficiency of the marine algae biomass is enhanced, and these materials become technologically viable.

One of the solutions proposed in the literature is the extraction of active compounds from marine algae biomass, such as alginate, agar, xylose, mannitol or caragenates, and their use in obtaining more efficient adsorbent materials [27,28]. In this way, the numerous superficial functional groups from the structure of marine algae biomass would become active to retain the heavy metal ions through adsorption, which will lead to an increase in the adsorptive performances of the obtained materials. In addition, if obtaining these materials does not require complicated preparation procedures, they can still be classified as low cost adsorbents, and retain all the advantages presented above.

Starting from these observations, in this study, marine red algae biomass (*Callithamnion corymbosum sp.*) was used as raw material for the extraction of alginate, in order to use the obtained materials (alginate and algae waste biomass (after alginate extraction)) as adsorbent for the removal of Cu(II) ions from aqueous solution. However, after precipitation and the separation of alginate, in the aqueous solution, there is still a significant amount of alginate that cannot be precipitated, due to its high solubility in water [29]. In order not to lose soluble alginate, this was used to obtain the iron nanoparticles functionalized with alginate, following an original procedure, described in a previous study. [30]. Thus from marine red algae biomass (*Callithamnion corymbosum*

sp.), three new adsorbent materials were obtained: algae waste biomass (after alginate extraction), alginate (extracted from red marine algae) and iron nanoparticles functionalized with alginate, and these adsorbents have been tested for the removal of Cu(II) ions from aqueous media, compared with the raw marine red algae biomass. The selection of Cu(II) ions for experimental studies was made taking into account the chemical properties and its industrial importance [31,32].

The novelty of this study is that it highlights the possibility of integrated use of marine algae biomass in the removal processes of metal ions from aqueous environments, in accordance with the principles of circular economy. Thus, from a low-performance adsorbent material, such as marine red algae biomass, three adsorbent materials, which can be more efficiently used to retain Cu(II) ions, are obtained by a simple and low-cost experimental procedure. To the best of our knowledge, such approach has not been presented so far in the literature.

In this study, the adsorptive performances of marine red algae biomass (RAB), algae waste biomass (AWB), alginate (Alg) and iron nanoparticles (Fe-NPs-Alg) functionalized with alginate were examined for different values of initial Cu(II) ions concentration and contact time, in the optimal experimental conditions (initial solution pH of 4.4 and adsorbent dose of 2 g/L). The experimental results obtained were modelled using isothermal and kinetic models to allow a quantitative evaluation of the adsorption processes. Also, desorption experiments were performed to test the recovery efficiency of the retained Cu(II) ions. The obtained results show that the extraction of alginate from marine red algae biomass (*Callithamnion corymbosum sp.*) could be a viable solution for obtaining efficient adsorbent materials for the removal of heavy metal ions from aqueous solution, and will allow for a better valorisation of these renewable resources.

2. Materials and Methods

2.1. Preparation and Characterization of the Adsorbent Materials

The red marine algae (*Callithamnion corymbosum*) were collected from the Black Sea coast, in August 2016. The collected biomass was washed with distilled water (several times) to remove solid impurities and dried in air for 8 hours, at 70 °C. After drying, the biomass was processed properly until the particle size was less than 1.5 mm and was kept desiccant for further use.

The alginate was extracted in alkaline media, when 5 g red marine algae biomass (*Callithamnion corymbosum*) was mixed with 100 mL of 1M NaOH solution for 4 hours, for the dissolution of sodium alginate from marine algae. The obtained liquid phase has been heated for 24 hours at 50 °C and then cooled to 10 °C, using an ice bath. The could solution was treated with 100 mL of 1M $CaCl_2$ solution and vigorously stirred for 2 hours, to precipitate the alginate salt. The obtained precipitate of calcium alginate was filtered, washed with distilled water and dried in air.

The iron nanoparticles functionalized with alginate were obtained by mixing 100 mL of $FeCl_2$ solution with 50 mL of $FeCl_3$ solution and adding 1 N NaOH solution until a pH of 10–11 was reached. The solution of $FeCl_2$ was obtained by dissolving 3.976 g of $FeCl_2$ in 100 mL of alginate solution (obtained after extraction from marine algae biomass), while the solution of $FeCl_3$ was prepared by dissolving 5.406 g of $FeCl_3$ in 50 mL of alginate solution. The mixture was stirred vigorously for 1 hour and then filtered, washed with distilled water and dried in air. More technical details about the preparation of iron nanoparticles functionalized with alginate have been presented previously [30].

The superficial functional groups of each adsorbent were examined by FTIR spectrometry (FTIR Bio-Rad Spectrometer (Perkin Elmer, Waltham, MA, USA), 400–4000 cm^{-1} spectral domain, 4 cm^{-1} resolution, KBr pellet technique), while the SEM images were recorded using SEM-Hitach S 3000N microscope (Hitach, Berlin, Germany).

2.2. Chemical Reagents

All the reagents used in the experiments were of analytical grade. The stock solution of copper (635 mg Cu(II)/L) was prepared by copper sulphate (Chemical Company, Iaşi, Romania) dissolving

in distilled water. Fresh working solutions were used for each experiment, which were obtained by diluting an exact volume of stock solution with distilled water. A solution of 0.1 N HNO$_3$ (Chemical Company, Iaşi, Romania) was used for the adjustment of initial solution pH, and in desorption studies.

2.3. Adsorption/Desorption Methodology

The adsorptive performances of the studied adsorbent materials (marine red algae biomass (RAB), algae waste biomass (AWB), alginate (Alg) and iron nanoparticles functionalized with alginate (Fe-NPs-Alg)) was tested in the removal processes of Cu(II) ions from aqueous solution. The experiments were performed in batch systems at different values of the initial concentration of Cu (II) ions and the contact time. Thus, 25 mL of Cu(II) ions solution (12–240 mg/L) and pH 4.4 were mixed with 0.05 g of each adsorbent, at room temperature (25 ± 1 °C) and well-defined time interval (24 h). The experimental conditions, initial solution pH 4.4, adsorbent dose of 2.0 g/L and room temperature (25 ± 1 °C) have been established as optimal in a previous study [30]. The liquid and solid phases were separated trough 0.45 mm filter paper, and the Cu(II) ions concentration was analyzed using a spectrophotometric method (Digital Spectrophotometer S 104D (JKI, Shanghai, China), rubeanic acid, λ = 390 nm, 1 cm glass cell, against distilled water, linear dynamic range = 0.5–3.5 mg Cu(II)/L). The same optimal conditions (initial solution pH of 4.4, room temperature) were used and in kinetics experiments, when 25 mL of Cu(II) ion solution with the initial concentration of 48 mg/L was added to 0.05 g of from each adsorbent, but the contact time between the two phases was varied between 5 and 180 min. After filtration, the analysis of Cu(II) ions in the solution was performed according to the method presented above.

The adsorption capacity (q, mg/g) and the removal percent (R, %) were calculated using the relations:

$$q = \frac{(c_0 - c) \times V}{m} \tag{1}$$

$$R = \frac{c_0 - c}{c_0} \times 100 \tag{2}$$

where c_0 and c are the initial and equilibrium Cu(II) ions concentration in solution (mg/g), *V* is a measure of solution (L), and *m* is the mass of adsorbent used in experiments (g).

In desorption experiments, 0.5 g of AWB and Fe-NPs-Alg adsorbents loaded with a known amount of Cu(II) ions (29.2–31.5 mg Cu(II)/g adsorbent) was mixed with 10 mL of 0.1N HNO$_3$ solution for 3 hours, and then filtered (0.45 mm filter paper). The concentration of Cu(II) ions in the resulted solution was spectrophotometrically analyzed as is described above. The desorption percent (D, %) of Cu(II) ions from each adsorbent material was calculated using the relation:

$$D = \frac{c_d}{q \times m} \times 100 \tag{3}$$

where: c_d is the concentration of Cu(II) ions desorbed from adsorbent (mg/L); *q* is the adsorption capacity (mg/g) and *m* is the amount of adsorbent used in desorption experiments.

2.4. Isotherm and Kinetics Modelling of Adsorption Processes

The quantitative description of the adsorption process of Cu(II) ions on each type of adsorbent was done using two isotherm (Langmuir and Freundlich models) and two kinetics models (pseudo-first order and pseudo-second order models). The linear equations of these models are well known in literature [33,34], and are summarized in Table 1.

Table 1. Linear equations of isotherm and kinetics models used for the analysis of the experimental results [33,34].

| Model	Equation	Notations
	Kinetics models	
Pseudo-first order	$\lg(q_e - q_t) = \lg q_t - k_1 \times t$	q_e, q_t—adsorption capacity at equilibrium and at time t;
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e}$	k_1—the rate constant of pseudo-first order kinetic equation; k_2—the pseudo-second order rate constant
	Isotherm models	
Langmuir	$\frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{q_{max} \times K_L} \times \frac{1}{c}$	q—adsorption capacity at equilibrium; q_{max}—the maximum adsorption capacity; K_L—Langmuir constant; K_F—Freundlich
Freundlich	$\lg q = \lg K_F + \frac{1}{n} \times \lg c$	constant; n—the heterogeneity factor

The best model that fits with experimental data was selected based on the values of correlation coefficients (R^2), obtained from the ANOVA statistical analysis.

3. Results and Discussion

3.1. Structural Characteristics of Adsorbents

It is well known that the performances of an adsorbent material in the adsorption processes of heavy metal ions from aqueous solution depend by its structural characteristics [35,36]. The most important structural characteristics of an adsorbent are determined by: (i) the number and nature of superficial functional groups, and (ii) the surface porosity. If the number of superficial functional groups is large and the surface is porous, the studied material has the potential to be used in the removal processes of heavy metal ions by adsorption.

In order to highlight the nature of superficial functional groups, FTIR spectra have been recorded for each adsorbent material considered in this study (RAB, AWB, Alg and Fe-NPs-Alg), and are presented in Figure 1. In all cases, the broadband at 3400–3500 cm^{-1} indicates the overlap of the O–H bonds in the hydroxyl groups (alcohols or phenols) and the N–H bonds in the aliphatic amines, followed by the presence of bands 2850–3000 cm^{-1}, which correspond to the C–H bond from aliphatic radicals.
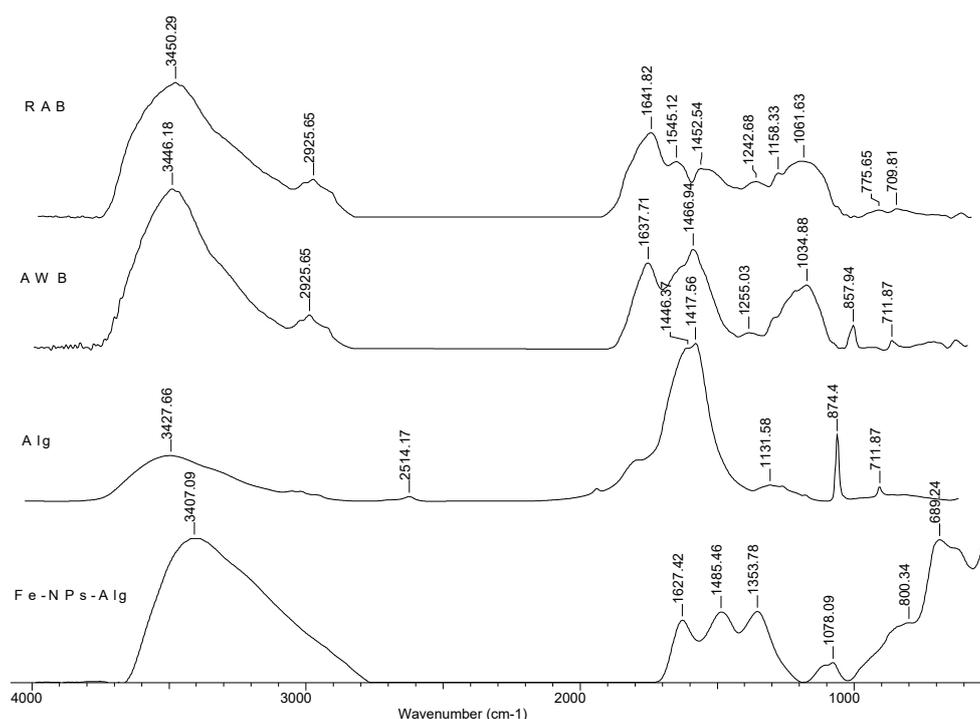
Figure 1. FTIR spectra of studied adsorbent materials.

The bands at 1600–1700 cm^{-1} can be assigned to the C=O bonds of carboxylic or/and carbonyl compounds, while the intense bands from 1000–1100 cm^{-1} are attributed to the axial deformation of the C–O bonds of ethers, esters, etc. The strong absorption band from 1450–1500 cm^{-1} which corresponds to the asymmetric deformation of C–OH bonds, indicates that these types of functional groups are present in all the adsorbent materials. The high intensity of this band in case of Alg shows that in this material, these functional groups are more numerous compared with the others. These observations suggest that the studied adsorbent materials have different types of superficial functional groups, and these functional groups can bind Cu(II) ions from aqueous solution. On the other hand, SEM images (Figure 2) indicate that all adsorbents have porous structure and opening shapes, which is also important from the perspective of their use as adsorbent materials. It should be also noted that, compared with RAB and AWB, on those surfaces large cracks can be observed (Figure 2a,b), Alg and Fe-NPs-Alg (Figure 2c,d) have a more aggregated morphology. This difference is a consequence of the way of preparing the adsorbent materials.
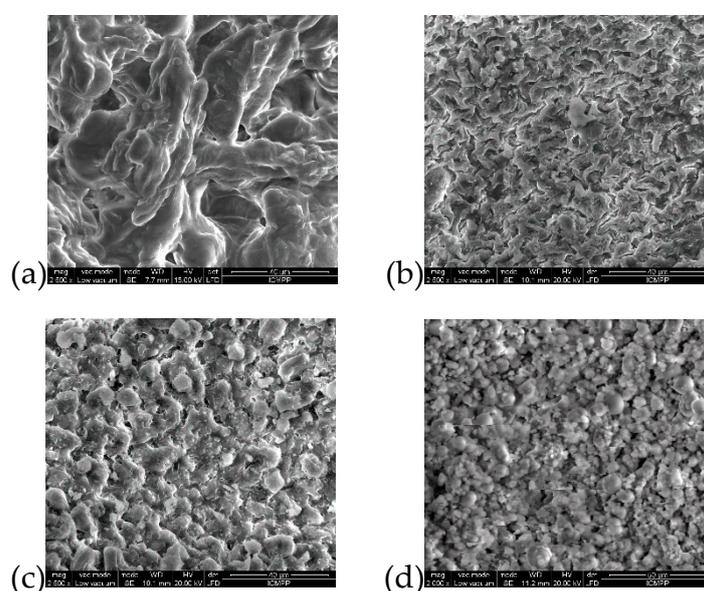

Figure 2. SEM images of RAB (**a**), AWB (**b**), Alg (**c**) and Fe-NPs_alg (**d**).

These observations suggest that the studied adsorbent materials have different types of functional groups on their surface, and these functional groups can play the role of binding sites for Cu(II) ions in aqueous media. On the other hand, SEM images (Figure 2) indicate that all adsorbents have porous structure and opening shapes, which is also important from the perspective of their use as adsorbent materials.

Therefore, in view of all these observations, it can be concluded that all the considered materials have a porous structure and numerous functional groups on their surface and can be used as adsorbents for removing Cu(II) ions from an aqueous solution.

3.2. Influence of Contact Time and Kinetics Modelling

At industrial scale, the equilibrium contact time is an important parameter for adsorption process optimization. Figure 3 shows the effect of contact time on the adsorption of Cu(II) ions using as adsorbents the four materials considered in this study, under optimal experimental conditions.
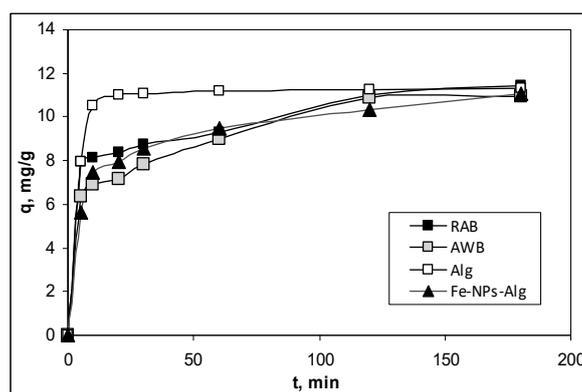
Figure 3. Influence of contact time on Cu(II) adsorption efficiency on considered adsorbent materials (initial pH = 4.4; 2.0 g adsorbent/L, c_0 = 25.41 mg Cu(II)/L, temperature = 25 °C).

As the contact time between the two phases of the adsorption system increases, the amount of Cu(II) ions retained on the adsorbent materials increases, in all the cases (Figure 3). This increase is more pronounced in the initial stage and depends on the nature of adsorbent material. In the case of RAB and AWB, this initial step lasts up to 30 minutes, and the amount of Cu(II) ions retained is 8.724 mg/g for RAB and 7.817 for AWB, while for Alg and Fe-NPs-Alg, the initial step lasts for up to 20 min, and the amount of Cu(II) retained varies from 11.004 mg/g for Alg and 7.928 mg/g, for Fe-NPs-Alg, respectively.

As the contact time between the solid and liquid phases of the adsorption system increases, the amount of Cu(II) ions retained on the adsorbent materials increases, in all the cases (Figure 3). This increase is more pronounced in the initial stage and depends on the nature of adsorbent material. In the case of RAB and AWB, this initial step lasts up to 30 minutes, and the amount of Cu(II) ions retained is 8.724 mg/g for RAB and 7.817 for AWB, while for Alg and Fe-NPs-Alg, the initial step lasts for up to 20 min, and the amount of Cu(II) retained varies from 11.004 mg/g for Alg and 7.928 mg/g, for Fe-NPs-Alg, respectively. After this initial stage, the adsorption process becomes much slower, and the values of adsorption capacity increase only by 10%–15% until the end of the experiments. From these observations, it can be considered that a contact time value of 60 min is sufficient to reach the equilibrium state in the case of the retention of Cu(II) ions for all studied adsorbent materials.

In the kinetic modelling of the adsorption process of Cu(II) ions from aqueous media on the considered adsorbent materials, two kinetic models, namely: the pseudo-first kinetic model and the pseudo-second kinetic model, were used. The selection of the most suitable kinetic model that fit the experimental data was made using linear regression. The kinetic parameters of the adsorption process of Cu(II) ions on the considered adsorbent materials, corresponding to the pseudo-first and pseudo-second order models, were calculated from the slopes and the intercept of the linear dependencies $lg(q_e − q_t)$ vs. t and t/q_t vs. t [33], shown in Figure 4, and the obtained values are summarized in Table 2.
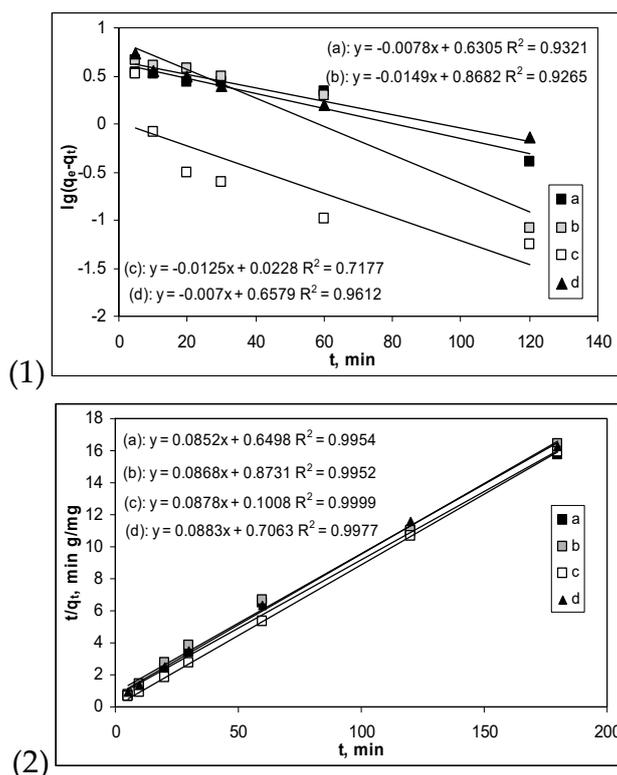
Figure 4. Linear dependences for pseudo-first kinetic model (**1**) and pseudo-second kinetic model (**2**) for Cu(II) ions adsorption on considered adsorbent materials ((a): RAB; (b): AWB; (c): Alg; (d): Fe-NPs-Alg).

Table 2. Parameter values of pseudo-first order and pseudo-second order kinetics models.

Adsorbent	RAB	AWB	Alg	Fe-NPs-Alg
q_e^{exp}, mg/g	11.4332	10.9632	11.3153	11.0621
Pseudo-first order kinetic model				
q_e, mg/g	4.2707	7.3824	1.0539	4.5488
k_1, 1/min	0.0078	0.0149	0.0125	0.0070
R^2	0.9321	0.9265	0.7177	0.9612
Pseudo-second order kinetic model				
q_e, mg/g	11.7371	11.5207	11.3895	11.3250
k_2, g/mg min	0.0072	0.0086	0.0764	0.0110
R^2	0.9954	0.9952	0.9999	0.9977

Comparing the values of the regression coefficients (R^2), it can be observed that the experimental kinetic data obtained for the adsorption of Cu(II) ions from aqueous solutions are best described by the pseudo-second order kinetic model ($R^2 > 0.99$), for all the cases. The values of calculated equilibrium adsorption capacities (q_e, mg/g) are similar with the experimental values (q_e^{exp}, mg/g), for all types of adsorbent materials used in this study.

Consequently, it can be said that in the mechanism of the adsorption process of Cu(II) ions from aqueous solutions on these adsorbent materials, an important role has the chemical interaction (probably electrostatic type) between the metal ions from aqueous media and the functional groups on the adsorbent surface.

Even if the values of adsorption capacities are similar for all adsorbent materials considered in this study (11.32–11.73 mg/g), suggesting that on the adsorbents surface are the same type of functional

groups, some important differences between the rate constants can be observed (Table 2). Thus, the rate constants calculated from the pseudo-second order kinetic model (k_2, g/mg min) increases in the order: RAB < AWB < Fe-NPs-Alg << Alg, and indicates that alginate has the most of superficial functional groups accessible for interactions with Cu(II) ions, and therefore in this case, the adsorption process will be the fastest. The very fast adsorption process of Cu(II) ions on Alg (ten times higher than in case of RAB—Table 2) represent an important argument which support the idea of extraction of active compounds from marine algae biomass, and using them to obtain adsorbent materials with increased efficiency. AWB and Fe-NPs-Alg have also better kinetics performances compared with RAB (see Table 2), and these are most likely due to the enlargement of the specific surface due to the breaking of the cell walls (in the case of AWB), or the binding of alginate chains on the nanoparticles surface (in case of Fe-NPs-Alg).

3.3. Influence of Initial Cu(II) Ions Concentration and Isotherm Modelling

The efficiency of the adsorption process is significantly influenced by the variation of the initial concentration of metal ions in the aqueous solution [34,36]. The influence of initial Cu(II) ions concentration on the adsorptive performances of considered adsorbent materials was examined in the concentration interval between 17.70 and 177.89 mg Cu(II)/L, at the optimum pH values (4.40) and adsorbent dose (0.05 g/L). The obtained experimental results are presented in Figure 5.
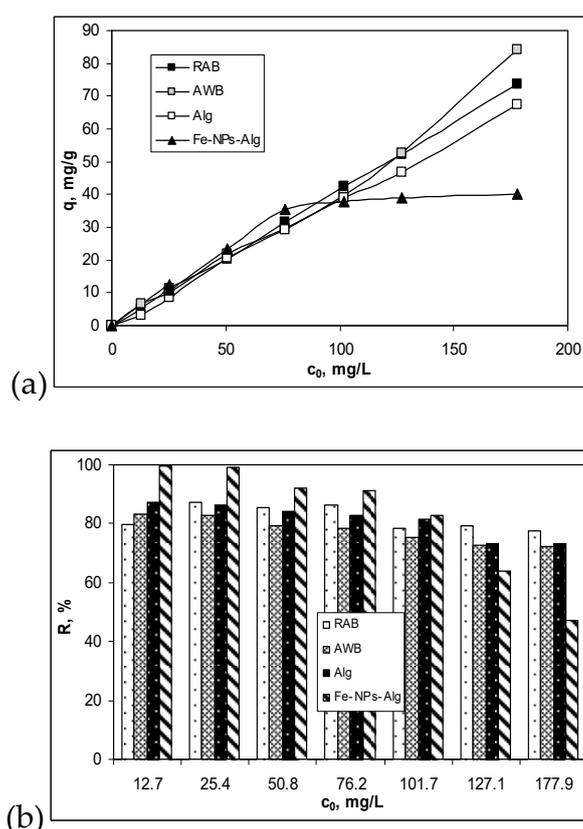

Figure 5. Influence of initial Cu(II) ions concentration on the adsorption capacity (**a**) and removal percent (**b**) for the studied adsorption processes.

It can be seen from Figure 5a that the experimental isotherms obtained for the adsorption of Cu(II) ions on the considered adsorbent materials are nonlinear, in the studied concentration range and two regions can be delimited in each case. In the first region, corresponding to the low concentrations of Cu(II) ions (0–30 mg/L), the all adsorbent materials have similar adsorptive performances, while in the second region (at initial Cu(II) ions concentration higher than 30 mg/L), the differences between

the adsorption capacities are much more obvious. Thus, at high initial Cu(II) ions concentration (177.89 mg/L), the most efficient seems to be AWB (q = 84.24 mg/g), followed by RAB (q = 73.47 mg/g), Alg (q = 67.58 mg/g) and Fe-NPs-Alg (q = 40.05 mg/g).

On the other hand, the removal percents (Figure 5b) decrease with the increasing of initial Cu(II) ions concentration 79% to 70% in case of RAB, from 83% to 72% in case AWB, from 72% to 42% in the case of Alg, and from 99% to 47% in case of iron Fe-NPs-Alg. This decrease is the direct consequence of the limited number of active centres available on the surface of the adsorbent materials, and this is a common behaviour for the adsorption processes [20,31,34].

The quantitative description of the adsorption efficiency of Cu(II) ions on considered adsorbent materials can be done by isotherm modelling. Two isotherm models, namely Langmuir and Freundlich models [34], have been used for the mathematical modelling of the experimental isotherms presented in Figure 5. The values of the characteristic parameters for each model were obtained from the linear representations (Figure 6) and are summarized in Table 3.
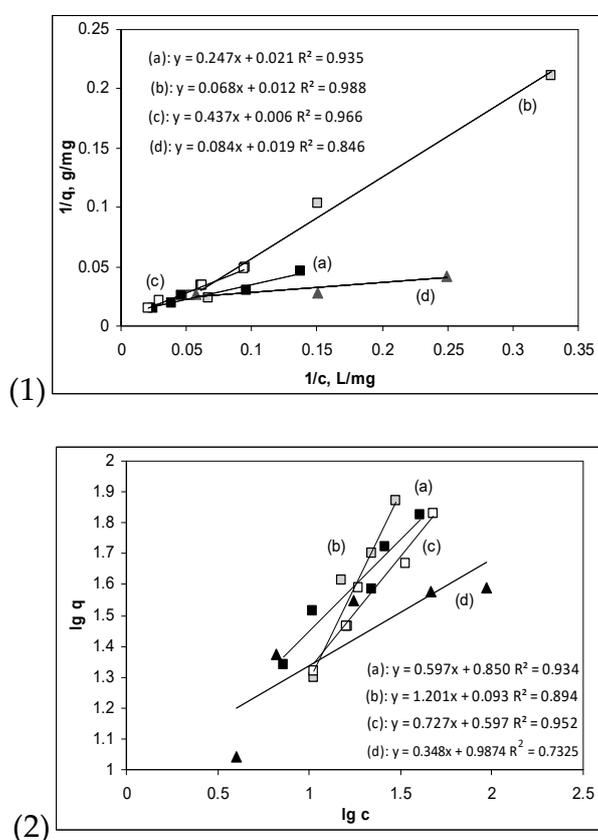
Figure 6. Linear representation of Langmuir isotherm model (**1**) and Freundlich isotherm model (**2**) for the adsorption of Cu(II) ions on studied adsorbent materials ((**a**): RAB; (**b**): AWB; (**c**): Alg; (**d**): Fe-NPs-Alg).

Table 3. Isotherm parameters for Cu(II) ions adsorption on considered adsorbent materials.

Adsorbent	RAB	AWB	Alg	Fe-NPs-Alg
Langmuir isotherm model				
q_{max}, mg/g	47.62	83.33	166.66	52.63
K_L, g/L	12.81	8.82	16.92	9.54
R^2	0.935	0.988	0.966	0.846
Freundlich isotherm model				
1/n	0.59	1.20	0.73	0.35
K_F, g/L	7.07	1.23	3.95	30.19
R^2	0.934	0.894	0.952	0.732

As can be seen from Figure 6, the Langmuir isotherm model better describes the experimental results compared with Freundlich model, for all considered adsorbent materials. Therefore, it can be said that the adsorption of Cu(II) ions from aqueous solutions is performed on the surface of the adsorbents until a monolayer coverage is completed, after which the intensity of the adsorption process decreases significantly and reaches equilibrium [36]. The amount of Cu(II) ions required for the complete formation of the monolayer coverage depends on the nature of adsorbent material, and the values of the maximum absorption capacity (q_{max}, mg/g), calculated based on the Langmuir model (see Table 3), indicate that Alg has the higher adsorption capacity, followed by AWB resulted after alginate extraction, Fe-NPs-Alg and RAB.

The different values of the maximum adsorption capacity show that in the adsorption process of Cu(II) ions from aqueous solution, an important role has the structural characteristics of the adsorbent material. Thus, Alg extracted from RAB has a large number of functional groups on its surface and can adsorb highest quantities of Cu(II) ions from aqueous media. In the case of AWB, the higher value of maximum adsorption capacity compared with RAB is mainly due to the increase of specific surface area, due to the breakdown of the cell walls during the extraction process of alginate [29]. Somewhat surprising is the maximum adsorption capacity obtained for Fe-NPs-Alg. The lower value of the maximum adsorption capacity compared to the values obtained for Alg and AWB (Table 3) shows that this adsorbent material has moderate adsorption performance for Cu(II) ions, and its efficiency can be increased by increasing the concentration of alginate used for functionalization. However, Fe-NPs-Alg is a more efficient adsorbent for the retention of Cu(II) ions from aqueous media than RAB (Table 3).

3.4. Practical Applicability

Considering all the observations presented above, it can be said that the extraction of alginate from the marine red algae biomass allows for obtaining more efficient adsorbent materials, which can be successfully used to remove metal ions from aqueous effluents. However, for practical applications, the following two aspects should be considered.

First, in the case of AWB and Alg, the variation of the removal percent is quite small (9%–13%) on studied initial Cu(II) ions concentration range, which means that these adsorbent have enough functional groups on their surface so that they can retain Cu(II) ions even at high concentrations. Unfortunately, the retention of Cu(II) ions from the aqueous solution on these materials is not quantitative even at low concentrations, and this suggest that not all the functional groups of these adsorbents are available to interact with Cu(II) ions from aqueous media. However, the adsorbents AWB and Alg can be used successfully in the first stage of treatment of industrial wastewater containing Cu(II) ions, when most of the metal ions can be removed. However, after such treatment, the Cu(II) ions concentration in residual solutions (obtained after filtration) (c, mg/L) is higher than the maximum permissible limit (according with Romanian regulation [37]) (see Figure 7a), and therefore a second stage of adsorption is required. In this second stage of adsorption should be used as adsorbent another

material, because as can be seen from Figure 5b, the removal percent obtained in case of AWB and Alg does not exceed 83% even at very low Cu(II) ions concentrations (12 mg/L).
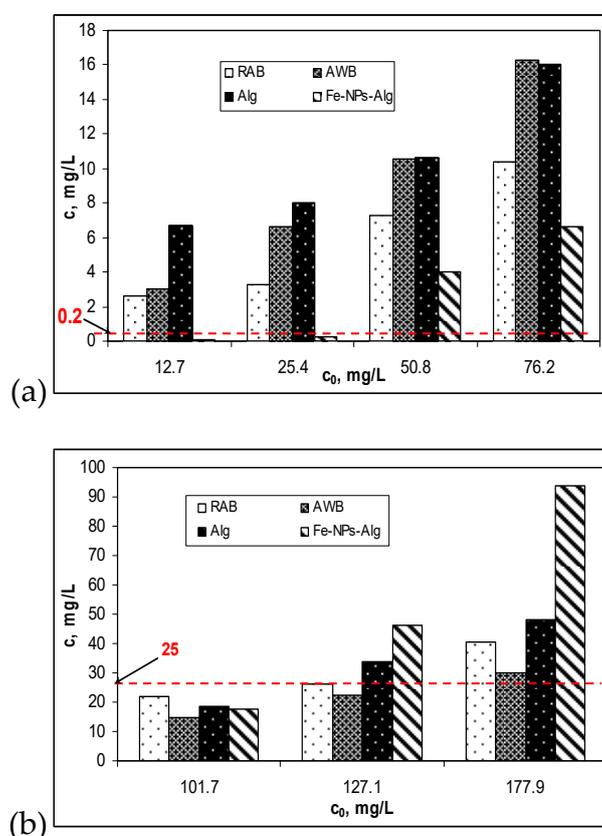

Figure 7. Variation of c (mg/L) vs. c_0 (mg/L), in low (**a**) and high (**b**) concentration range of Cu(II) ions.

Secondly, in the case of Fe-NPs-Alg, the obtained values of the removal percentage are higher than 99% in the concentration range of Cu(II) ions between 12–25 mg/L, and significantly decrease at the higher initial concentrations (Figure 5b). This variation indicate that the functional groups of Fe-NPs-Alg adsorbent are available for quantitative interaction with Cu(II) ions from aqueous solution, but their number is relatively small, so the removal of Cu(II) ions cannot be done quantitatively at concentrations greater than 25 mg/L (Figure 7a). Therefore, to improve the adsorptive performances of Fe-NPs-Alg, their preparation methodology should be improved, and this will be done in a further study.

Therefore, from a practical point of view, it is more advantageous to use AWB and Fe-NPs-Alg in two consecutive treatment steps, instead of using RAB for the removal of Cu(II) ions from industrial effluents. This is because the modest adsorbent performance of RAB in the removal of Cu(II) ions (Figure 5b) will not allow their concentration to fall below the maximum permissible limit (0.2 mg/L [37]), even if the treatment wastewater is carried out in two or more stages. The residual concentration of Cu(II) ions, even at lowest initial concentration (12.71 mg/L), is ten times higher than the maximum permissible limit (Figure 7a), which clearly indicates that the quantitative removal of Cu(II) ions cannot be made by using this adsorbent.

In contrast, if for the removal of Cu(II) ions is used AWB and Fe-NPs-Alg adsorbents in two successive stages: (i) first stage—AWB—for the removal of most Cu(II) ions, and (ii) second stage—Fe-NPs-Alg – for the quantitative removal of low concentration of Cu(II) ions, the treated industrial effluent will have a Cu(II) ions concentration lower that the maximum permissible limit [37], and the treatment system can be considered an efficient one. However, such treatment system can be

applied for the industrial effluents where the initial Cu(II) ions concentration is not higher than 170 mg/L (Figure 8).
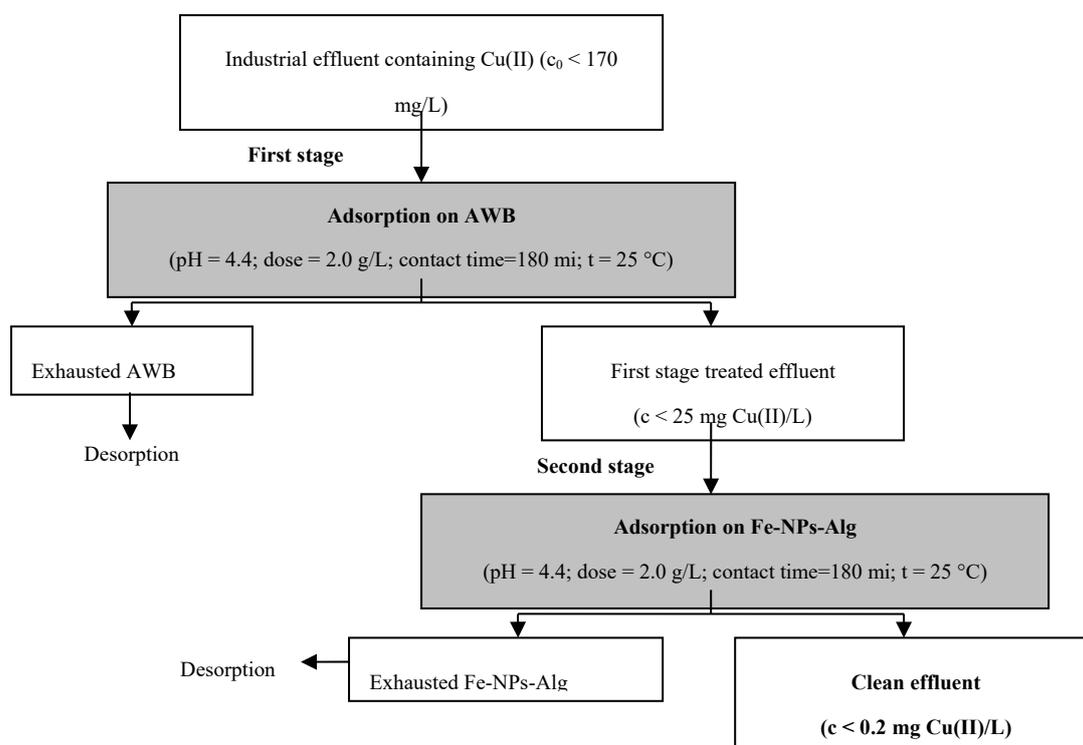
Figure 8. Schematic representation of the successive steps required to treat industrial effluents using AWB and Fe-NPs-Alg adsorbents.

All these estimations have been done bases of the experimental results presented above, which indicate that if the aqueous solution contains up to 170 mg Cu(II)/L and AWB is used as adsorbent, then after adsorption, the residual concentration of Cu(II) ions in aqueous solution is below 25 mg/L (Figure 7b). Under these conditions, the use of Fe-NPs-Alg as adsorbent in the second treatment stage will allow the quantitative removal of Cu(II) ions, and their concentration after adsorption decreases below 0.2 mg/L (Figure 7a). In this way, an efficient and simple treatment system for wastewater containing Cu(II) ions is obtained, which can be successfully used in industrial practice.

On the other hand, the extraction of alginate from marine red algae biomass allows a better valorisation of this type of renewable biomass, from adsorption processes point of view. This is because, after extraction AWB and alginate solution is obtained. If AWB can be used directly as adsorbent for the coarse removal of Cu(II) ions (with higher efficiency than RAB (see Figure 5a), the alginate solution is used to prepare Fe-NPs-Alg adsorbent, which is then used in the second stage of treatment (Figure 8). Therefore, compared with RAB, which is an adsorbent with moderate adsorptive performances regardless of the initial Cu(II) ions concentration (Figure 5a,b), AWB and Fe-NPs-Alg (obtained from RAB) can ensure the quantitative removal of Cu(II) ions from aqueous effluents. In addition, the experimental procedure used for this is simple, inexpensive and fast, and can be easily adapted to industrial scale.

3.5. Desorption and Recovery of Cu(II) Ions

The recovery of Cu(II) ions from exhausted AWB and Fe-NPs-Alg was done by treating 0.5 g of exhausted adsorbents (AWB and Fe-NPs-Alg, respectively) with 10 mL of 0.1 N HNO_3 solution and mixed for three hours. After filtration and analysis of solutions, the amount of Cu(II) ions desorbed

from exhausted adsorbents and desorption percents were calculated, and the obtained results are summarized in Table 4.

Table 4. Desorption efficiency of Cu(II) ions on exhausted AWB and Fe-NPs-Alg adsorbents.

Adsorbent	q, mg/g	$q_{desorbed}$, mg/g	D, %
AWB	31.72	30.96	97.61
Fe-NPs-Alg	29.58	29.07	98.28

As can be observed from Table 4, a quantitative recovery of retained Cu(II) ions is obtained in case of both adsorbent materials. In addition, the volume of the HNO_3 solution is relatively small, which allows a concentrated solution of Cu(II) ions to be obtained after desorption, which can then be reintroduced into the technological process.

All these experimental results highlight once again the possible uses of the studied adsorbents in the treatment of industrial effluents containing Cu(II) ions.

4. Conclusions

In this study, the adsorptive performances of the three adsorbents obtained from marine red algae biomass, namely: Alg, AWB (resulted after alginate extraction), and Fe-NPs-Alg, were studied comparatively with RAB, for the removal of Cu(II) ions from aqueous media. In all experiments, 0.05 g of each adsorbent was added to 25 mL of Cu(II) ions solution (12–240 mg/L), at pH 4.4 or 5.0, and ambient temperature (25 ± 1 °C). The increase of the initial Cu(II) ions concentration and the contact time leads to an increase of the adsorption capacity (q, mg/g), in all the cases. The pseudo-second order model was the best model in describing the kinetics of the adsorption process, while the experimental isotherms were best described by the Langmuir model. The values of the maximum adsorption capacity, obtained from the Langmuir model, follows the order: Alg > AWB > Fe-NPs-Alg > RAB, while the rate constant, calculated from the pseudo-second order model, increases in the order: RAB < AWB < Fe-NPs-Alg < Alg. The experimental results included in this study shows that the adsorbent materials separated from marine red algae biomass have better adsorptive characteristics than RAB, for the removal of Cu(II) ions from aqueous solution. The quantitative removal of Cu(II) ions from aqueous effluents can be done in two successive adsorption stages, using AWB (in the first stage) and Fe-NPs-Alg (in the second stage), when the treated solution has a Cu(II) ions concentration below the maximum permissible limit (0.2 mg/L). In addition, the quantitative recovery of retained Cu(II) ions from AWB and Fe-NPs-Alg highlight the possible uses of these adsorbents in the treatment of industrial effluents containing Cu(II) ions. Therefore, the extraction of active compounds from marine algae, and then their use as adsorbents for the removal of metal ions can be a viable solution, which can improve the practical applicability of marine algae in the environmental decontamination processes.

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