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# Effective removal of nickel(II) and zinc(II) in mono-compound and binary systems from aqueous solutions by application of alginate-based materials

A. Benettayeb<sup>a,b</sup>, E. Guibal<sup>b</sup>, A. Bhatnagar<sup>c</sup>, A. Morsli<sup>a,d</sup> and R. Kessas<sup>a</sup>

<sup>a</sup>Département de Génie Chimique, Laboratoire de Génie Chimique et de catalyse hétérogène, Université de Sciences et de la Technologie-mohamed Boudiaf, Oran, Algérie; <sup>b</sup>Polymers Composites and Hybrids (PCH), IMT Mines Ales, Alès Cedex, France; <sup>c</sup>Department of Separation Science, LUT School of Engineering Science, LUT University, Mikkeli, Finland; <sup>d</sup>Laboratoire de Chimie des Matériaux, Université Oran Ahmed Ben Bella, Oran, Algérie

## ABSTRACT

In the present study, beads of alginate, alginate-biuret and alginate-urea, were synthesised for the removal of Ni(II) and Zn(II) metal ions from aqueous solution (in single and in the bimetallic component solution). The properties of the synthesised sorbents were investigated by  $\text{pH}_{\text{PCZ}}$ , ESEM-EDX and ESEM. The modelling of experimental data demonstrate that the PSORE equation fits well the kinetic profiles, while Langmuir and also Sips models correspond well to the results of sorption isotherms (heterogeneous surface). Also, the spontaneous of process and endothermic nature of sorption was demonstrated by thermodynamic study. The maximum sorption capacity of 3.22, 4.73 and 8.53  $\text{mmol g}^{-1}$  was found for the beads of alginate, alginate-biuret and alginate-urea, respectively, in case of Ni(II) while it was 6.77, 6.97 and 7.14  $\text{mmol g}^{-1}$  for alginate, alginate-biuret and alginate-urea, respectively, in case of Zn(II). It was found that at 0.3  $\text{mmol L}^{-1}$  concentration, Zn(II) was selectively adsorbed while Ni(II) ions were concentrated/enriched in the solution in the case of alginate-urea, but alginate-biuret and alginate beads adsorbed almost the same amount of Ni(II) and Zn(II). In the bimetallic solution, the study of selectivity coefficients ( $K_s$ ) shows that the alginate-urea is a selective sorbent for Zn(II) and alginate-biuret for Ni(II) ions. Therefore, the two functionalised polysaccharides do not show the same harmony in front of the two-chemical species, thus, giving the possibility of their use as selective adsorbents in solutions containing these elements and can be used in applications of different interest.

## 1. Introduction

Various toxic heavy metal ions have been released (and still being discharged) into the environmental medium as a result of anthropogenic activities, causing serious soil and water pollution. Some of the common metals like Hg(II), Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) are that tend to accumulate in living organisms, and cause numerous diseases and

disorders. These metals are highly toxic and carcinogenic even at low concentrations in the range of 0.1–0.3 mg.L<sup>-1</sup> [1]. Over time, these metals are dispersed in nature in an uncontrolled way and can bioaccumulate and biomagnify in the food chain and may pose a serious threat to the environment and living organisms. Nickel and zinc are two important metals which are used in a large industrial processes, including; alloy preparation, metal plating, electronics, welds, fertilisers, fungicides, also these metals are used in manufacturing of paints, pigments, batteries, in the refinery and in the manufacturing of catalysts. These metals are among the essentials trace elements that can be found naturally and can be beneficial for the normal performance of biological cycles [2,3], but an increase in their concentrations can cause pollution and serious health problems for human health.

The releases of metal ions are a hazard to public health and the environment when discharged inappropriately. Many methods have been used to remove the metal ions from the wastewater, such as precipitation or solvent extraction process [4,5] (for the concentrated effluents), and reduction, precipitation, coagulation, flotation, membrane technologies, electrolysis and adsorption (*for the dilute effluents*).

Particularly, the sorption is considered to be one of the most promising techniques for heavy metal removal from wastewater [6,7], and we can use it in batch or column which is a preferable method to pass or real solution. This adsorption is the best economical method for an efficient elimination of these metals and this sorption operation can be carried out using chelation and/or ion exchange process. Several types of adsorbents are used for the treatment of heavy metals, and in addition to the classic normal-sized shapes, nanomaterials remain more advantageous in heavy metal removal and wastewater treatment because of their unique properties [8–10]. But the manufacturing cost remains high compared to some other type of adsorbent. However, because of the reduced cost of this process (process is inexpensive), the use of the biosorbents in the adsorption system can again reduce this cost and thus increase the efficiency of this process, it is for this reason that low-cost biosorbents have received increased attention in recent years. The use of biomaterials like chitin, chitosan, cellulose, algae and alginate for metals removal has increased significantly. Particularly, the alginate and chitosan gel beads have demonstrated as one of the most effective absorbents for eliminating low levels of heavy metal ions from the wastewater stream [11,12].

In particular, alginate and its derivatives have been used in wastewater treatment due to its high capacity of sorption of some heavy metal ions at their natural form also for its abundance, non-toxicity, biocompatibility, biodegradability. Also, it is not expensive compared to organic complex materials that are expensive and not useful [13].

The objective of this study was to examine the ability to use of the derivatives of alginate 'Alginate-urea and Alginate-biuret' [14] that were synthesised as biosorbent materials for the removal of Ni(II) and Zn(II) cations from water and the efficiency of these biomaterials was also examined in bimetallic solutions. This flexible modification has a capability of increasing the% of – N with simple ways in the matrix of alginate (grafting of urea and biuret in the alginate which increased the % of – N which slightly increased the efficiency, these materials synthesised from alginate is not expensive, and its obtained by a simple bio-grafting (1 g of alginate can produce a sufficient quantity).

The three models "Langmuir, Sips and Temkin" were used to fit the resultants of equilibrium isotherm. The behaviour of biosorption was examined by studying the effect

of initial metal ion concentration, adsorbent mass(SD), contact time and the efficiency of materials in binary systems was also examined in this work. The effect of temperature of the solution and thermodynamic parameters were also evaluated from the adsorption measurements. To present the kinetic results the two models of Pseudo first-order rate equation (PFORE) and pseudo-second-order rate equation (PSORE) were used.

## 2. Materials and Methods

### 2.1. Chemicals and materials

Sodium alginate (reference: *Protanal LF-240D*) was supplied by FMC (Cork, Ireland), La Madeleine, France, viscosity 11.5 mPa.s, molecular weight kDa, in alginate extracted from *L. digitata* the M/G fractions were 0.35/0.65 [15].

Calcium chloride (>99.5%) was purchased from Chem-Lab (Chem-Lab NV, Zedelgem, Belgium), urea and biuret (>99.0%) were obtained from Sigma-Aldrich (Taufkirchen, Germany). Deionised water (Milli-Q Millipore) was used in all experiments. The stock solutions of 1000 mg.L<sup>-1</sup> of Ni(II) and Zn(II) were prepared by dissolving the exact quantity of ZnCl<sub>2</sub> and (Ni(NO<sub>3</sub>)<sub>2</sub> + 6H<sub>2</sub>O) in an aqueous medium Milli-Q water. The solutions used in this work were prepared by diluting the stock solution to the desired concentrations

In this study, the change in the values of pH was assessed before and after the sorption process, when preparing solutions the pH of each one was fix to the desired value by using 1 M HCl or NaOH and the change in the final pH is checked severely in order to evaluate the potential precipitation phenomena associated with pH variation we used a pH-metre cyber scan pH 6000 with four digit (Eutech Instruments, Nijkerk, Netherlands). The analysis of C<sub>0</sub> and C<sub>eq</sub> after the sorption test was calculated by inductively coupled plasma atomic emission spectrometry (ICP-AES, JY Activa M, Jobin-Yvon, Horiba, Longjumeau, France).

### 2.2. Biosorbents preparation

Alginate and his derivatives, Alginate-urea and Alginate-biuret, was prepared following the procedures of study of [14]. In brief, for preparing alginate beads, sodium alginate was dissolved in Milli-Q water (about 3.4% w/v) by mixing 3 g of the biopolymer with 84 mL of water. And for alginate-urea and alginate-biuret a known mass of the Alginate was added to water (3 g + 84 ml Milli-Q water) in a presence of urea or biuret (1.116 g) and the mixture was heated under reflux at a specific conditions (50°C for 3 h). The chemically modified alginate solution was distributed dropwise in the ionotropic gelation solution (0.2 M CaCl<sub>2</sub> solution) [14]. For more detail see supplementary material (**Section I, Additional material section**).

### 2.3. Characterisation of materials

The pH of zero point of charge (pH<sub>zpc</sub>) was determined in the study of (A. Benettayeb et al., 2017, Section I, See Additional material section), by the pH drift method following the protocol described in [16–18].

The morphological structure of the alginate-urea, alginate-biuret and alginate were visualised by Environmental scanning electron microscopy ESEM (Quanta FEG 200, FEI France, Thermo Fisher Scientific, Mérignac, France) and ESEM-EDX (SEM coupled with energy dispersive X-ray diffraction analysis), equipped with an Oxford Inca 350 energy-dispersive Xray (EDX) system for chemical analysis, micro-analyser (Oxford Instruments France, Saclay, France).

Some samples of sorbents were analysed before and after sorption (T: 20°C; pH:5.5; SD: 0.1 g (d.w.) L<sup>-1</sup>; agitation speed: 150 rpm; t: 8 h; C<sub>0</sub>: 0.3 mmol L<sup>-1</sup>), ESEM-EDX analysis was used to detect the major elements exist on the surface of the sorbents for the analysis of the semi-quantitatively composition of the beads.

## 2.4. Sorption tests

A known amount (0.005 g) of sorbent was agitated with a volume of 50 mL of aqueous metals solution, (adsorbent dose;SD = 0.1 g/L; moist weight; sorbent mass, m (g) and volume of solution, V (L)). The flasks were agitated for 8 h at 150 rpm at room temperature (i.e. T: 20 ± 1°C).

The initial nickel and zinc concentration (i.e., C<sub>0</sub>, mg metal L<sup>-1</sup>) were varied between 4 and 300 mg metal L<sup>-1</sup>. at equilibrium the samples are filtered and the residual zinc and nickel ions concentrations (C<sub>eq</sub>, mg metal L<sup>-1</sup>) in the aqueous phase were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, JY Activa M, Jobin-Yvon, Horiba, Longjumeau, France).

The sorption capacity (q<sub>eq</sub>, mg metal g<sup>-1</sup>) was calculated by the mass balance equation;

$$q(\text{mg g}^{-1}) = V/m(C_0 - C_{\text{eq}}) \quad (1)$$

and the percent of removal (%) was calculated using the following equation:

$$\% \text{ Removal} = \frac{(C_0 - C_{\text{eq}})}{C_0} \times 100 \quad (2)$$

The distribution coefficient, K<sub>d</sub> is obtained by the q<sub>eq</sub>/C<sub>eq</sub> ratio using the following equation:

$$K_d = V/m[(C_0 - C_{\text{eq}})/C_{\text{eq}}] \quad (3)$$

The information important for the experimental conditions are methodically reported in the figures caption: in most cases, SD = 0.1 g/L, the equilibrium time was 8 h (experiments were performed at room temperature; i.e. 20 ± 1°C) and the pH was set at 5.5. It is noteworthy that the sorbents were practically used as wet beads (*to prevent the irreversible collapse of the porous structure of the hydrogel*) while the sorption capacity was determined on the basis of dry sorbent weight [14].

## 2.5. Modelling of kinetics and sorption process

As is summarised in the work of S. Wang et al., (2017) the sorption isotherms represent the solute distribution at equilibrium between the liquid and the solid phases for different initial metal concentrations. The sorption capacity (q) is plotted vs. the residual metal

concentration ( $C_{eq}$ ) [19]. To evaluate the results obtained in this study, some important equations have been reported and tested for the modelling of the results of sorption isotherms; the Langmuir (see Supplementary Information, Section V, Equation AM1 [20]), Sips (see Supplementary Information, Section V, Equation AM2 [21]), and Temkin equations (see Supplementary Information, Section V, Equation AM3 [20]).

The most common models used to fit the kinetic sorption experiments are pseudo-first-order model (PFORE, see Supplementary Information, Section V, Equation AM4) [22–24], and pseudo-second-order model (PSORE, see Supplementary Information, Section V, Equation AM5 [25,26]). For more details on the models used in this part see Additional Material Section V. Knowing that the choice of the best model which is adapted to the experimental data is chosen according to estimated variance (i.e. EV) or/and the coefficient of determination (i.e.  $R^2$ ).

### 3. Results and Discussion

#### 3.1. Characterisation of materials

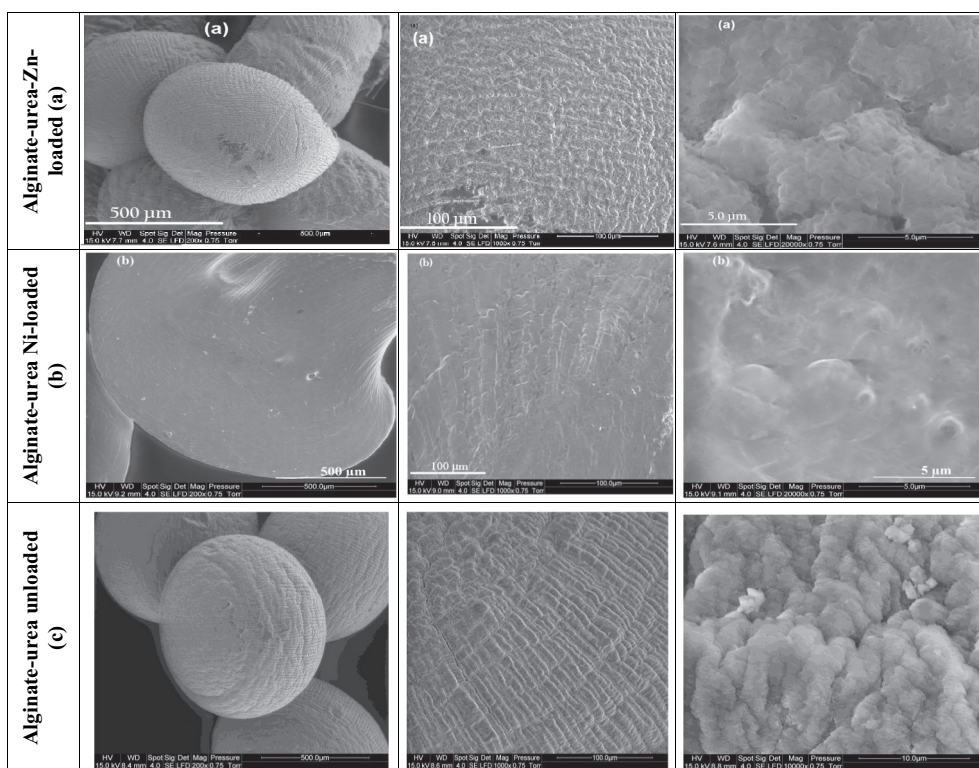
The beads obtained have a percentage of water of almost 98% for the different beads, for more detail see the additional material (see section I, and work A. Benettayeb et al., (2017) [14]). The reaction of alginate with urea and biuret, in order to produce the alginate-urea and alginate-biuret, is clearly discussed in the work of A. Benettayeb et al., (2017) [14]. This grafting is believed to occur through the reaction of –OH of alginate with the –NH<sub>2</sub> on the urea/biuret with simultaneous release of NH<sub>3</sub>, this simultaneous release of ammonia (NH<sub>3</sub>) is characterised by alkalisation of the reactive medium and consequently the increase in pH. According to S. Gan et al., (2014) alkalisation is confirmed by a small increase in pH value of the reagent medium during synthesis, this slight increase is generally negligible [27]. Thus, the FT-IR was done to justify the success of the reaction and to know the structure of the materials synthesised during this research [14].

Scanning electron microscopy (SEM) and SEM-EDX were used for characterising the sorption of nickel and zinc ions on alginate-based sorbent (Figure 1 and Fig. AM1, see Supplementary Information, Section I). Knowing that, An energy-dispersive X-ray (EDX) is an analytical method that is used for the identification of elemental compositions in the sample [28]. The distributions of Ni(II) and Zn(II) ions were found uniformly homogeneous on the surface of sorbents, as shown by SEM–EDX analysis. This has been confirmed by analysis of the same bead on different parts of the surface and different beads.

The morphology and topography of these biomaterial, also the main constituents (we can clearly see that the spectrum shows well-defined peaks for these elements C, Ca, O, Cl, Na and N) of the natural alginate and the new elements that do not exist in the structure of the alginate are represented in the **Figure AM1** (see Supplementary Information, Section I).

The EDX spectrum is presented with element cartography, from a collection of important information about the nature of our materials, it is important to note that it is likely that the elements O and C are associated to the matrix of sorbent while the Cl and Ca elements are associated to Ni(II) and Zn(II).

When doing a comparative study for micrographs of Alginate-urea-Zn(II)-loaded, Alginate-urea-Ni(II)-loaded and Alginate-urea unloaded it was found that the bulky



**Figure 1.** Scanning electron microscopy-energydispersive X-ray analysis (SEM-EDX) micrographs of Alginate-urea-Zn-loaded(a), Alginate-urea-Ni-loaded (b) and Alginate-urea unloaded (c) (T: 20°C; pH:5.5; SD: 0.1 g (d.w.) L<sup>-1</sup>; agitation speed: 150 rpm; t: 8 h; C<sub>0</sub>: 0.3 mmol L<sup>-1</sup>).

particles are present on the surface of Zn(II)-loaded biomass. In addition, we noted that the pores become dark in Figure 1(a). After nickel and zinc sorption (Figure AM1b, see Supplementary Information, Section I) important changes can be observed: (a) the disappearance of Na element, (b) the decrease in the intensity of the signals of Cl and Ca elements and (c) the appearance of signals representatives of Ni(II) and Zn(II) elements. SEM images confirmed that there is no damage effect or cutting on the structure of the beads after sorption of Ni(II) and Zn(II) in the working conditions for the synthesised beads. On the other hand there are changes in the beads of alginate, other researchers have used this analysis to confirm the structural strength under some conditions [29,30].

### 3.2. Effect of pH on metal sorption

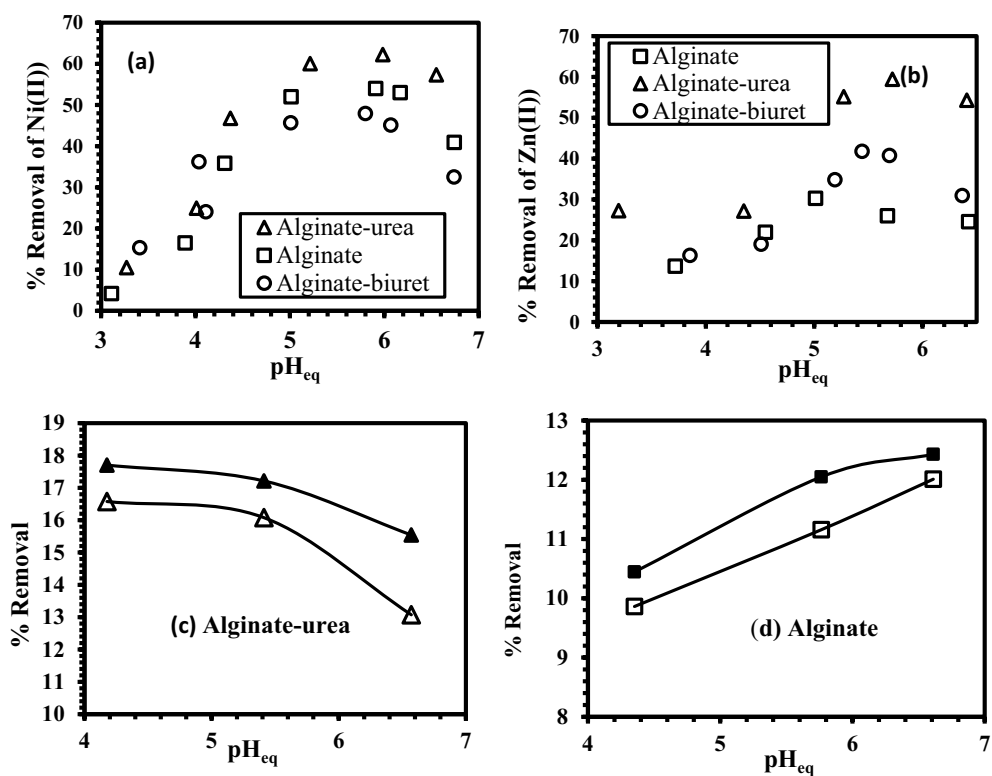
The pH is the main factor that controls the sorption of Zn(II) and Ni(II) ions. It also affects the surface charge of the adsorbents as well as the degree of ionisation of different pollutants [31]. Change of the pH affects the adsorptive process through dissociation of functional groups on the adsorbent's surface [32]. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process.

There was dependence on zinc and nickel ions sorption in relation to the pH. When the pH value is low, Zn(II) and Ni(II) ions faced competition with abundance of H<sup>+</sup> ions for the



available sites, so the sorption of Zn(II) and Ni(II) ions onto the three sorbents is limited (low). While at high pH value, this competition decreases, and thus, more Zn(II), Ni(II) ions are adsorbed onto alginate, alginate-urea and alginate-biuret, up to the pH value of 6. Above pH 6, the sorption is decreased due to the precipitation. Therefore, all experiments were conducted at pH below 5.5 to prevent metal hydrolysis and precipitation, which has been reported in several studies (*for Ni(II) is at pH > 7.6 and for Zn(II) is at pH = 7*) [33,34].

Adsorption percentage of Zn(II) and Ni(II) ions onto three sorbents is shown in Figure 2 (a-b) at temperature of 20°C; sorbent dosage of 0.1 g (d.w.) L<sup>-1</sup>, contact time of 8 h and concentration initial of 0.3 mmol L<sup>-1</sup>. The effect of the pH<sub>eq</sub> value variation on the sorption efficiency for Ni(II) and Zn(II) using alginate-based sorbents is represented in this figure. What remarkable is that the sorption efficiency of Ni(II) and Zn(II) increases significantly with the increase of pH value, in particular until reaching the ceiling at a pH of 5.5 for the alginate-urea and alginate-biuret and 4.6 for alginate unmodified. After the pH value of 6.5, the removal efficiency decreases by 5 to 10%, the sorption efficiency increases in the order: Ni(II) > Zn(II) for the three sorbents but the alginate-urea and alginate-biuret are more effective than alginate with a percentage for Ni(II) [Alginate-urea (80%); Alginate-biuret (47%); Alginate (40%)] and for Zn(II) [Alginate-urea (60%); Alginate-biuret (41%); Alginate (24%)].

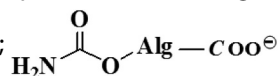


**Figure 2.** (a-b) Effect of pH on Ni(II) and Zn(II) using Alginate beads (squares), Alginate-urea (triangles) and Alginate-biuret (circles) and (c-d) Effect of pH on the % removal of Ni(II) (white symbols) and Zn(II) (black symbols) in the solution bi-metallic using Alginate beads (squares) and Alginate-urea (triangles) (T: 20°C; sorbent dosage, SD: 0.1 g (d.w.) L<sup>-1</sup>; agitation speed: 150 rpm; contact time: 8 h; C<sub>0</sub>: 0.3 mmol L<sup>-1</sup>).



Alginate (30%). pH variation ( $pH_{eq}$  vs.  $pH_i$ ) during the sorption of Ni(II) and Zn(II) are represented in Figure AM5 (see Supplementary Information, Section IV).

Alginate consists of carboxylic acid groups while the proposed product obtained in grafting with either urea or biuret has a carboxylic and amine groups as;



The reaction mechanism is suggested to be performed on –OH groups of alginate and –NH<sub>2</sub> of urea/biuret as discussed in previous work [14]. So, both –NH<sub>2</sub> and –COOH are the major functional groups in our material and the main sorption mechanism is limited to ion exchange between metal cations (*i.e.* Zn(II), Ni(III)) and the protons on carboxylic groups or calcium ions, bound to carboxyl groups [19]. It is noteworthy that the intensity of Ca element significantly decreases after metal binding (*Figure AM1b, see Supplementary Information, Section I*). This is associated to the ion-exchange of calcium with metal ions for both free alginate and grafted one.

The carboxyl and unprotonated amino groups are used in several coordination and electrostatic interaction studies of metals [35]. According to *O. Monteiro et al.,(1999)*, the metal ions (*i.e.* Ni(III)) can be adsorbed by one –NH<sub>2</sub> group as well as two –OH groups of the glucose residue, and the fourth ligand site is probably occupied by a water molecule [36].

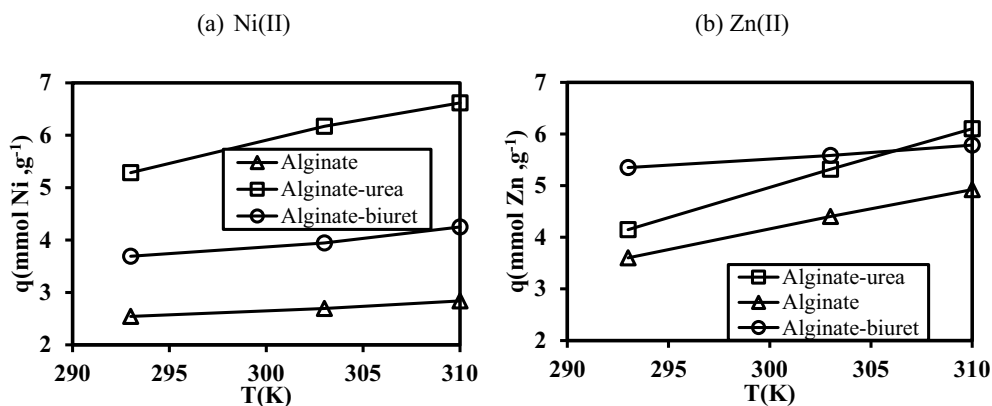
Researchers are investigated that, in alginate, the electrostatic attraction cannot be one of the sorption mechanism; because the contribution is minimised since, there is no reactive groups are directly available for binding of these metals [37], but when the surface of the sorbents are positively charged, the electrostatic attraction should be one of the sorption mechanism [37].

Knowing that the  $pK_a$  of carboxylic acid groups of mannuronic and guluronic acid units are 3.38 and 3.65, respectively [38]. Under the value of 3.5, the majority of carboxylate groups are protonated and thus, less reactive for the binding of metal cations, while, above pH 3.5 the carboxylate groups are more favourable for metal binding [14]. The amine groups in urea and biuret are characterised by a  $pK_a$  value close to 0.18 [39], this meaning that under current working conditions –NH<sub>2</sub> should not be protonated and should be available for chelation of metal cations (vacant site) [14]. This justifies the results obtained in this work. So, the possible interaction of Ni(II) and Zn(II) with alginate-urea /alginate-biuret are coordination, electrostatic interaction. In the selected pH, and under the selected conditions, the protonation of amine groups decreases progressively. Therefore, the metals ions are bound with –N of the amine groups through coordination. Moreover, the negatively charged of carboxylic group holds the positively charged of metals ions though electrostatic forces also there is a possibility of ion exchange.

When using bimetallic solutions, we can increase the pH range in the case of alginate-urea by 4 to 5.5. On the other hand, we have detected increases in the percent of adsorption in the case of alginate up to 6.5 (See [Figure 2\(c,Figure 2d\)](#)).

### 3.3. Effect of temperature and sorption thermodynamics

To study the effect of the temperature, adsorption studies were also performed at 20, 30 and 37°C. [Figure 3\(a-b\)](#) illustrates the relationship between temperature and the amount of Zn(II) and Ni(II) cations adsorbed onto different adsorbents. The study was realised in



**Figure 3. (a-b)** The uptake capacity of Zn(II) and Ni(II) ions at different concentration and different temperature (pH 5.5, t = 8 h, initial metal concentration, T = 20, 30 and 37°C, adsorbent dosage; SD = 0.1 g/L, 150 rpm).

three different concentrations in the range of 40 to 250 mg metal.L<sup>-1</sup> (equivalent to mmol metal.L<sup>-1</sup> for each metal), it was found that temperature has an effect on adsorption, and this effect increased with increasing the concentrations, which becomes remarkable at 200 and 250 mg metal.L<sup>-1</sup>.

As seen, at an initial concentration of 200 mg/L, the sorption of Ni(II) cations increased from 5.29 to 6.62 mmol.g<sup>-1</sup> on alginate-urea, 3.69 to 4.248 mmol.g<sup>-1</sup> on alginate-biuret and 2.54 to 2.84 mmol.L<sup>-1</sup> on alginate when the temperature goes from 20 to 37°C

Also, the adsorption of Zn(II) cations increased from 4.15 to 6.10 mmol.g<sup>-1</sup> on alginate-urea, 5.347 to 5.784 mmol.g<sup>-1</sup> on alginate-biuret and 3.6 to 4.92 mmol.g<sup>-1</sup> on alginate when the temperature goes from 20 to 37°C at an initial concentration of 250 mg/L.

This could be the result of an increase in the mobility of the Zn(II) and Ni(II) cations with increasing temperature. Also an increasing number of molecules could acquire sufficient energy to undergo an interaction with active sites at the surface. In addition, the increasing of the temperature may create a swelling effect within the internal structure enabling large metal ions to penetrate further [40].

In order to understand the nature of adsorption, thermodynamics parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ), were calculated using following equations [41–45].

The free energy change of the sorption reaction can be given by the following equation:

$$\Delta G^\circ = -RT \ln K_d \quad (4)$$

$$\ln K_d = \left( -\Delta H^\circ / R \right) 1/T + \Delta S^\circ / R \quad (5)$$

where  $\Delta G^\circ$  is the standard free energy change (J), R is the universal gas constant, 8.314 J/mol K and T is the absolute temperature (K).

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

The distribution coefficient  $K_d$  ( $\text{Lg}^{-1}$ ), which was calculated by the ratio  $\frac{q_{\text{eq}}}{C_{\text{eq}}}$  for each temperature, by the relationship;

$$K_d = V/m[(C_0 - C_{\text{eq}})/C_{\text{eq}}] \quad (7)$$

Is correlated to enthalpy change  $\Delta H^\circ$ , and entropy change  $\Delta S^\circ$  by the van't Hoff equation (Eq. 2), while the free energy  $\Delta G^\circ$  change can be deduced from Eq. 4 and 6 [46].

Distribution coefficient ( $K_d$ ) indicates the capability of the alginate beads to retain a solute and also the extent of its movement in a solution phase [47]. According to P. Gomes et al., (2001),  $K_d$  is a useful parameter for comparing the adsorptive capacities of different adsorbent materials for any particular ion [48], when measured under same experimental conditions [49].

The distribution ratio ( $K_d$ ) values increased with rising temperature (see Additional Material Section, Section VI, Figure AM8(c-d)), Table 1(a) and Table AM1(bc), indicating the endothermic nature of sorption. A plot of Gibbs free energy changes,  $\Delta G^\circ$  versus temperature, T(K), was found to be linear. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and intercept of the plots. The thermodynamic parameters of Gibbs free energy change  $\Delta G^\circ$  also other parameters are shown in Table 1(a).

The positive values of  $\Delta H^\circ$  confirm the endothermic nature of the sorption process [50]; also the slope is negative  $-\frac{\Delta H^\circ}{R}$  and as the temperature increases, the equilibrium constant also increases. The negative values of  $\Delta G^\circ$  indicate that the sorption reaction is spontaneous. The decrease in  $\Delta G^\circ$  with increasing temperature confirms the spontaneity of the sorption process [43]. At different temperatures, the values of free enthalpy are negative, except for the case of sorption of nickel on alginate. This value reflects the non-spontaneity of the reaction, and this theoretically means that alginate does not show any affinity for nickel, which is not quite consistent with our results.

In addition, the fact that regardless of temperature,  $|\Delta H^\circ| < |T\Delta S^\circ|$  means that the sorption process was dominated by entropic rather than enthalpic changes [46]. It is noteworthy that the two sorbents show very similar thermodynamic parameters. The positive value of entropy indicates the randomness at solid/liquid interface of the system which increases with metal sorption during the reaction (*probably associated to the release of water, which comes from water hydration of metals species*) [43].

The thermodynamic parameters indicate that the sorption process is endothermic, feasible and thermodynamically favoured. Based on the obtained results, it appears that

**Table 1.** (a) Thermodynamic parameters of Ni(II) and Zn(II) in single systems and Variation of the distribution ratio ( $K_d$ ) at different concentration and different temperature (b) Ni(II) and (c) Zn(II) (pH 5.5,  $t = 8$  h, initial metal concentration,  $T = 20, 30$  and  $37^\circ\text{C}$ , adsorbent dosage; SD = 0.1 g/L, 150 rpm).

		(a) Thermodynamic parameters								
Metals	Adsorbent	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )			$T\Delta S^\circ$ (kJ mol <sup>-1</sup> )			
				293 K	303 K	310 K	293 K	303 K	310 K	
Ni(II)	Alginate beads	5.25	16.38	0.44	0.29	0.17	4.8	4.96	5.07	
	Alginate-urea beads	12.24	47.19	-1.59	-2.06	-2.38	13.82	14.3	14.63	
	Alginate-biuret beads	6.99	25.73	-0.55	-0.81	-0.99	7.54	7.79	7.97	
Zn(II)	Alginate beads	15.65	53.56	-0.04	-0.58	-0.95	15.7	16.2	16.60	
	Alginate-urea beads	19.79	69.02	-0.43	-1.12	-1.60	20.2	20.9	21.40	
	Alginate-biuret beads	4.00	17.48	-1.12	-1.30	-1.42	5.12	5.30	5.42	

the alginate modified by the urea and biuret is a good adsorbent for removing these heavy metal ions from water (*in the temperature of 20°C*).

### 3.4. Uptake kinetics- Uptake kinetics at mono and bi-component metals

A study of the kinetics of sorption is desirable as it provides information about the mechanism of adsorption [51], which is important for the efficiency of the process. The tested of capability to use of the pseudo-first-order rate equation, and/or the pseudo-second-order rate equation (PFORE 'Equation AM5', Figure AM7, Table AM1 and for PSORE 'Equation AM4'), and/or the model of resistance to intraparticle diffusion (see Additional Material Section, Section V, RIDE 'Equations AM6', for complementary information) were tested in this study for the biosorption of nickel and zinc onto three sorbents.

The choice of stirring speed was selected after a series of tests which were carried out with some heavy metals ions on three sorbents, the agitation speed of 150 rpm turned out to be sufficient to reduce effect of the diffusion resistance of the film [14].

The kinetics was studied at the fixed initial concentrations, by mixing volumes of 500 mL of ion solutions of Ni(II) and Zn(II) at concentrations of  $0.3 \text{ mmol L}^{-1}$ , with masses of 2.5 g (dosage; SD = 0.1 g/L) of the three adsorbents; alginate, alginate-urea and alginate-biuret at a room temperature at 20°C and pH 5.5. The homogenisation of mixtures was done by a shaker with constant stirring of 150 rpm. The samples were taken at different intervals of time after separation of adsorbent-adsorbate. The equilibrium concentration in solution was determined by ICP-AES.

The effect of contact time on the sorption of metal ions was investigated at initial metal concentration ( $19 \text{ mg metal L}^{-1}$  equivalent to  $0.3 \text{ mmol L}^{-1}$  for each metal).

It can be noticed from Figure AM6 (see Supplementary Information, Section V) that the removal of nickel and zinc by sorption on the three sorbents was found to be quick at the initial period of contact time and then it slowed down with time. The reason for this is the attractive forces between the metals ion and the sorbent such as *van der Waals forces* and *electrostatic attractions*. The stages of sorption are; the fast diffusion onto the external surface was followed by the fast pore diffusion into the intra-particle matrix and then it slowed down with time to attain equilibrium in 8 h. The results are presented in Table 2.

The same study is established in bi-metallic solutions (Zn(II) + Ni(II)) in order to estimate the selectivity of our materials towards the two elements. Such a study approaching the real conditions, since, heavy metals are generally in the form of multi-components pollutants in wastewater.

At fixed concentration (0.3 mmol/L), the adsorption of heavy metals decreases in the order: Zn(II) (2.39 mmol/g) < Zn(II)(Ni(II)+Zn(II)) (2.32 mmol/g) < Ni(II) (Ni(II)+Zn(II)) (2.13 mmol/g) < Ni(II) (1.49 mmol/g) for the alginate-urea. In case of alginate-biuret, the following order was noticed: Ni(II) (Ni(II)+Zn(II)) (2.24 mmol/g) < Ni(II) (1.58 mmol/g) < Zn(II) (1.32 mmol/g) < Zn(II)(Ni(II)+Zn(II)) (1.28 mmol/g), but for the alginate, the order was: Zn(II) (1.04 mmol/g) < Zn(II)(Ni(II)+Zn(II)) (0.86 mmol/g)  $\approx$  Ni(II) (Ni(II)+Zn(II)) (0.88 mmol/g) < Ni(II) (0.79 mmol/g) at 293 K and pH = 5.5.

These results show that nickel is better retained by the three adsorbents in the bimetallic solution (Ni + Zn) than when it exists alone in solution (see Supplementary Information, Section VI, Figure AM9). Thus, the sorption capacity of Ni(II) in the two-component solution increases by 10.7% for alginate, 43.2% for alginate-urea and 42% for

**Table 2.** Maximum adsorption capacity at fixed initial concentration ( $\text{mmol.g}^{-1}$ ) at  $0.3 \text{ mmol.L}^{-1}$  in mono and bimetallic solution and (b) The operating parameters and the results of the selectivity factor for the two cases Ni(II) and Zn(II) for the three sorbents Alginate, Alginate-urea and Alginate-biuret (SD:  $0.1 \text{ g (d.w.) L}^{-1}$ ;  $C_0$ :  $0.3 \text{ mM}$  – mono-component solutions; T:  $20^\circ\text{C}$ ; pH 5.5).

(a)				
Adsorbents	Maximum adsorption capacity at fixed initial concentration( $\text{mmol.g}^{-1}$ ) at $0.3 \text{ mmol.L}^{-1}$			
	Ni(II)	Zn(II)	Ni(II)(Ni(II)+Zn(II))	Zn(II)(Ni(II)+Zn(II))
Alginate	0.79	1.04	0.88	0.86
Alginate-urea	1.49	2.39	2.13	2.32
Alginate-biuret	1.58	1.32	2.24	1.29

(b)				
Solution(Ni(II)+Zn(II))				
	Parameters	Alginate	Alginate-urea	Alginate-biuret
Zn(II)	$C_0$ (mg/L)	19.71	19.71	19.71
	$C_{eq}$ (mg/L)	14.58	5.01	11.89
	Separation factor Zn(II)/Ni(II)( $K_s$ )	0.99	2.21	0.75
Ni(II)	$C_0$ (mg/L)	19.01	19.01	19.01
	$C_{eq}$ (mg/L)	14.01	8.17	10.11
	Separation factor Ni(II)/Zn(II)( $K_s$ )	1.01	0.45	1.34

alginate-biuret. However, no improvement has been recorded for the adsorption of zinc in the bimetallic solution. The calculated capacities were found to decrease by 21% for alginate and remained almost stable for two alginate-modified sorbents.

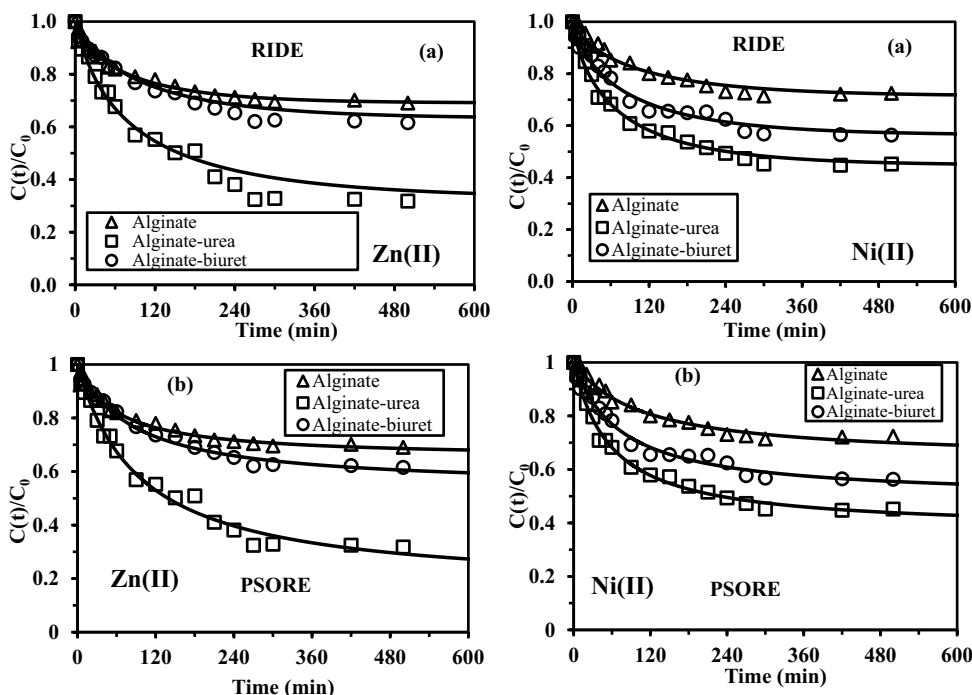
However, it was observed that the adsorption sequence for nickel follows the order: Alginate < Alginate-urea < Alginate-biuret, whereas zinc follows the order: alginate < alginate-biuret < alginate-urea.

As we see in Figure 4(a, Figure 4b) the best fit that matches well to the experimental data is obtained by PSORE and also by the RIDE model. The coefficients obtained during the modelling using these two models are summarised in Table 3. When comparing intraparticle diffusion coefficients we noticed that the maximum diffusivity get us with alginate-urea beads for Ni(II) (i.e.  $0.055 \times 10^{-9} \text{ m}^2 \text{ min}^{-1}$ ), and for Zn(II) (i.e.  $0.068 \times 10^{-9} \text{ m}^2 \text{ min}^{-1}$ ) with alginate beads.

The model PSORE (see Figure 4(b), Table 3) gives an excellent fit of experimental profiles and the largest error is obtained with alginate-urea/beads/Zn(II) and alginate-biuret/beads/Ni(II). The results obtained by the PSORE model suggests that the adsorption process is a chemical interaction between metal ions and active sites rather than a simple physical adsorption process.

Knowing that according to A. Benettayeb et al., (2017) and S. Wang et al., (2017) the two models of **PFOR** and **PSOR** were initially established to describe the homogeneous chemical reaction, the extrapolating of these equations to heterogeneous systems means that the rate parameters implicitly integrate the contribution of mechanisms of diffusion and should be considered as apparent rate parameters [14,19].

The apparent rate parameters keep the same trends as previously observed with intraparticle diffusion coefficients. So, it is not possible to find a clear trend in the evolution of these two parameters with these types of biosorbent and with Ni(II)/Zn(II). The rate coefficients are for Zn(II) (in the range  $6.39 \times 10^{-3} - 2.52 \times 10^{-2} \text{ g mmol}$



**Figure 4.** Ni(II) and Zn(II) uptake kinetics on Alginates, Alginates-urea and Alginates-biuret beads (SD: 0.1 g (d.w.) L<sup>-1</sup>; C<sub>0</sub>: 0.3 mM – mono-component solutions; T: 20°C; pH 5.5) solid-lines: **(a)** modelling of kinetic profile with the RIDE (Crank equation), **(b)** modelling of kinetic profile with the PSORE and all parameters from Table 3

min<sup>-1</sup>) and for Ni(II) (in the range 1.38 × 10<sup>-2</sup> – 1.44 × 10<sup>-2</sup> g mmol<sup>-1</sup> min<sup>-1</sup>). It is observable that the equilibrium sorption capacities are close to the calculated values, So, it can be concluded that PSORE (Figure 4(b), Table 3, PSORE) is more appropriate than PFORE (Equation AM5, Figure AM7 and Table AM1) for describing experimental data, for complementary information about PFORE (see Additional Material Section, Section V)

To test the selectivity of synthesised adsorbents, the competitive sorption was conducted in the binary system, Ni(II)/Zn(II) at the initial concentration of each metal ion in the mixed solution was 19 mg/L (equivalent of 0.3 mmol L<sup>-1</sup> for each metal). The selectivity coefficients (K<sub>s</sub>) or the factor of separation (S<sub>1/2</sub>), on the metal ion Ni(II) and Zn(II) in the presence of the mixture of (Ni(II)+Zn(II)) ions have been calculated according to the equation Eq. 8 [52], for example, for the Zn(II) ions in the solution of Zn(II)+Ni(II), we can write the equation as follows:

$$K_s = S_{Zn(II)/Ni(II)} = \frac{Q_{Zn(II)}/Q_{Ni(II)}}{C_{eNi(II)}/C_{eZn(II)}} = \frac{Q_{Zn(II)} \times C_{eNi(II)}}{Q_{Ni(II)} \times C_{eZn(II)}} = \frac{(C_{0Zn(II)} - C_{eZn(II)}) \times C_{eNi(II)}}{(C_{0Ni(II)} - C_{eNi(II)}) \times C_{eZn(II)}} \quad (8)$$

where; Q<sub>Zn(II)</sub> and Q<sub>Ni(II)</sub> are the equilibrium adsorption capacities of Zn(II) and other metal ions, respectively. For this case of study Ni(II), C<sub>eNi(II)</sub> and C<sub>eZn(II)</sub> are the equilibrium concentrations of Zn(II) and Ni(II). For the choice of selectivity of the metal ion in the mixture solutions of Ni(II)+Zn(II), generally we need to use the selectivity factor 'K<sub>s</sub>', and

**Table 3.** Sorption isotherms – Parameters of the Langmuir, Sips and Temkin models and Modelling of uptake kinetics using the Crank equation (RIDE) and PSORE – Mono-component solutions (Initial pH: 5.5, 0.3 mM, SD: 0.1 g (d.w.) L<sup>-1</sup>).

Metal	Sorbent	Langmuir model			Sips model			Temkin model						
		q <sub>m,exp</sub> (mmol/g)	q <sub>m</sub> (mmol/g)	b (L/mmol)	q <sub>m</sub> × b (L/g)	R <sup>2</sup>	q <sub>m</sub> (mmol/g)	K <sub>s</sub> (L/mmol)	n <sub>s</sub>	R <sup>2</sup>	A <sub>T</sub> (L/mg)	b <sub>T</sub>	ΔQ <sub>s</sub> (KJ/mol)	R <sup>2</sup>
Ni(II)	Alginate	2.900	3.220	2.480	7.980	0.976	2.980	3.480	1.219	0.973	27.939	3906.100	0.634	0.968
	Alginate-urea	6.480	8.530	0.790	6.740	0.995	7.950	0.930	1.118	0.994	11.685	1511.370	1.640	0.969
	Alginate-biuret	4.260	4.730	2.850	13.480	0.984	4.410	4.780	1.316	0.973	32.592	2637.670	0.940	0.956
Zn(II)	Alginate	4.800	6.760	0.780	5.270	0.995	5.450	1.200	1.486	0.987	13.426	1990.650	1.244	0.952
	Alginate-urea	6.140	7.140	2.310	16.490	0.996	7.320	1.700	0.836	0.993	40.740	2018.520	1.227	0.995
	Alginate-biuret	5.820	6.970	1.710	11.920	0.981	6.390	2.140	1.169	0.983	51.836	2292.220	1.080	0.940
Ride														
Metal	Sorbent	D <sub>e</sub> × 10 <sup>9</sup> (m <sup>2</sup> min <sup>-1</sup> )	Estimated Variance	q <sub>e,exp.</sub> (mmol g <sup>-1</sup> )	q <sub>e,calc.</sub> (mmol g <sup>-1</sup> )	k <sub>2</sub> × 10 <sup>2</sup> (g mmol <sup>-1</sup> min <sup>-1</sup> )	Estimated Variance							
Zn(II)	Alginate	0.011	3.371	60.40	68.362	0.0252	2.660							
	Alginate-urea	0.055	1.475	133.0	164.269	0.0064	29.578							
	Alginate-biuret	0.029	2.490	75.0	90.173	0.01297	9.770							
Ni(II)	Alginate	0.068	2.553	52.4	69.030	0.0138	7.294							
	Alginate-urea	0.020	2.500	104.2	119.176	0.0144	4.706							
	Alginate-biuret	0.037	2.555	83.0	96.819	0.0142	15.159							



adsorbent has a selectivity towards Zn(II) or Ni(II) when  $K_s > 1$ . Otherwise, if  $K_s < 1$  it has no selectivity, Table 2(b) summarises the operating parameters and the results of the selectivity factor for the two cases.

The separation factor calculated for Zn(II) in a mixed solution (Ni(II)+Zn(II)) reveals a high selectivity of alginate-urea compared to the other two materials, while the adsorption of Ni(II) in the same bimetallic solution is more favourable by alginate-biuret compared to the other two forms materials, the parent material, alginate, has almost the same affinity towards of the two elements.

In addition, it is interesting to note that the two functionalised polysaccharides do not show the same harmony in front of the two-chemical species, thus giving the possibility of their use as specific adsorbents in solutions containing these elements.

### 3.5. Sorption isotherms

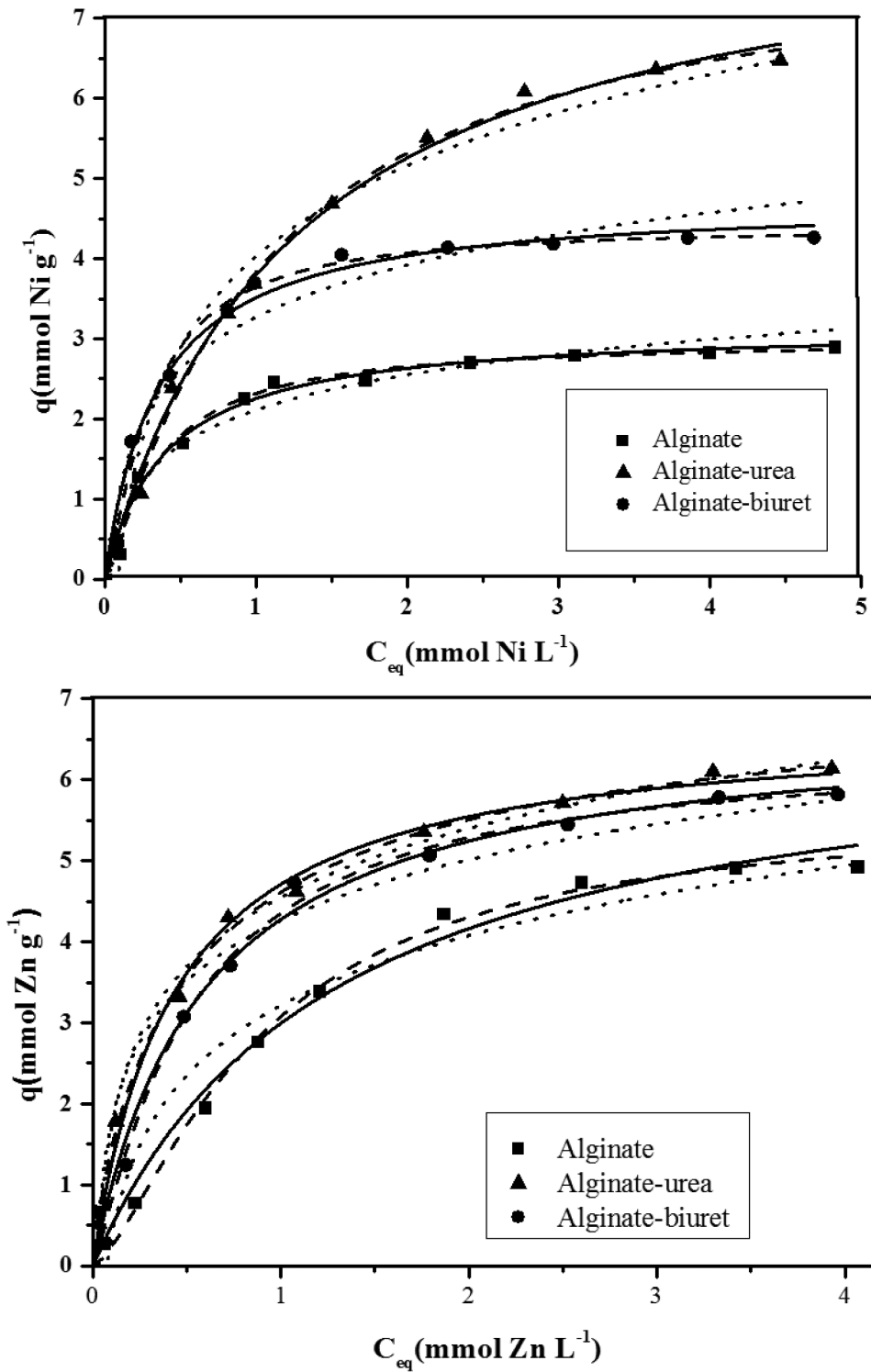
The sorption capacity of three biosorbents for the removal of Ni(II) and Zn(II) ions was examined at room temperature. The resultants of the sorption isotherms for these metals using alginate beads, alginate-urea beads and alginate-biuret beads are shown in Figure 5.

The profiles obtained for the two metals when plotting the curve  $q_{eq} = f(C_{eq})$  are characteristics of saturation plateau at equilibrium and these curves can modelled by the Langmuir equation, this modelling is different to the using of freundlich model which does not contain this plateau [53,54]. We noticed a progressive increase of the sorption capacity followed by a saturation plateau for the two metal ions Ni(II) and Zn(II) and the plateau of saturation reached for a residual concentration close 2 to 3 mmol metal  $L^{-1}$  these curves show are a very favourable sorption. The sorption isotherms for Ni(II) and Zn(II) show the same trends the alginate-modified with urea and biuret have higher sorption capacities compared with the alginate beads.

According to the Langmuir isotherm model, the adsorption capacity for Ni(II) was 3.22, 4.73 and 8.53 mmol/g while for Zn(II), it was 6.77, 6.97 and 7.14 mmol metal  $g^{-1}$  for alginate, alginate-biuret and alginate-urea, respectively (Figure 5, Table 3).

In reason of the richness of structure of the modified materials (*heterogeneous character of structure with a new morphology*) it is interesting to test other model, as it is the case of Sips and Temkin. As it is already known, the Langmuir equation, despite having a good adjustment of the saturation plateau, fails to describe the zone of maximum curvature and it may be interesting to use a more complex mathematical equation which takes into account consideration of other parameters such as the Sips equation and the Temkin equation.

As shown in Figure 5, the Langmuir (solid lines) and Sips model (dashed lines) are superimposed, the experimental data and all parameters of these three models, respectively Langmuir (solid lines), Sips model (dashed lines) and Temkin (dotted lines) are summarised in Table 3. Despite almost total superposition for three models, it is noted that the best fit is found by the model of sips which is normal compared to the character of our biosorbents (better graphical representation of results particularly in the zone of highest curvature). knowing that this better adjustment is due to the introduction of a third parameter which is the heterogeneity factor. Generally, the mathematical fit is obviously improved while introducing a new parameter in the model (*three estimated*



**Figure 5.** Sorption isotherms for Ni(II) and Zn(II) recovery using alginate-based sorbents ((Initial pH: 5.5, 0.3 mM, SD: 0.1 g (d.w.) L<sup>-1</sup>- solid lines: Langmuir model; dotted lines: Temkin model; dashed lines: Sips model with parameters from Table 3).

parameters ( $q_m$ ,  $K_s$  and  $n$ ) vs. two parameters ( $q_m$  and  $B$ ) [14]. And, when compare the experimental sorption capacities at saturation we find it very proximate to the values obtained by the Langmuir model. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given by the following equation [55]:

$$R_L = 1/(1 + K_a \times C_0) \quad (9)$$

where  $C_0$  (mg/L) is the initial concentration of adsorbate and  $K_a$  (L/mg) is Langmuir constant. The value of  $R_L$  indicates the shape of the isotherm which can be unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ) [55]. The values of  $R_L$  parameters for the sorption of synthesised adsorbents onto nickel and zinc are summarised in Additional Material Section, are observed to be in the range 1–0.8, indicating that the adsorption was a favourable process for more complementary information (See Additional Material Section, Section III, Figure AM4).

The coefficients of correlation show a perfect agreement between the experimental data of the adsorption and the different models (see Table 3). The Sips model gave the best results during the sorption of Ni(II) and Zn(II) on the alginate-urea, and the sorption of Zn(II) on alginate. For alginate/Ni(II) and alginate-biuret, the results are almost similar for both models: Sips and Langmuir. But, generally, it can be said that both models give practically the same tendencies. According to the results obtained, the sorption isotherms for two metals show the similar trends, the sorption capacity of alginate-modified is almost twice that of alginate beads.

The value of the affinity coefficient (i.e.  $b_L$ ) is slightly increased with increasing of  $q_m$  for the sorption of Zn(II), on the opposite site for Ni(II), it was decreased with increasing of the sorption capacity. These changes in the order of parameter values can be associated with the effect of increasing occupancy of sorption sites [56]. For the Ni(II) sorption the coefficients 'b' are in the same order of magnitude for alginate and alginate-biuret beads and lower than the affinity coefficients 'b' obtained with alginate-urea beads, but, for the Zn(II) sorption, the affinity coefficients are the same order of magnitude for the alginate-urea and alginate-biuret and higher than alginate (see Table 3).

In addition, the parameter  $q_m \times b$  ( $L g^{-1}$ ) which corresponds to the initial slope of the sorption isotherm, is in the range 5.27 – 16.49  $L g^{-1}$  for Zn(II) while it was in the range of 6.74 – 13.48  $L g^{-1}$  for Ni(II). On the other hand, the Sips and Langmuir model provides the similar fit with the experimental results, for two metals studied. But, the obtained heterogeneity index ( $n_s$ ) greater than 1 for the three sorbents (except for *Alginate-urea /Zn(II)*), which shows that the sorbent is almost heterogeneous, these parameters can confirm the heterogeneous nature of our sorbents in this study.

The result of this study is coherent with the findings of other researchers who reported that if  $1/n$  ranges between 0.5 (or  $n_s > 1$ ), the increased heterogeneity and if it is about  $1/n = 1.0$  or higher ( $1 < n_s > 0$ ), it is almost homogeneous sorbent (Sips equation = Langmuir equation). When the two models are applied (Sips and Langmuir), the Sips equation is reduced to the Langmuir model, indicating that the preferential binding of metals on all sites of adsorbent is neglected, which can act as a homogeneous surface [57].

All parameters of the three theoretical models (Langmuir, Sips and Temkin) used to test experimental values, are summarised in Table 3. These results can be interpreted using

the theory of Pearson; hard-soft-acid-base theory (HSAB) [58], Marcus [59] and the classification of Nieboer and Richardson [60].

The Zn(II) cations are less soft than Ni(II) cations and belong to the first row of transition metals together with Cu(II), Co(II) and Ni(II). According to Hard & Soft Acid-Base theory 'Pearson's rule' and the classification of Nieboer and Richardson, the Ni(II) and Zn(II) are in the range of borderline acids, but the classification of the ion softness parameters ( $\sigma_M$ ) suggested by Marcus; Zn(II) and Cu(II) are classified as class C 'borderline-Intermediate' [58,59], while Ni(II) and Co(II) are classified as hard cations (class A) [59], and indicates the softness parameter for Hg(II) (+1.28) > Cd(II) (+0.58) > Pb(II) (+0.41) > Cu(II) (+0.39)  $\geq$  Zn(II) (+0.38) > Ni(II) (-0.11) > Co(II) (-0.18).

The softness parameters for Zn(II) is close to Cu(II) (borderline, lower than 0.5) and soft acid greater than 0.5 (as is the case with Cd(II)) that while borderline acids (as is the cases of Cu(II), Pb(II) and Zn(II)) between less than 0.5 up to 0 and the negative values of ( $\sigma_M$ ) for hard acids. According to Pearson's rule, Hard & Soft Acid-Base theory, hard acids prefer to associate with hard bases in equilibrium and soft acids prefer to associate with soft bases in equilibrium [58]. And, on the basis of the principle rule of the HSAB theory, we can conclude that O-ligands (such as in our case - COOH) have more affinity for hard acids than N-ligands (-NH<sub>2</sub>) and soft acids have more affinity for -N ligands (-NH<sub>2</sub>) than -O (such as in our case -COOH) base ligands. This may justify the increase in the sorption efficiency for amine-rich alginate derivatives (*grafting result with urea and biuret*) due to the higher density of sorption sites and the specific reactivity of these new groups (-NH<sub>2</sub>) for the sorption of metals tested. Also the use of hydrogels beads with the opened-porous structure maybe can explain the fast transfer of metal ions (accessibility) and strong sorption (availability) [14].

It is known that 'Class A', which belongs to the Nieboer and Richardson (1980) classification, groups elements have an affinity for ligand containing oxygen atoms, and 'Class B' groups elements have an affinity for ligands containing nitrogen atoms and sulphur, while 'Class C' (borderline, intermediate) groups elements having an affinity for both oxygen, nitrogen and sulphur [60]. Which approximately correspond to hard acids (class A), soft acid (class B) and intermediate class of metals (borderline) [58,60].

The interest of this classification is to predict the potential binding sites of the metals within the adsorbents and to select the best adsorbent for each metal and the best modification, if necessary. Therefore, for this reason, we chose the functionalization by amine groups.

I. Persson, (2010) discussed in their work the influence of hydration of metal ions on their structure (size/dimension and structural change due to hydration) [61]. The two selected metal ions have almost the same configurations: Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> (0.74 Å) octahedron structure and Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> (0.715 Å) octahedron, green structure, and considers Ni(II) and Zn(II) as borderline Lewis acids.

I. Pletnev et V. Zernov, (2002) inter-correlated the stability constants of 24 metals with numerous ligands in order to establish a mapping of the metal ions in function of their complexation properties [62]. This classification does not contradict the well-known scheme by Pearson but complements it, so it allows to examine the complexing properties in more detail. According to these researchers, there appear six classes of metals; Ni(II) and Zn(II) metal ions are members of the same zones and seem to have same behaviours

(class V with Co(II) and Cu(II)). This classification is based on the dimension of the metal radii and classed metals of the smallest ionic radius up to the largest.

The sorption isotherms were obtained by varying metal concentrations of the solution, but the change in mass of sorbents at a fixed volume and concentration or the change in the volume of pollutant at a fixed sorbent mass and a fixed pollutant concentration is very important in a sorption study, with give a importance for the dosage study (SD), therefore, the complementary experiments have been achieved by changing the sorbent dosage. The effect of adsorbent dose on the percentage sorption of Zn(II) and Ni(II) is summarised in the additional material section. It was noted that the increase in the adsorbent dosage of 0.05 to 1.50 g L<sup>-1</sup> resulted in a decrease in the absorption capacity (see Section II, Figures AM2 and AM3).

At an initial concentration of metal ions of 0.3 mmol.L<sup>-1</sup>, it was found that increasing the adsorbent dose increased the percentage sorption of Zn(II) and Ni(II) ions. So, It can be concluded that the sorption percentage increased with increasing the adsorbent dose because increasing the sorbent dose give a larger surface area, consequently more adsorption sites are available For Ni(II); sorption increased from 21 to 45% for alginate, 47 to 82% for alginate-urea and 47 to 71% for alginate-biuret and in the case of Zn(II); an increase from 23 to 67% for alginate, the 38 to 78% for alginate-urea and 26 to 77% for alginate-biuret was observed. Sorption capacities of the synthesised sorbents for Zn(II) and Ni(II) removal are compared with other famous biosorbents in the literature (*see table AM2, Section VI, Additional Material Section*), it is clear that the synthesised materials are high in capacities than the most of other materials.

#### 4. Conclusions

The alginate-urea and alginate-biuret have been proven to be effective sorbents for Ni(II) and Zn(II) removal from water and show a greater affinity for these metals(for Ni(II): 3.22, 4.73 and 8.53 mmol g<sup>-1</sup> was found for the beads of alginate, alginate-biuret and alginate-urea, while it was 6.77, 6.97 and 7.14 mmol g<sup>-1</sup> for alginate, alginate-biuret and alginate-urea in the case of Zn(II)). The sorption is correlated with the softness parameters of these metal ions, the characteristics of the functional groups of the sorbents; – COOH for alginate beads and both – COOH and – NH<sub>2</sub> for modified alginate beads).

The sorption was studied in single and binary systems, equilibrium and kinetic studies were carried out onto different beads for the removal of Ni(II) and Zn(II) ions. The process was found to be pH-dependent and the maximum removal was attained an optimal pH value of

5.5. The equilibrium was achieved in a contact time of 6–8 h. Other parameters such as initial adsorbent dose, metal ion concentration, agitation speed and temperature of the solution had an influence on adsorption. And, kinetic data were well fitted to the PSORE kinetic model compared to PFORE model.

Sorption isotherm studies clearly indicated that among the Langmuir and Sips models, Langmuir showed a better fit for sorption of nickel and zinc ions by alginate and alginate-biuret, implying a monolayer/homogeneous binding surface. On the other hand, the Sips model provides the best fit with the experimental results ( $R^2 = 0.99$ ), for the adsorption of

two metals studied on the alginate-urea in this work, which confirms the great heterogeneity of the surface of the last.

According to SEM-EDX analysis and the HASB theory, the affinity for Ni(II) and Zn(II) could be related to the presence of amino groups at the surface of the biosorbents. The thermodynamic parameters were also evaluated using equilibrium constants with a change in temperature. The thermodynamic parameters,  $\Delta G^\circ$  and  $\Delta H^\circ$  indicated a spontaneous endothermic physico-chemical sorption process. The study indicates that prepared adsorbents can be successfully used as effective adsorbents for the removal of metal ions from water.

Selectivity studies of the two functionalised polysaccharide sorbents is showing the possibility of their use as selective adsorbents in solutions included these elements. Due to the complexity of the polysaccharides and their specific characteristics, we can predict different types of interactions that used in the adsorption mechanism, like our case, ion exchange and others as; electrostatic attraction and coordination/chelation. These two groups – COOH and – NH<sub>2</sub> are used in the coordination and electrostatic interaction of metals.

According to the results obtained in this study, it is necessary to choose well the added function (-NH<sub>2</sub> or others function), the way and above all the cost because generally we want to modify the biosorbents to reduce the cost of the biosorption to keep or/and modify the basic properties. So the researchers must compare the need for modification with respect to the basic materials, and for each modification, we ask the question what are the contributions for each modification compared to the basic materials.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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