



## Comparative removal of nickel ions from aqueous solution using adsorbents derived from agricultural biomasses: a kinetic modeling

Ángel Villabona-Ortiz<sup>a</sup>, Candelaria Tejada-Tovar<sup>a</sup>, Ángel D. González-Delgado<sup>b,\*</sup>

<sup>a</sup>Chemical Engineering Department, Process Design and Biomass Utilization Research Group (IDAB), University of Cartagena, Cartagena, Bolívar, Colombia

<sup>b</sup>Chemical Engineering Department, Nanomaterials and Computer Aided Process Engineering Research Group (NIPAC), University of Cartagena, Cartagena, Bolívar, Colombia, email: agonzalezd1@unicartagena.edu.co

Received 19 April 2020; Accepted 1 November 2020

---

### ABSTRACT

The waste generation in the agricultural sector in North-Colombia represents a serious environmental problem owing to the attraction of vector-borne diseases, an increase in organic matter concentration, and an unsustainable life cycle of derived products. This leads to an increasing need for the identification of potential uses to these wastes, increasing its value-added. The aim of this work is to evaluate the adsorption capacity of five different biomasses from *Theobroma cacao*, *Citrus lemon*, *Manihot esculenta*, *Dioscorea rotundata*, and *Elaeis guineensis* crops to be used as promising biosorbents in the removal of nickel ions. This work provides insights into the current body of knowledge regarding the adsorption performance of different types of biomasses through the comparison of adsorption properties of five agricultural wastes under fixed operating parameters. The adsorption process was analyzed by defining optimum conditions of particle size and initial pH. The resulting adsorption data overtime was used to construct kinetic curves and study the phenomenon taking place during Ni(II) uptake. Results revealed higher removal yields for lemon peels (LP) biomass up to 96% compared with the other biosorbents. The optimum conditions for adsorption were observed at pH = 6 and particle size = 1 mm. The experimental data of cassava peels (CP), oil palm bagasse, and yam peels (YP) agreed with chemical adsorption nature of Elovich model, accounting for the sum of square errors at 0.14 and 0.46. The LP and cocoa (cocoa pod husk) biomasses were not properly fitted by these kinetic models. The resulting comparative study of adsorption kinetics allowed to prioritize those agricultural residues with the highest adsorption rates.

*Keywords:* Adsorption; Biomass; Nickel; Removal

---

### 1. Introduction

The disposal of agricultural residues in North Colombia represents a serious problem in terms of the environment and public health. The Colombian Institute of Hydrology, Meteorology, and Environmental Studies (IDEAM) and the National Planning Department (DNP) estimated that agriculture has significant repercussions in the total volume of solid waste generation and the agricultural nonpoint sources contribute at 84% to the biochemical oxygen demand of surface waters [1]. These residues cause contamination

of water sources as well as the attraction of vector-borne diseases because of the lack of proper waste management and valorization alternatives [2]. Based on the current environmental concerns of agricultural practices, there is a need to develop potential applications for residues that link the United Nation Sustainable Development Goals by responsible consumption and production within the whole processing chain of crop cultivation and commercialization.

Colombia exhibits competitive advantages in the global production of agricultural and forest biomass owing to its location in the tropics. Based on the Atlas of the Energy

---

\* Corresponding author.

Potential of Biomass Residual, Colombia generates more than 71 million tons/y of agricultural residues during the cultivation of rice, corn, banana, sugar cane, coffee, panela, oil palm, and plantain [3]. In the North-Colombia region, agricultural production is focused on cassava *Manihot esculenta* and yam *Dioscorea rotundata*, accounting for 35% and 18% of total production, respectively [4]. Besides, African palm oil *Elaeis guineensis* is widely cultivated positioning Colombia as the first Latin-America producer [5]. In 2015, more than 150,000 ha of oil palm fruits were harvested to cover the Colombian demand in food and industrial applications [6]. Other crops such as *Theobroma cacao* and *Citrus lemon* contribute to 20% of national production [4]. This high contribution of the North-Colombia region for derived food products has a direct relationship with the waste generation, which must be addressed for reducing its effects on the environment.

The agricultural residues have proved to be potential sources of adsorbents to treat wastewater highly contaminated with heavy metals and dyes; however, the current body of knowledge is focused on showing how a given type of biomass can efficiently adsorb contaminants, without comparing the performance of different materials under the same operating conditions. This leads to a more difficult selection of biomasses from a numerous set of agricultural wastes since the information available in the open literature corresponds to different operating conditions difficult to compare among works. Dai et al. [7] conducted a literature review regarding the utilization of agricultural wastes as an adsorbent for the removal of contaminants such as heavy metals, dyes, nitrogen, and phosphorus and organic contaminants. The influence of operating conditions on the adsorption performance was evident in such review, and consequently, comparing removal yields from different works may be challenging to accurately identify what material is more efficient among the large set.

In this work, five agricultural biomasses from *T. cacao*, *C. lemon*, *M. esculenta*, *D. rotundata*, and *E. guineensis* crops widely available in North-Colombia are used to prepare biosorbents for the removal of nickel ions. The optimum conditions of pH and particle size were assessed in batch adsorption mode. Kinetic modeling was also conducted by studying the adsorption capacity of these materials overtime. The findings derived from this work will be useful to screen potential biomasses in further adsorption studies considering standardized operating conditions and optimum removal yields.

## 2. Materials and methods

### 2.1. Biomass preparation

This work follows the methodological procedure proposed in previous work [8]. The agricultural biomasses were collected from local farms in North-Colombia and cut into small pieces for further pretreatment. The cocoa pod husk (CPH) is derived from the local processing of *T. cacao* trees. The peels from *C. lemon* (LP) were selected among a wide variety of fruit residues. The cassava peels (CP), yam peels (YP), and oil palm bagasse (OPB) derived from crops of *M. esculenta*, *D. rotundata*, and *E. guineensis*, respectively.

These biomaterials were washed thoroughly to remove adhered particles that may affect the adsorption process. Then, biomasses were subjected to drying in an oven at 80°C for 24 h. The particle size was reduced to 0.5, 0.355, and 1 mm by grinding and sieve meshing.

### 2.2. Adsorption experiments

The synthetic solution of nickel ions at 100 ppm was prepared by adding 0.275 g of nickel sulfate into 1 L of deionized water. The operating temperature and adsorbent amount during adsorption experiments were fixed at 25°C and 0.5 g, respectively. The particle size was varied at 0.355, 0.5, and 1 mm in order to assess the effect of this parameter on the adsorption yield [9]. The initial pH was varied to 2, 4, and 6, using HCl and NaOH solutions as reported by García-Padilla et al. [10]. The optimum conditions of particle size and pH were identified for the selected biomasses depending on its removal yields. The latter was calculated by Eq. (1), where  $C_0$  and  $C_e$  are defined as the initial and remaining concentrations in mg/L, respectively:

$$\text{Removal yield}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

Statistical analysis via Statgraphics Centurion XVI.II software was conducted to evaluate the significance of each variable on the removal yield. The kinetic modeling of the adsorption process was analyzed by collecting aliquots after 10, 30, 60, 120, 180, and 240 min. Then, the remaining concentration of heavy metal ions was measured using UV-vis spectrometry at 232 nm. The adsorption capacities  $q_e$  in mg/g were quantified as given by Eq. (2), where  $V$  is the volume of the solution in liters and  $m$  is the mass of adsorbent in grams [11]:

$$q_e = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

The experimental data were fitted to kinetic models of pseudo-first-order, pseudo-second-order, and Elovich to analyze the adsorption performance of nickel ions onto the biomass surface. The fitting parameters provide important information about the rate at which heavy metal ions are removed from the aqueous solution. Table 1 summarizes the mathematical modeling of pseudo-first-order, pseudo-second-order, and Elovich, as well as their parameters [12].

## 3. Results and discussions

### 3.1. Effect of particle size

As shown in Fig. 1, the effect of particle size on removal yield varied according to the type of biomass. The lemon peels and cocoa pod husk biomasses reached the highest adsorption yield of 95.8% and 79.96%, respectively, at 0.5 mm particle size. The CP, YP, and OPB biomasses reported that particle size at 1 mm provides the optimum condition for removal yields around 75.69%. Such particle size shows favorability towards efficient adsorption

Table 1  
Adsorption kinetic modeling in batch mode

Model	Equation	Parameters
Pseudo-first-order	$q_t = q_e (1 - e^{-k_1 t})$	$q_t$ (mmol/g): adsorption capacity at time $t$ $q_e$ (mmol/g): adsorption capacity at the equilibrium $k_1$ (min <sup>-1</sup> ): first-order-kinetic constant
Pseudo-second-order	$q_t = \frac{t}{\left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right)}$	$k_2$ (g/mmol min): kinetic constant of pseudo-second-order and the initial adsorption rate $q_e$ : adsorption capacity in equilibrium
Elovich	$q_t = q_e (1 - e^{-\alpha t})$	$\alpha$ (mmol/g min): initial rate of adsorption $\beta$ (mmol/g): related to the surface area covered and the activation energy by chemical adsorption

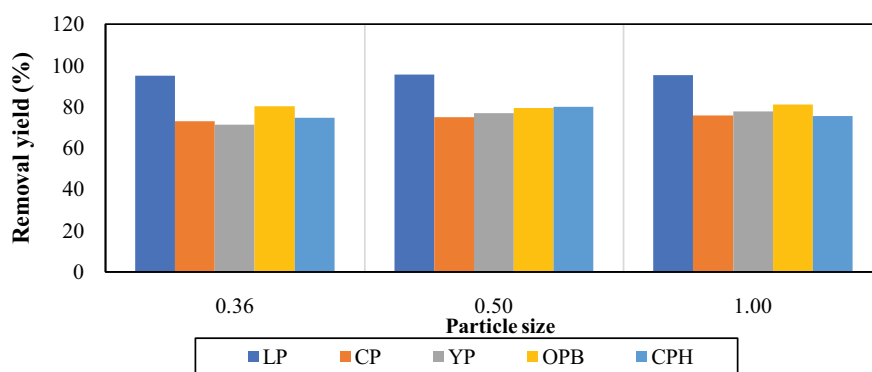


Fig. 1. Effect of particle size on nickel removal yields at pH = 6.

performance for most of the biomasses. These results revealed that the surface area of the biomass is independent of the particle size and/or the shape thereof [13]. Previous studies reported a similar tendency for large particles with spherical shapes since they exhibited higher adsorption yields caused by the high mass transfer of sorbate [14]. Other works reported that small-sized particles (<1 mm) enhance the adsorption process, especially close to 0.25 mm, for example, cocoa pod husk biomass (0.25 mm) [15], coconut peels (0.2 mm) [13], and orange peels (0.25 mm) [16].

### 3.2. Effect of initial solution pH

Fig. 2 shows the influence of initial solution pH on the adsorption performance of nickel ions using agricultural biomasses. The highest removal yields were reached for these biomaterials when using initial solution pH = 6, followed by pH = 4. According to these findings, the adsorption efficiency increases as the system becomes more alkaline, which is supported by several contributions that assess the effect of solution pH. For example, Bartczak et al. [17] evaluated acidic, neutral, and alkaline pH values in the removal of nickel using peat as a low-cost adsorbent. They found that the lowest effectiveness (42.7%) was obtained when the process took place in an acidic

environment. Shen et al. [18] reported an increase in Ni(II) removal percentage using biochar from wheat straw pellets and rice husk when increasing the initial solution pH in the range 2–10. The maximum removal yields for LP, CP, YP, OPB, and CPH were 94.5%, 75.69%, 77.65%, 81.15%, and 75.455%, respectively. According to Zhang and Wang [19], the repulsive interactions decrease as increasing solution pH, and consequently, it was expected the changes in removal yields when varying this parameter. The Ni(II) adsorption increased because of an ion-exchange mechanism between the surface protons and the heavy metal ions.

### 3.3. Statistical analysis

The statistical analysis of experimental data was conducted via Statgraphics Centurion XVI.II software. Fig. 3 shows the standardized Pareto graphs for the statistical significance of pH solution and particle size on the removal efficiency. This analysis showed a significant effect of pH solution as the  $p$ -values were closer to 0 for all the biomasses. At pH = 6, the H<sup>+</sup> concentration is relatively lower, facilitating the deprotonation of the adsorbent surface and, consequently, the bioadsorption capacity reaches higher values [2]. The deprotonation of the functional groups serving as binding sites makes them easily accessible to metal ions since low solubility salts such as NiCO<sub>3</sub> and

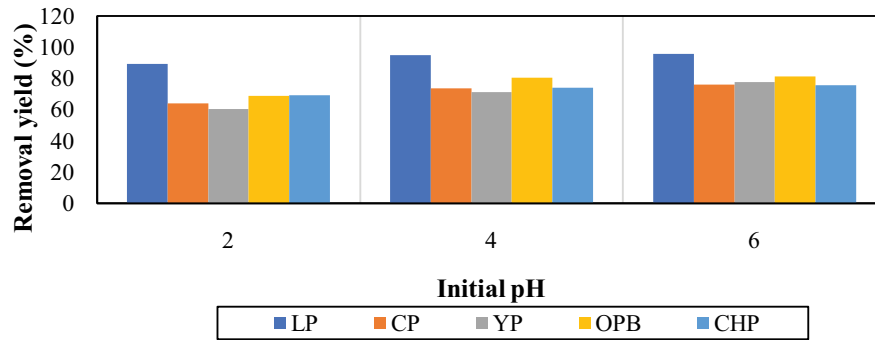


Fig. 2. Effect of initial pH on nickel removal yields at a particle size of 1 mm.

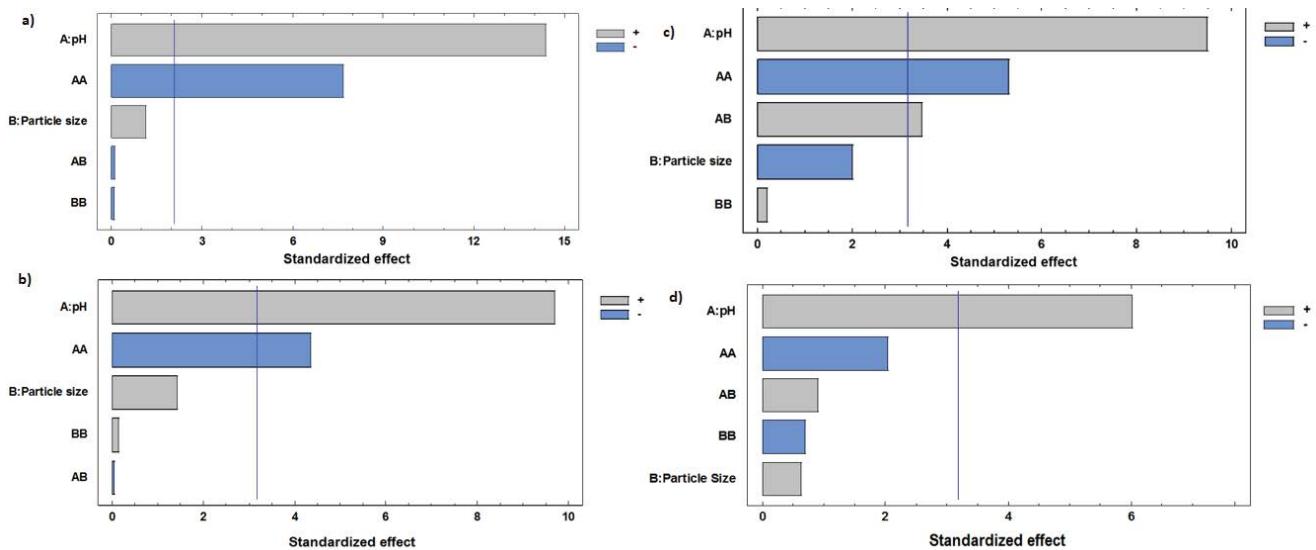


Fig. 3. Pareto chart for: (a) LP, (b) CP, (c) OPB, and (d) YP biomass.

NiHCO<sub>3</sub> are formed, therefore, it would favor ion exchange on the surface of the adsorbent [3]. The standardized effects were lower for particle size, having no significant contribution to the removal efficiency.

### 3.4. Kinetic modeling

The adsorption kinetics describe the rate of removal of Ni(II) ions from an aqueous environment to the solid-phase interface of the biosorbent [20]. The experimental data for kinetic modeling included the changes in adsorption capacity overtime in the range of 0–240 min. Fig. 4 depicts the curves for the biosorbents. The lemon peel biomass reached the highest adsorption capacity in the first 30 min. At this time interval, a rapid increase in capacities was observed for the CP, YP, OPB, and CHP biosorbents; however, best adsorption results were achieved after 180 min of contact time between biomass surface and sorbate (nickel ions). This phenomenon may be explained as follows: the sites in biosorbent surface are open and available at the beginning of the adsorption process and Ni(II) can interact easily with these sites. After adsorption

took place, nickel ions were accumulated in the surface, which leads to the occupation of surface binding sites and reducing the adsorption capacity of the material [21].

#### 3.4.1. Pseudo-first-order model

Fig. 5 depicts the kinetic curves following pseudo-first-order model for the selected adsorbents. The YP biomass reached the lowest sum of square error (SSE) at 0.61, which suggests a good fitting of experimental data. Such fitting to the pseudo-first-order model establishes that the adsorption rate depends on a mechanism operating at an active site on the biomass surface [22]. These findings revealed that sorption rates for lemon peels and cocoa pod husks are not accurately described by first-order model.

#### 3.4.2. Pseudo-second-order model

Fig. 6 shows the curves from kinetic modeling of biosorbents and the SSE for the data fitting. It is found that biosorbents from cassava peels and yam peels follows the pseudo-second-order model, in which the rate-limiting

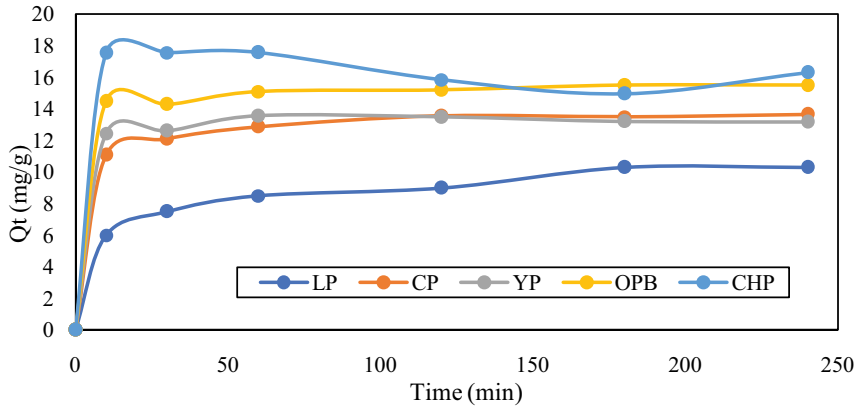


Fig. 4. Adsorption kinetic curves for Ni(II) adsorption onto the biomasses.

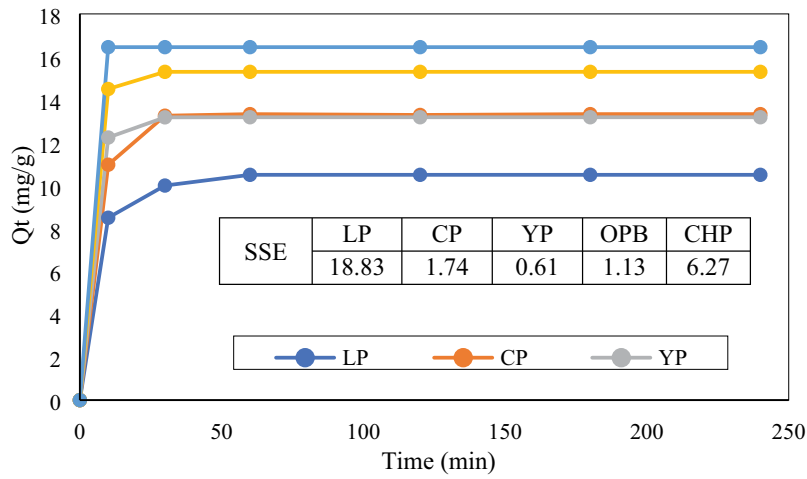


Fig. 5. Pseudo-first-order modeling of experimental data.

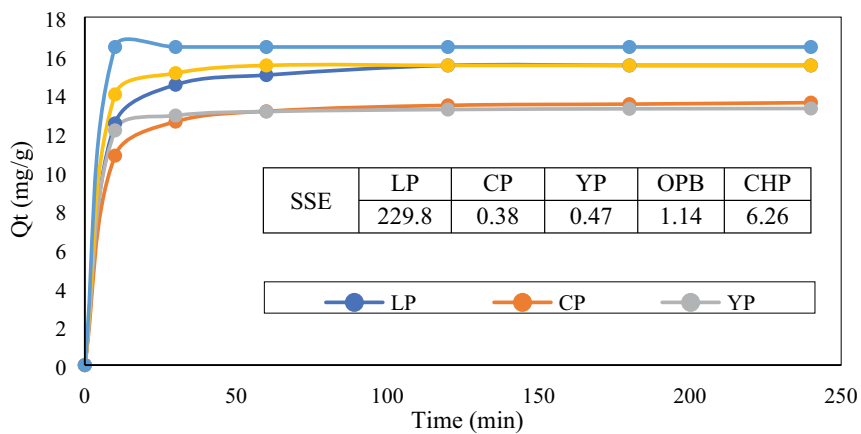


Fig. 6. Pseudo-second-order modeling of experimental data.

step is the chemisorption due to physicochemical interactions between the two phases [23]. The lemon peels biomass reached the highest SSE value, suggesting that experimental data is not well-described by pseudo-second-order model.

3.4.3. Elovich model

The Elovich model was used to fit experimental data and the resulting curves are shown in Fig. 7. Based on the SSE values, the adsorption process using biosorbents derived

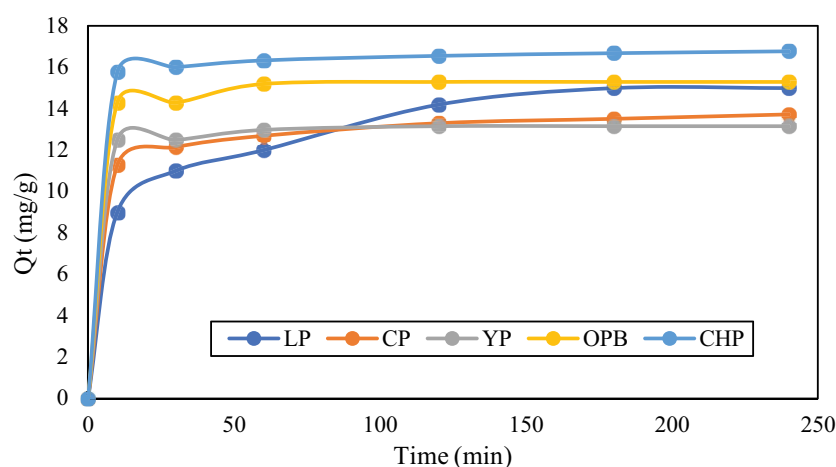


Fig. 7. Elovich modeling of experimental data.

from cassava peels and OPB was better described by Elovich model compared with the other biosorbents. Taking into account the previous results for all kinetic models, it can be concluded that LP is not well-described by neither of the models, however, the SSE was lower for pseudo-first-order model. The CP, YP, and OPB biomasses agreed with the chemical adsorption nature of Elovich model. The adsorption data for CHP biomass do not fit the kinetic models, and Elovich was the one with the most significant SSE.

#### 4. Conclusions

This work attempted to provide alternatives for agricultural waste valorization as well as reduce contamination of heavy metal ions in aqueous environments. Five agricultural residues available in North-Colombia were selected to perform this work, which is collected from *T. cacao*, *C. lemon*, *M. esculenta*, *D. rotundata*, and *E. guineensis* crops. The adsorption capacity of these biomaterials for Ni(II) uptake from aqueous solution was evaluated by varying operating conditions such as initial pH and particle size. Also, experimental data was fitted to kinetic models of pseudo-first-order, pseudo-second-order, and Elovich. Results revealed that the most favorable particle size in the nickel adsorption process is the largest one (1 mm) for most of the biosorbents. The highest removal yields were reached when using initial solution pH = 6, followed by pH = 4. It can be concluded that high adsorption efficiencies can be obtained using these agricultural wastes at optimum pH = 6 and particle size = 1 mm. The most promising results were observed for lemon peels suggesting that fruit wastes may represent a good alternative to treat wastewater highly contaminated with nickel ions.

#### Acknowledgments

Authors express their gratitude to University of Cartagena for providing reagents and equipment to successfully conclude this research.

#### References

- [1] A. Blackman, R. Morgenstern, L. Montenegro, J. García de Brigard, Review of the Efficiency and Effectiveness of Colombia's Environmental Policies, An RFF Report, 2006.
- [2] R. Herrera-Aristizábal, J. Salgado-Dueñas, Y. Peralta-Ruiz, A. González-Delgado, Environmental evaluation of a palm-based biorefinery under North-Colombian conditions, *Chem. Eng. Trans.*, 57 (2017) 193–198.
- [3] K. Rodríguez-Cáceres, F.G. Blanco-Patiño, J.A. Araque-Duarte, V. Kafarov, Assessment of the energy potential of agricultural residues in non-interconnected zones of Colombia: case study of Chocó and Putumayo, *Chem. Eng. Sci.*, 50 (2016) 349–354.
- [4] I. Paz-Astudillo, C. Rivera-Barrero, L. Buelvas, Puello, G. Franco-Arnedo, D. Marsiglia-Lopez, Diagnostic of the main agricultural residues produced in the Bolivar region, *Sci. Agroaliment.*, 2 (2015) 39–50.
- [5] L.E. Rincón, J. Moncada, C.A. Cardona, Analysis of potential technological schemes for the development of oil palm industry in Colombia: a biorefinery point of view, *Ind. Crops Prod.*, 52 (2014) 457–465.
- [6] L.E. Rincón, M.J. Valencia, V. Hernández, L.G. Matallana, C.A. Cardona, Optimization of the Colombian biodiesel supply chain from oil palm crop based on techno-economical and environmental criteria, *Energy Econ.*, 47 (2020) 154–167.
- [7] Y. Dai, Q. Sun, W. Wang, L. Lu, M. Liu, J. Li, S. Yang, Y. Sun, K. Zhang, J. Xu, W. Zheng, Z. Hu, Y. Yang, Y. Gao, Y. Chen, X. Zhang, F. Gao, Y. Zhang, Utilizations of agricultural waste as adsorbent for the removal of contaminants: a review, *Chemosphere*, 211 (2018) 235–253.
- [8] C. Tejada-Tovar, A. Gonzalez-Delgado, A. Villabona-Ortiz, Characterization of residual biomasses and its application for the removal of lead ions from aqueous solution, *Appl. Sci.*, 9 (2019) 1–14.
- [9] J. Lara, C. Tejada-Tovar, A. Villabona-Ortiz, A. Arrieta, Adsorption of lead and cadmium in continuous of fixed bed on cocoa waste, *Rev. Ion*, 29 (2016) 113–124.
- [10] Á. García-Padilla, K. Moreno-Sader, A. Realpe, M. Acevedo-Morantes, J.B.P. Soares, Evaluation of adsorption capacities of nanocomposites prepared from bean starch and montmorillonite, *Sustainable Chem. Pharm.*, 17 (2020) 1–13, doi:10.1016/j.scp.2020.100292.
- [11] K. Moreno-Sader, A. García-Padilla, A. Realpe, M. Acevedo-Morantes, J. Soares, Removal of heavy metal water pollutants (Co<sup>2+</sup> and Ni<sup>2+</sup>) using polyacrylamide/sodium montmorillonite (PAM/Na-MMT) nanocomposites, *ACS Omega*, 4 (2019) 10834–10844.
- [12] S. Madala, S.K. Nadavala, S. Vudagandla, V.M. Boddu, K. Abburi, Equilibrium, kinetics and thermodynamics of

- Cadmium(II) biosorption on to composite chitosan biosorbent, *Arabian J. Chem.*, 10 (2017) S1883–S1893.
- [13] A. Natasia, J. Febrianto, J. Sunarso, Y. Ju, N. Indraswati, S. Ismadji, Sequestering of Cu(II) from aqueous solution using cassava peel (*Manihot esculenta*), *J. Hazard. Mater.*, 180 (2010) 366–374.
- [14] G. Huamán, L. Torem, Biosorción de Metales Pesados Contenidos en Efluentes Utilizando Biomasa Orgánica, Convención Minera Arequipa, 2009.
- [15] C. Ardila, S. Carreño, Aprovechamiento de la Cáscara de la Mazorca de Cacao Como Adsorbente, Universidad Industrial de Santander, 2011.
- [16] E. Soto, Estudio de la Remoción de Cu(II) en Medio Acuoso Utilizando el Albedo de la Cáscara de Naranja, Universidad Nacional de Ingeniería, 2009.
- [17] P. Bartczak, M. Norman, Ł. Klapiszewski, N. Karwańska, M. Kawalec, M. Baczyńska, M. Wysokowski, J. Zdzarta, F. Ciesielczyk, T. Jesionowski, Removal of nickel(II) and lead(II) ions from aqueous solution using peat as a low-cost adsorbent: a kinetic and equilibrium study, *Arabian J. Chem.*, 11 (2018) 1209–1222.
- [18] Z. Shen, Y. Zhang, O. McMillan, F. Jin, A. Al-Tabbaa, Characteristics and mechanisms of nickel adsorption on biochars produced from wheat straw pellets and rice husk, *Environ. Sci. Pollut. Res. Int.*, 24 (2017) 12809–12819.
- [19] X. Zhang, X. Wang, Adsorption and desorption of Nickel(II) ions from aqueous solution by a lignocellulose/montmorillonite nanocomposite, *PLoS One*, 10 (2015) 1–21, doi: 10.1371/journal.pone.0117077.
- [20] G. Kajjumba, S. Emik, A. Ongen, H. Ozcan, S. Aydin, Modelling of Adsorption Kinetic Processes—Errors, Theory and Application, S. Edebali, Ed., *Advanced Sorption Process Applications*, IntechOpen, 2018. Available at: <https://www.intechopen.com/books/advanced-sorption-process-applications/modelling-of-adsorption-kinetic-processes-errors-theory-and-application>
- [21] K. Kowanga, E. Gatebe, G. Mautin, E. Mauti, Kinetic, sorption isotherms, pseudo-first-order model and pseudo-second-order model studies of Cu(II) and Pb(II) using defatted *Moringa oleifera* seed powder, *J. Phytopharmacol.*, 5 (2016) 71–78.
- [22] E. Da'Na, A. Awad, Regeneration of spent activated carbon obtained from home filtration system and applying it for heavy metals adsorption, *J. Environ. Chem. Eng.*, 5 (2017) 3091–1099.
- [23] D. Robati, Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube, *J. Nanostruct. Chem.*, 55 (2013) 1–6.