

Multiple heavy metal removal simultaneously by a biomass-based porous carbon

Sari Tuomikoski , Hanna Runtti, Henrik Romar, Ulla Lassi, Teija Kangas

Research Unit of Sustainable
Chemistry, University of Oulu, Oulu, Finland

Received 15 December 2020; Revised 8
January 2021; Accepted 11 January 2021

ERDF project (WaterPro), Grant/Award
Number: A74635

Correspondence: Sari Tuomikoski,
Research Unit of Sustainable Chemistry,
University of Oulu, Oulu FI-90014, Finland.
Email: sari.tuomikoski@oulu.fi

DOI: 10.1002/wer.1514

© 2021 The Authors. *Water Environment
Research* published by Wiley Periodicals
LLC on behalf of Water Environment
Federation.

This is an open access article under the
terms of the Creative Commons Attribution
License, which permits use, distribution and
reproduction in any medium, provided the
original work is properly cited.

• Abstract

Activated carbon from sawdust was produced with an environmentally friendly process involving single-stage carbonization and activation with steam at 800°C. Production process is scalable because lignocellulosic biomass is ubiquitous worldwide as a waste or as a virgin material. Single-stage production without any cooling steps between carbonization and activation is easier in larger scale production. Monometal adsorption and multimetal adsorption of cobalt, nickel, and zinc were investigated by using the produced carbon, with a commercial one as control. Effect of pH, initial metal concentration, adsorbent dosage, and adsorption time was evaluated in batch experiments. Multimetal experiments showed the order of the maximum adsorption capacities: zinc > nickel > cobalt. Experimental adsorption capacities were 17.2, 6.6, and 4.5 mg/g for zinc, nickel, and cobalt, respectively, in multisolute adsorption. In case of monometal adsorption, adsorption capacity was notably lower. Experimental data fitted into the single-solute and multisolute Freundlich models. The best fit kinetic model varied among the metals. The Weber and Morris intraparticle diffusion model was used. Regeneration was performed with 0.1 M HNO₃, 0.1 M HCl, or 0.1 M H₂SO₄. The adsorption capacity remained at the same within three adsorption-desorption cycles. © 2021 Water Environment Federation

• Practitioner points

- Activated carbon was produced from sawdust with environmentally friendly process
- Monometal adsorption and multimetal adsorption with heavy metals were studied
- Best-fitting models to the experimental data were single-solute and multisolute Freundlich models
- Regeneration could be performed with diluted acids
- Worldwide available raw material successfully used as adsorbent for heavy metals

• Key words

adsorption; biomass; circular economy; heavy metals; regeneration

INTRODUCTION

Metals, such as zinc, are toxic substances, and they are released from anthropogenic sources, such as the metal industry and landfills, into the aquatic environment (Depci et al., 2012; Fernández et al., 2005; O'Connell et al., 2008; Rule et al., 2006). Heavy metals are not biodegradable, and they accumulate in living organisms causing several effects on health (Depci et al., 2012; Kurniawan et al., 2006). Several methods are suitable for the removal of metals from aqueous solutions; these methods include electrocoagulation (Mansoorian et al., 2014), ion exchange (Fernández et al., 2005), membrane filtration (Castelblanque & Salimbeni, 2004), coagulation-flocculation, flotation, and chemical precipitation (Kurniawan et al., 2006). Adsorption is one of the most widely used methods for heavy metal removal due to its simplicity, high efficiency, and regeneration potential (Depci et al., 2012; Runtti et al., 2014).

In several studies, adsorbents suitable for heavy metal removal were developed from a wide range of raw materials as precursor, including sesame straw biochar (Park et al., 2016), agricultural waste (apple pulp) (Depci et al., 2012), water hyacinth (Gwenzi et al., 2014), hazelnut shells (Demirbaş, 2003), *Barbula lambarenensis* (Diagboya & Dikio, 2018), fruit biomass (Mohubedu et al., 2019), and banana and orange peels (Annadurai et al., 2003). In addition, some kind of new class of functional adsorbents suitable for water treatment has been introduced in literature (Diagboya et al., 2020). Most of the reported adsorbents have been primarily used to remove individual metals. Thus, this study focused on multimetal adsorption, which offers various applications, such as in the purification of industrial wastewaters where several metals are typically found. Another novelty of this study is the usage of sawdust as a precursor for adsorbent production. Sawdust is ubiquitous worldwide, and from the perspective of circular economy and bioeconomy, there is huge potential with biomass-based raw materials in the field of water purification. Activated carbon production typically involves two steps: carbonization and activation. These processes can be performed in a two-stage system wherein carbonization and activation are performed as separate processes, that is, they are separately performed in a single-reaction system (Bergna et al., 2018). Meanwhile, activation can be done chemically or physically. The typical agents for physical activation are steam and carbon dioxide (Chand Bansal & Goyal, 2005).

Studies on the monometal adsorption of cobalt, nickel, or zinc by waste-based biomaterials have been reported in the literature. For instance, Depci et al. (2012) produced apple pulp-based activated carbon, which in turn was used to remove lead and zinc from monometal and multimetal systems. Bouhamed et al. (2016) also reported the removal of copper, nickel, and zinc by using activated carbon prepared from date stones. Hossain et al. (2014) used cabbage waste biosorbent for the removal of copper, nickel, cadmium, and zinc. However, a multimetal system used to remove cobalt, nickel, or zinc by using biomass-based activated carbon produced from a scalable precursor material has not yet been reported.

This study aimed to develop a carbon adsorbent from a renewable source (sawdust) and then activated physically with steam. This adsorbent was used for the monometal and multimetal adsorption of cobalt, nickel, and zinc. The advantages of this adsorbent are as follows: It is produced through an environmentally friendly single-stage process that involves steam, it is scalable given that lignocellulosic biomass in the form of virgin material or waste material is ubiquitous worldwide, it is suitable for adsorption in solutions containing low metal concentrations but with large flows, and it is regenerable multiple cycles. The sawdust used in this study was a sidestream from sawmills. The suitability of the obtained material as adsorbent for cobalt, nickel, and zinc was determined through monometal and multimetal adsorption experiments, which were conducted under the following conditions: pH 2–7, initial metal concentration of 30–900 mg/L, adsorbent dosage of 0.5–10 g/L, and adsorption time of 1–1440 min. Regeneration was investigated using three types of diluted acids. Typically, only traditional isotherm

models designed for single-compound systems are also used in multimetal systems. In this study, both single-solute models and multimetal isotherm models designed for multimetal adsorption were used. Moreover, pseudo-first-order, pseudo-second-order, and Elovich kinetic models were used to analyze the results.

EXPERIMENTAL SECTION

Preparation of biomass-based activated carbon

In a single-stage process, the biomass (spruce sawdust) was dried, carbonized, and activated with steam in a rotating quartz reactor (Nabertherm GmbH RSRB 80). The thermal profile during the entire process was divided into two parts. The first part is the carbonization step, wherein the temperature was raised to 800°C with a ramp of 6.7°C/min, leading to the complete carbonization of the biomass and then followed by the activation step. During the activation, the temperature was kept at 800°C for 120 min with a stream of water (120 g/h at 140°C), which facilitates proper surface activation. During the entire process, the reactor was flushed with an inert gas. In the ramping step, only N₂ (200 ml/min flow rate) was used, whereas in the activation step, a carrier gas (N₂ 200 ml/min flow rate) and steam (120 g/h at 140°C) were both utilized. The resulting activated carbon was crushed and sieved to a fraction size of 1.4–2 mm. In this paper, the carbonized and activated carbon from spruce sawdust is referred to as Sawdust. A commercial activated carbon (Norit GCN), referred to here as Norit, was used as reference material.

Characterization of activated carbon

Pore size, pore volume, and specific surface area of the produced activated carbons were analyzed using a Micromeritics ASAP 2020 system (Norcross, GA, USA). The analysis method is based on nitrogen adsorption–desorption isotherms at the temperature of liquid nitrogen. Prior to the measurements, the samples were pretreated at low pressures and at high temperatures to clean their surfaces. Sample tubes were immersed in liquid nitrogen (−197°C) and then nitrogen gas was added incrementally to the samples, and the resulting isotherms were obtained. Specific surface areas were calculated from the adsorption isotherms according to the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938), and pore-size distributions were calculated using the Barrett–Joyner–Halenda (BJH) algorithm. (Barrett et al., 1951) Sample degassing was performed by elevating the temperature to 50°C under the restricted pressure drop to 15 mmHg, and the temperature was held at 50°C for 10 min. Subsequently, the samples were heated at 10°C/min up to 140°C under free evacuation. Finally, the samples were degassed at 140°C for 3 h. This procedure gives a final, constant pressure of 2 μmHg.

The carbon, nitrogen, hydrogen, sulfur, and oxygen contents were determined through elemental analysis by using a Flash 2000 Analyzer (Thermo Fisher Scientific, Cambridge, UK). The analysis method is based on combustion wherein elements are converted into a simple gas, such as CO₂, in a pure oxygen atmosphere.

Adsorption experiments

The effect of initial pH, initial metal concentration, adsorbent dosage, and time was investigated through batch experiments involving Sawdust and Norit as adsorbents. The adsorption experiments began with pH optimization wherein the pH values 2, 4, 6, and 7 were tested under the following conditions: initial metal concentration of 90 mg/L, adsorbent dosage of 5 g/L, and adsorption time of 24 h at room temperature. The sample volume was 25 ml. The pH of the solution was adjusted by using 0.1 M HCl and/or NaOH, which were provided by FF Chemicals. pH was adjusted after mixing the adsorbent and the metal solution to prevent metal precipitation. Falcon tubes were placed on a laboratory shaker wherein the shaking speed was set to 300 rpm. Then, the effect of initial metal (cobalt, nickel, or zinc) concentration was studied at the optimum pH by using the following concentrations: 30–900 mg/L. Metal solutions were prepared from 1 g/L stock solution of cobalt, nickel, and zinc; the stock solutions were prepared by using CoCl_2 , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, or ZnCl_2 in Milli-Q water. The effect of adsorbent mass was studied at optimum pH and optimum initial metal concentration by using the following adsorbent dosages: 0.5, 1, 3, 5, 7, and 10 g/L. The effect of time was studied at optimum adsorption conditions, and the adsorption times used were 1–1440 min. Multimetal adsorption was investigated by using the same procedure applied for monometal adsorption and by using the same concentration ratio for the three metals. The concentrations of the metal solutions were analyzed by atomic absorption spectroscopy (AAAnalyst 200 Atomic Absorption Spectrometer; Perkin-Elmer).

The experimental adsorption capacity (q_e , mg/g) after equilibrium was calculated as follows (Equation 1):

$$q_e = \frac{(c_0 - c_e) V}{m_{\text{ads}}} \quad (1)$$

where c_0 and c_e are the initial and equilibrium concentrations (mg/L) of Co, Ni, or Zn, respectively. V (L) is the volume of the solution, and m_{ads} (g) is the amount of adsorbent.

Regeneration experiments

Regeneration experiments involving the adsorbents covered with metals were conducted in optimized conditions as follows: adsorbent dosage of 10 g/L, pH of 7, multimetal solution concentration of 30 mg/L, and contact time of 24 h. Regeneration experiments were performed using three types of acid: 0.1 M HNO_3 , 0.1 M HCl, or 0.1 M H_2SO_4 by mixing 0.4 g of used, air-dried adsorbent and 40 mL of regeneration solution. The mixture was shaken for 2 h in a laboratory shaker (300 rpm) and then filtrated through a 0.45- μm filter. Three adsorption – regeneration cycles were performed.

Adsorption isotherms

Both single-solute and multisolute Freundlich and Langmuir isotherm models were applied to the results obtained using the repaired sawdust-based adsorbent, the control adsorbent (Norit), and purified metal solutions of varying concentrations. The Langmuir isotherms can be presented as Equation

2 (Langmuir, 1918) and Freundlich isotherm with Equation 3 (Freundlich, 1906).

$$q_e = \frac{q_m b c_e}{1 + b c_e} \quad (2)$$

$$q_e = K c_e^n \quad (3)$$

In both equations, q_e is the adsorption capacity (mg/g) and C_e is the adsorbent concentration at equilibrium. The parameter q_m in the Langmuir equation represents the maximum adsorption capacity (mg/g), and the parameter b is an empirical constant (L/mg) that is related to adsorption energy. In Equation 3, K characterizes the strength of adsorption and is called the adsorption coefficient ((mg/g)/(mg/L)ⁿ), wherein the exponent represents both the adsorption intensity and the surface heterogeneity. If $n > 1$, adsorption is unfavorable; by contrast, when $n < 1$, the adsorption is favorable.

Multisolute adsorption was modeled using the extended Langmuir isotherm (Butler & Ockrent, 1930; Worch, 2012) and the Freundlich isotherm model for several components (Digiano et al., 1978). The extended Langmuir isotherm and the Freundlich isotherm for several components are introduced in Equations 4 and 5, respectively. In both equations, the parameters correspond to the parameters of single-solute isotherm in Equations 2 and 3.

$$q_{e,i} = \frac{q_{m,i} b_i c_i}{1 + \sum_{j=1}^N b_j c_j} \quad (4)$$

$$q_i = \frac{K_i^{1/n} c_i}{\left(\sum_{j=1}^N K_j^{1/n} c_j \right)^{1-n}} \quad (5)$$

The isotherm parameters were solved using nonlinear regression with the Microsoft Excel solver tool. The correlation coefficient R^2 and the residual root mean square error (RMSE) were also solved to evaluate the suitability of the isotherms. These values are defined in Equations 6 and 7.

$$R^2 = 1 - \frac{\sum_{n=1}^n (q_{e,exp,n} - q_{e,model,n})^2}{\sum_{n=1}^n (q_{e,exp,n} - \bar{q}_{e,exp,n})^2} \quad (6)$$

$$RMSE = \sqrt{\frac{1}{n-1} \sum_{n=1}^n (q_{e,exp,n} - q_{e,model,n})^2} \quad (7)$$

Kinetics

Three kinetic models, namely pseudo-first-order, pseudo-second-order, and Elovich, were applied to the experimental kinetic data obtained when the activated carbon prepared from sawdust and a comparable material (Norit) were utilized

to remove cobalt, nickel, and zinc ions. The nonlinear forms of the pseudo-first-order (Lagergren, 1898), pseudo-second-order (Ho & McKay, 1999), and Elovich (Zeldowitsch, 1934) models are presented in Equations 8, 9, and 10, respectively.

$$q_t = q_e (1 - e^{-k_1 \cdot t}) \quad (8)$$

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \quad (9)$$

$$q = \frac{1}{\beta} \ln \left(v_0 \beta + \frac{1}{\beta} \ln t \right), \quad (10)$$

In the pseudo-first-order model, q_t (mg/g) and q_e (mg/g) represent the amount of metal ions adsorbed at time t (min) and the equilibrium, respectively. The parameter k_1 (min^{-1}) is the pseudo-first-order rate constant in Equation 8 and the analogous parameter k_2 is the pseudo-second-order rate constant (g/mg min) in Equation 9. In Equation 10, the parameter β (g/mg) is the desorption constant and v_0 (mg/g min) is the initial adsorption rate. Nonlinear kinetic modeling was performed using the Origin 2018 Software.

The intraparticle diffusion model introduced by Weber and Morris (Equation 11) was used in analyzing diffusion mechanism.

$$q_t = k_{id} t^{1/2} + C \quad (11)$$

In this equation, k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion in the rate-determining step, and C is the intercept related to the thickness of the boundary layer (Weber & Morris, 1963).

RESULTS AND DISCUSSION

The biomass-based activated carbon, referred to here as Sawdust, was used to remove cobalt, nickel, and/or zinc. The effects of pH, initial metal concentration, adsorbent dosage, adsorption time, and desorption were studied through monometal and multimetal adsorption experiments. Isotherm analysis and kinetic modeling were also performed. A commercial activated carbon, Norit, was used as reference material. The results showed that the presence of other ions in a multimetal adsorption system influenced positively the adsorption efficiency. The results of the monometal adsorption experiments are not presented because the removal percentages were low compared with those for the multimetal adsorption. In the case of Sawdust, the maximum removal percentages for cobalt and zinc were 13.4% and 17.0%, respectively. In the case of Norit, the removal percentage for zinc and cobalt were 27.8% and 27.9%, respectively.

Characteristics of materials

The characterization results (elemental analysis and surface area, pore volume, and pore size measurements) for Sawdust

TABLE 1. Comparison of the characteristics of the produced activated carbon (Sawdust) and the commercial activated carbon (Norit). Porosity was calculated by BJH physisorption

PARAMETER	UNIT	NORIT	SAWDUST
C	%	91.9	90.8
H	%	0.5	0.7
N	%	<0.5	0.8
S	%	<2	0
O	%	2.6	2.1
Specific surface area	m^2/g	786	1010
Pore size (average)	nm	2.21	2.8
Micropore volume (total)	cm^3/g	0.394	0.28
Macropore + meso-volume (total)	cm^3/g	0.041	0.34

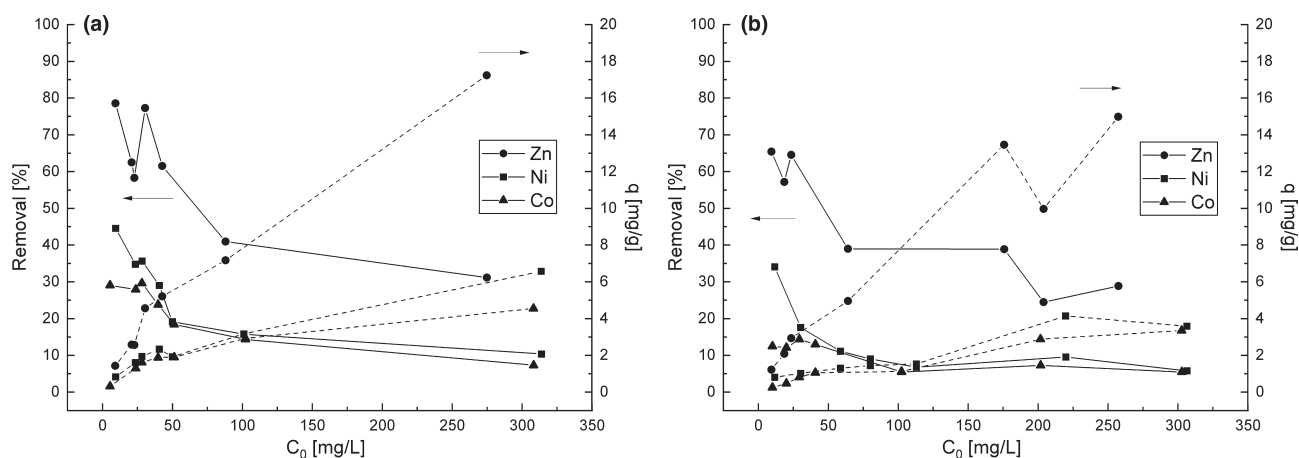
and Norit are presented in Table 1. The carbon content of the biomass-based activated carbon varies between 65% and 97% (Lahti et al., 2017), and the 90.8% carbon content of Sawdust is quite high and is nearly equal to that in Norit. Sawdust also contained elements other than carbon, and therefore, it is presumed to be heterogeneous. In the literature, specific surface areas for biomass-based activated carbons vary between 336 and 1080 m^2/g (Lahti et al., 2017). Compared with the specific surface area reported in other studies, that obtained in this study is considerably high. Typically, the pore volume varies between 0.02 cm^3/g and 0.80 cm^3/g (Lahti et al., 2017) for biomass-based activated carbons, consistent with the current results. During the activation step, a slow oxidation process occurs, resulting in the porosity of the material as a consequence of the reaction between carbon and oxygen (Marsh et al., 2006). The adsorption of different metals can be attributed to ionic radii, among other factors; however, in this study, the effect of ionic radii or hydrated ionic radii seems irrelevant given that the pore sizes of the studied adsorbents, as presented in Table 1, are notably larger (in nanometer) than the ionic radii (in picometers) of the studied metals (Depci et al., 2012). That is, the pore size is sufficiently large to facilitate adsorption.

Effect of pH

The surface charge of the adsorbent material, the degree of ionization, the speciation of metals, and the electrostatic interactions between an adsorbent and metals are determined by pH and thus is one of the most important parameters that control metal uptake from an aqueous solution (Cho et al., 2005; Özçimen & Ersoy-Meriçboyu, 2009). The effect of pH was studied within a pH range of 2 – 7 to prevent precipitation of metals by using the following conditions: 90 mg/L initial metal concentration, 5 g/L adsorbent dosage, and 24-h adsorption time at room temperature. Table 2 presents the results, which clearly show that the highest removal % and the optimum pH value for adsorption is 7 for both Norit and Sawdust. At an acidic pH, a negligible amount of metals was adsorbed. At low pH, metal cations in the solution compete with the H^+ ions for

TABLE 2. Effect of pH on the removal % of cobalt, nickel, and zinc with Sawdust or Norit as adsorbents

ADSORBENT	INITIAL PH	REMOVAL % COBALT	REMOVAL % NICKEL	REMOVAL % ZINC
Sawdust	2	3.79	4.65	0
	4	12.4	16.0	17.5
	6	24.7	23.4	60.2
	7	64.4	63.5	98.8
Norit	2	4.16	5.43	2.53
	4	6.87	9.99	9.18
	6	15.2	26.4	51.22
	7	51.0	60.2	91.0

**FIGURE 1.** Removal percentages as a function of the initial concentration of metals when (a) Sawdust or (b) Norit was used as adsorbent. The effect of initial concentrations was tested at pH 7, 5 g/L adsorbent dosage, and 24-h adsorption time at room temperature

the suitable adsorption sites, and this phenomenon explains the increase in the removal % with the increase in pH (Runtti et al., 2014).

A higher pH enables metal cations to form hydroxide complexes or to precipitate as hydroxides. In the pH optimization experiments, the final pH after adsorption was measured to ensure that the metals do not precipitate as metal hydroxides. (Chen & Wang, 2000; El-Ashtouky et al., 2008; Özçimen & Ersoy-Meriçboyu, 2009) Based on the Eh-pH diagrams, cobalt, nickel, and zinc exist as ions within the studied pH range under both oxidative and reductive conditions. This finding may indicate that the metal removal capacity is based on adsorption and that no major precipitation occurred (National Institute of Advanced Industrial Science and Technology Research Center for Deep Geological Environments Naoto TAKENO, 2005). The results of the regeneration experiments support this finding. Therefore, pH 7 was selected for all the other adsorption experiments.

Effect of initial metal concentration

Experimental results for the removal of cobalt, nickel, and zinc by Sawdust and Norit within the initial metal concentration of 30–900 mg/L at the optimum initial pH for each metal are shown in Figure 1. The results show that Sawdust is slightly better as a adsorbent material than Norit. The q values

obtained in this study were favorable compared with the values presented in the literature. For example, Onundi et al. (2010) prepared an activated carbon from palm kernel shell and used it as an adsorbent for lead, copper, and nickel removal. The nickel removal capacity was 0.130 mg/g at 1 g/L adsorbent dosage, 75 min adsorption time, and pH 5.

Results showed that, especially in the case of zinc, the adsorption capacity q increased sharply as a function of initial metal concentration. This finding indicates that suitable specific adsorption sites are available on the surface of the fresh adsorbent. The same effect can be seen in the removal %, which decreased sharply as a function of initial metal concentration, indicating that the surface is occupied and that metal removal through adsorption is no longer effective. (Bhatnagar et al., 2010; Katal et al., 2012).

Effect of adsorbent dosage

The effect of the adsorbent dosage of Sawdust and Norit on the adsorption of cobalt, nickel, and zinc is presented in Figure 2. The adsorption capacity decreased slightly as a function of increasing adsorbent dosage (dashed lines in Figure 2). This phenomenon can be attributed to the increased adsorbent-to-adsorbate ratio wherein the number of available adsorption sites increases as a function of adsorbent dosage, and thus, more adsorption sites become available to the metal ions. However,

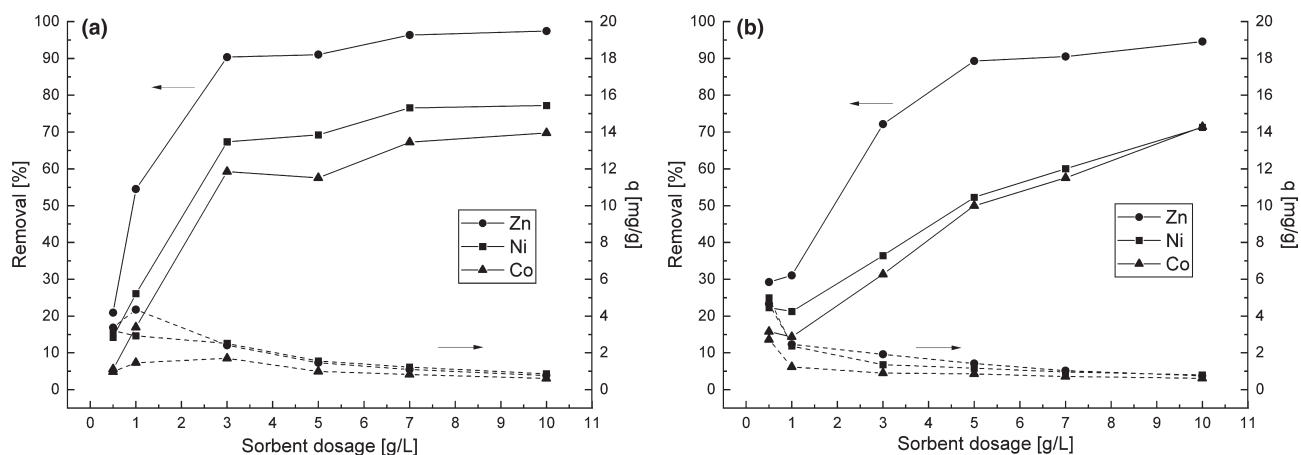


FIGURE 2. Effect of adsorbent dosage on metal removal by using (a) Sawdust or (b) Norit as adsorbent. The experiments were performed under the following conditions: pH 7, initial concentration of 30 mg/L (10 mg/L for each metal), and 24-h adsorption time at room temperature

adsorption capacity decreases at higher adsorbent dosage due to the unsaturation of the adsorption sites (Dimitrova & Mehanjiev, 2000; Lataye et al., 2009; Özacar & Şengil, 2005; Shukla et al., 2002). Overall, the results of the experiments on the effect of adsorbent dosage suggested that Sawdust was a slightly better adsorbent than Norit.

Isotherm analysis

Both single-solute and multisolute Langmuir and Freundlich models were applied to the experimental results. The obtained parameters are shown in Table 3. The results show that both models give satisfactory correlation for the adsorption onto both materials; however, for Sawdust, the Freundlich model leads to slightly higher R^2 values and to smaller error values than the Langmuir model. A better correlation in the Freundlich model reveals the heterogeneity of the adsorbent material. This result agrees with the characterization results (Chapter 3.1).

Given that the obtained values for the Freundlich isotherm exponent n were < 1 , adsorption is considered favorable in both of the studied materials. The q values obtained from the models are somewhat higher than the experimental ones, but the order of adsorbent capacities toward the adsorbates is the same in both adsorbents as follows: zinc $>$ nickel $>$ cobalt. Based on the q values, Sawdust is at least as good as or is even better than Norit.

If we explore the values of the parameter b of the Langmuir model and the parameter K of the Freundlich model, we can see that the value for the main metal is obviously higher than the values for the side components in nearly all cases. This finding means that the proportion of the side component is not high in Equations 4 and 5 and that the multisolute model reduces almost to the single-solute form. This phenomenon can also be seen in the identical or almost identical correlation coefficients. These observations might reveal that the multisolute models cannot sufficiently describe our experiment results. It is known that multisolute isotherm models are developed for competitive adsorption (Worch, 2012). However, in our experiments,

competition did not affect the adsorption. Rather, the adsorption was synergistic given that the q values were clearly higher in multisolute adsorption than in the single-solute adsorption.

Effect of contact time

The effect of contact time between the adsorbent and the adsorbates was studied at a time range of 1 min to 24 h (Fig. 3). The maximum removal % was attained quite quickly, and it remained constant thereafter for both the adsorbents and for all the studied metals. Under the described adsorption conditions, the highest removal efficiencies for the studied metals were in this order: zinc $>$ nickel $>$ cobalt, consistent with the results of the isotherm analysis. The adsorption of nickel and zinc onto Sawdust was slower than that of cobalt. By contrast, the adsorption of nickel and cobalt was faster onto Norit than onto Sawdust.

Kinetic modeling

Pseudo-first-order, pseudo-second-order, and Elovich models were applied to the experimental results. The parameters of the models are presented in Table 4, and graphs are shown in Figures 4 and 5. For all the studied cases, at least one model was found to show a correlation that is higher than 0.95. On the basis of $RMSE$ and R^2 values, we found that the Elovich model could describe the adsorption of cobalt and nickel onto Sawdust and that the pseudo-second-order model was the best model for zinc removal. As for Norit, both the pseudo-second-order and Elovich models demonstrated a satisfactory correlation for cobalt and nickel; as for zinc, the highest correlation was obtained using the pseudo-first-order model.

As can be seen in Figures 4 and 5, it can be concluded that generally Elovich is suitable for slow adsorption that increases over time, that the pseudo-first-order model describes fast adsorption, and that the pseudo-second-order model is suitable for the intermediate conditions.

In addition to the kinetic model, the Weber–Morris intraparticle diffusion model was applied to the results of the time optimization experiments (Figure 6). The data for

metal adsorption onto Sawdust show three plots representing the three stages in the adsorption mechanism. The first plot with the highest slope is attributed to the instantaneous or external surface adsorption. Most metal ions are adsorbed in this stage. In the second stage, which is attributed to the slow diffusion of metal ions from the surface sites into the inner pores, the adsorption capacity increases only slightly. In the third stage, the adsorption rate stays nearly constant due to the low concentration of metal ions left in the solution. In

the case of Norit, adsorption was either two-phased or three-phased depending on the metal. In the case of zinc, wherein the pseudo-first-order model fitted best to the results, the adsorption was two-phased. In the case of other metals, it was three-phased.

Regeneration

Reuse of the adsorbents is vital in improving cost efficiency. The used adsorbents can be reused via regeneration wherein

TABLE 3. Parameters of the single and multisolute adsorption isotherms

	ADSORBENT						
	MATERIAL	SAWDUST			NORIT		
	VARIABLE	CO	NI	ZN	CO	NI	ZN
Experiments	Max. q_e [mg/g]	4.547	6.573	17.230	3.486	3.588	14.978
Langmuir	q_m [mg/g]	5.371	8.580	23.413	6.909	6.771	22.557
	b [L/mg]	0.016	0.010	0.013	0.003	0.005	0.010
	R^2	0.975	0.911	0.917	0.935	0.865	0.962
	RMSE	0.212	0.562	1.552	0.307	0.481	1.159
Freundlich	n	0.438	0.509	0.544	0.686	0.587	0.588
	K [(mg/g)/(mg/L) ⁿ]	0.389	0.364	0.976	0.071	0.145	0.711
	R^2	0.977	0.972	0.966	0.948	0.870	0.961
	RMSE	0.204	0.315	0.993	0.275	0.472	1.187
Multisolute Langmuir	q_m [mg/g]	5.375	8.811	23.635	18.942	8.336	39.737
	b_{Co} [L/mg]	0.016	$2.5 \cdot 10^{-4}$	$8.41 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$	0.00071	$1 \cdot 10^{-6}$
	b_{Ni} [L/mg]	$1.26 \cdot 10^{-5}$	$9.6 \cdot 10^{-3}$	$9 \cdot 10^{-8}$	$1.9 \cdot 10^{-3}$	0.00384	$3.1 \cdot 10^{-3}$
	b_{Zn} [L/mg]	$1 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	0.013	$4.9 \cdot 10^{-3}$	$1 \cdot 10^{-5}$	$5.7 \cdot 10^{-3}$
	R^2	0.975	0.911	0.917	0.931	0.903	0.967
	RMSE	0.299	0.794	2.196	0.448	0.684	1.534
Multisolute Freundlich	n	0.439	0.520	0.544	0.686	0.587	0.588
	K_{Co} [(mg/g)/(mg/L) ⁿ]	6.295	$1 \cdot 10^{-4}$	$4.9 \cdot 10^{-4}$	0.071	$2 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
	K_{Ni} [(mg/g)/(mg/L) ⁿ]	56.077	0.370	$3 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	0.145	$3 \cdot 10^{-5}$
	K_{Zn} [(mg/g)/(mg/L) ⁿ]	1.859	0.181	0.977	$1 \cdot 10^{-5}$	$2 \cdot 10^{-4}$	0.711
	R^2	0.985	0.972	0.966	0.947	0.870	0.961
	RMSE	0.230	0.445	1.405	0.389	0.667	1.678

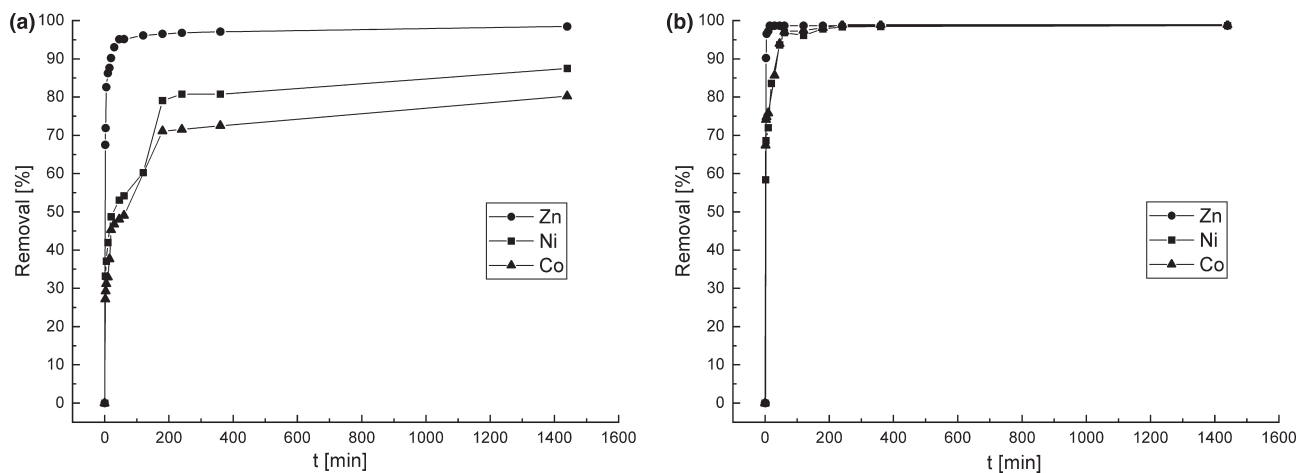


FIGURE 3. Effect of contact time on the removal efficiency toward cobalt, nickel, and zinc by (a) Sawdust or (b) Norit. The conditions for the kinetic experiments were as follows: pH value of 7, adsorbent dosage of 10 g/L, initial metal concentration of 30 mg/L, and adsorption time of 24 h at room temperature

TABLE 4. Parameters of the applied kinetic models

MODEL	ADSORBENT MATERIAL	SAWDUST			NORIT		
	PARAMETER	CO	NI	ZN	CO	NI	ZN
Experiments	$q_{e(exp)}$ [mg/g]	0.738	0.847	0.697	0.861	0.891	0.678
Pseudo-1st-order	$q_{e(cal)}$ [mg/g]	0.605	0.674	0.663	0.810	0.840	0.677
	k_1 [1/min]	0.066	0.113	0.541	0.479	0.411	1.213
	R^2	0.731	0.735	0.974	0.915	0.924	0.999
	RMSE	0.110	0.132	0.029	0.072	0.076	0.002
Pseudo-2nd-order	$q_{e(cal)}$ [mg/g]	0.648	0.731	0.683	0.838	0.874	0.678
	k_2 [g/mg min]	0.116	0.188	1.547	0.977	0.674	9.088
	R^2	0.858	0.843	0.996	0.966	0.972	0.989
	RMSE	0.080	0.102	0.011	0.046	0.046	0.002
Elovich	β [g/mg]	11.853	10.947	31.788	19.447	15.783	168.485
	ν_0 [mg/g min]	0.515	0.922	458857.159	3161.131	281.872	$4.6 \cdot 10^{44}$
	R^2	0.971	0.961	0.969	0.973	0.958	0.927
	RMSE	0.036	0.051	0.032	0.041	0.056	0.006

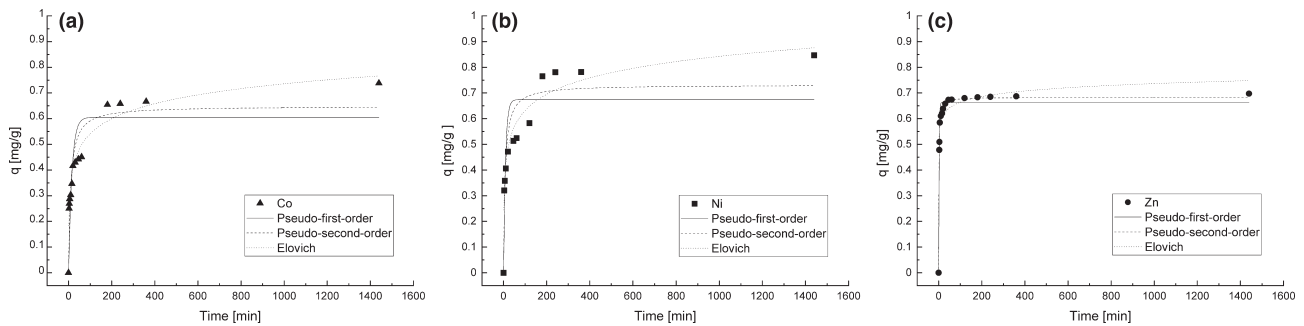


FIGURE 4. Pseudo-first-order, pseudo-second-order, and Elovich models applied to the experimental results for Sawdust

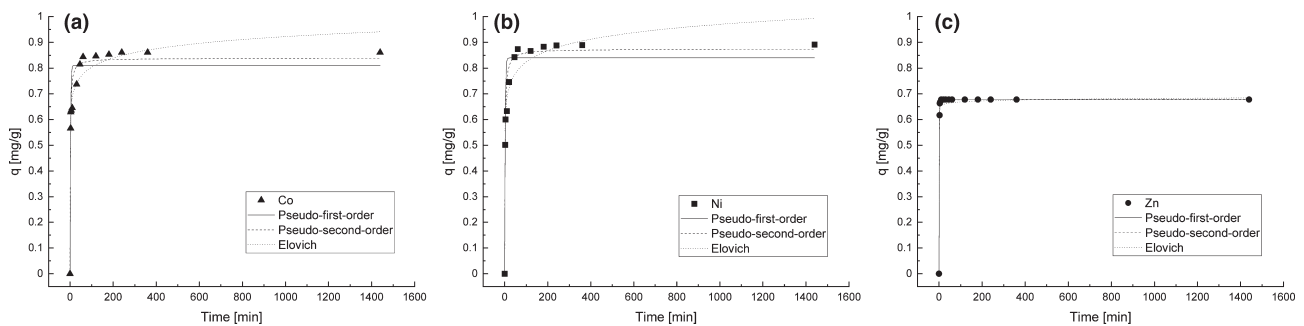


FIGURE 5. Pseudo-first-order, pseudo-second-order, and Elovich models applied to the experimental results for Norit

metals are recovered in the solution form. A regeneration solution, which is produced by a regeneration system, is an example of a secondary pollution; thus, nonhazardous regeneration solutions are preferred. (Tzou et al., 2007) Regeneration is typically performed using acids, such as HCl (Iqbal et al., 2002; Saeed et al., 2005) or H₂SO₄ (Motsi et al., 2009) or salts such as KCl (Katsou et al., 2011), NaNO₃ (Hu & Shipley, 2012), or NaCl (Xu et al., 2012). In this study, regeneration experiments were performed using 0.1 M HCl, 0.1 M HNO₃, or 0.1 M H₂SO₄ for Sawdust and Norit to recover cobalt, nickel, and zinc. Based on the results, all acids were suitable for regeneration,

and the adsorption capacity remained the same within three adsorption–desorption cycles. Therefore, it is possible to regenerate biomass-based activated carbon by using nonhazardous and diluted chemicals.

Comparison with other adsorbents

The obtained Langmuir adsorption capacity was compared with the capacities presented in the literature for other carbonaceous adsorbents used in the removal of cobalt, nickel, and/or zinc in monometal or multimetal solutions. The comparison is shown in Table 5. The Langmuir adsorption

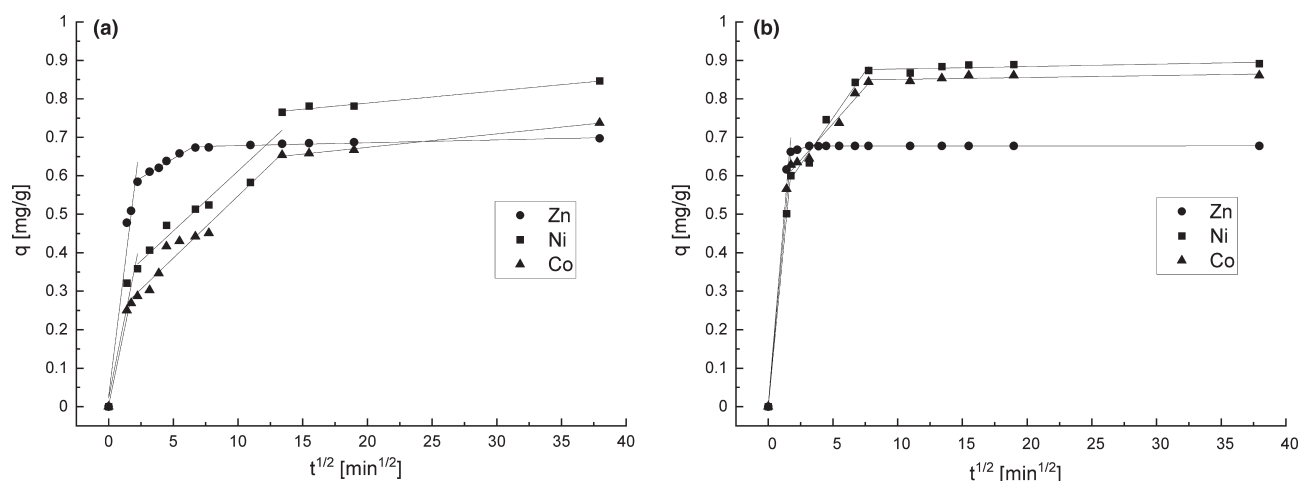


FIGURE 6. The Weber and Morris intraparticle diffusion model plots of cobalt, nickel, and zinc by using (a) Sawdust or (b) Norit as an adsorbent

capacities presented in the literature vary between 4.76 and 12.19 mg/g for zinc (multimetal adsorption), and in this study, the obtained Langmuir adsorption capacity was 24.413 mg/g. Therefore, the result obtained in this study can be compared favorably to the previously reported results. In the literature, the highest Langmuir adsorption capacity for multimetal nickel removal was 16.12 mg/g, which is notably higher than the current Langmuir adsorption capacity (8.580 mg/g). Monometal adsorption studies for cobalt were found in the literature, but their results cannot be directly compared with the present results. The number of studies on the multimetal adsorption of cobalt and/or nickel is very limited. Several studies on the monometal or multimetal adsorption of zinc on carbonaceous adsorbents have been reported, and some of those are listed in Table 5.

In multimetal adsorption system, synergistic, antagonistic or noninteractive adsorption can occur between interacting metals (Jain et al., 2016; Ting & Teo, 1994). The present results showed that adsorption in the monometal experiments was weak and that the behavior of the same metals in the multimetal adsorption experiments was totally different. Therefore, a notable synergy exists among the studied metals in the adsorption system. In the literature, the adsorption capacity during monometal or multimetal adsorption varies depending on the material used. Seo et al. also observed that the adsorption capacities during monometal and multimetal adsorption in a sediment differed, and they noticed that competitive adsorption between metals increased the mobility of the metals (Seo et al., 2008). Jain et al. reported higher adsorption capacities in monometal adsorption than in multimetal experiments for the removal of nickel, cadmium, and chromium by the carbon prepared from sunflower biomass (Jain et al., 2016). Also Park et al. described the experiments wherein the monometal adsorption capacity of pulp-based activated carbon toward lead and zinc was higher compared with its multimetal adsorption capacity. However, in multimetal experiments, more metal ions were adsorbed although the individual metal ion adsorption

decreased compared with the monometal adsorption (Depci et al., 2012).

Park et al. (2016) reported that sesame straw biochar demonstrated higher adsorption capacities in multimetal adsorption than in monometal adsorption. In addition, the order of the adsorption capacities of different metals differed between monometal adsorption and multimetal adsorption. Depci et al. (2012) also found that the degree of monometal adsorption is obviously higher than that of multimetal adsorption. Consistent with this finding, the result obtained by Hossain et al. (2014) demonstrated a higher adsorption capacity toward lead and cadmium in a monometal condition than in binary, ternary, and quaternary multimetal experiments; moreover, they found that the adsorption capacity decreased due to the interference between the studied metals. Meanwhile, Bouhamed et al. (2016) found that the competitive effects upon the adsorption were clearly indicated by adsorption isotherms.

CONCLUSIONS

The adsorption of cobalt, nickel, and zinc ions onto Sawdust, a biomass-based activated carbon, was studied as a function of pH, initial metal ion concentration, adsorbent dosage, and adsorption time in monometal and multimetal adsorption. Norit, a commercial activated carbon, was used as reference material. The highest adsorption capacity was obtained at pH 7 for Sawdust and Norit at an adsorbent dosage of 10 g/L, initial metal concentration of 30 mg/L (10 mg/L for each metal), and adsorption time of 24 h at room temperature. The order of the maximum adsorption capacities was as follows: zinc > nickel > cobalt. In summary, regenerable activated carbon from lignocellulosic biomass (Sawdust) was produced through an environmentally friendly production process involving single-stage carbonization and activation with steam at 800°C, and the material was found to be suitable for multimetal adsorption of cobalt, nickel, and zinc.

TABLE 5. Adsorption capacities of carbonaceous adsorbents toward cobalt, nickel, and/or zinc in single or multimetal solutions

ADSORBENT	SINGLE/ MULTIMETAL	PH	ADSORBENT DOSAGE [G/L]	INITIAL METAL		ADSORPTION TIME	TEMPERATURE	REF.
				CONCENTRATION [MG/L]	ADSORPTION CAPAC- ITY [MG/G]			
Activated carbon from apple pulp	Multimetal Pb + Zn at molar ratio 1:1	5	4	20-50	7.54 for Zn (Pb + Zn) (Langmuir)	60 min	298 K	Depci et al. (2012)
Activated carbon from apple pulp	Multimetal Pb + Zn at molar ratio 1:1	5	4	20-50	8.27 for Zn (Pb + Zn) (Langmuir)	60 min	308 K	Depci et al. (2012)
Activated carbon from apple pulp	Multimetal Pb + Zn at molar ratio 1:1	5	4	20-50	8.69 for Zn (Pb + Zn) (Langmuir)	60 min	318 K	Depci et al. (2012)
Activated carbon from apple pulp	Single metal Zn	5	4	20-50	11.72 (Langmuir)	60 min	298	Depci et al. (2012)
Activated carbon from apple pulp	Single metal Zn	5	4	20-50	12.91 (Langmuir)	60 min	308	Depci et al. (2012)
Activated carbon from apple pulp	Single metal Zn	5	4	20-50	13.09 (Langmuir)	60 min	318	Depci et al. (2012)
Activated carbon from date stones	Multimetal Cu, Ni, Zn	5.5	2.5	10-100	16.12 for Ni, and 12.19 for Zn (pseudo-Langmuir)	2 h	293 K	Bouhamed et al. (2016)
Cabbage waste biosorbent	Multimetal Cu(II), Zn(II)	6-6.5	5	1-500	4.76 for Zn (Langmuir)	2 h	R.T	Hossain et al. (2014)
Cabbage waste biosorbent	Single metal Zn(II)	6-6.5	5	1-500	10.890 (Langmuir)	2 h	R.T	Hossain et al. (2014)
Cabbage waste biosorbent	Multimetal Cu(II), Cd(II), Zn(II)	6-6.5	5	1-500	5.844 for Zn (Langmuir)	2 h	R.T	Hossain et al. (2014)
Apricot stone activated carbon	Single metal Co	9	5	10-80	111.11 (Langmuir)	90 min	298 K	Abbas et al. (2014)
Chemically activated carbon residue from biomass gasification	Single metal Ni	8	5	25-125	62.9 (Langmuir)	24 h	R.T	Runtti et al. (2014)
Sawdust based activated carbon	Multimetal Co, Ni, Zn	7	5	30-900	Co: 5.371, Ni: 8.580, Zn: 24.413 (Langmuir)	24 h	R.T	This study
Commercial activated carbon, Norit	Multimetal Co, Ni, Zn	7	5	30-900	Co: 6.909, Ni: 6.771, Zn: 22.557 (Langmuir)	24 h	R.T	This study

The production process is scalable because lignocellulosic biomass is ubiquitous worldwide as a waste material or as a virgin material, making this production process even more meaningful.

ACKNOWLEDGMENTS

This study was conducted under the auspices of the WaterPro project (ERDF project number: A74635, funded by the Central Ostrobothnia Regional Council, European Union, European Regional Development Fund and Leverage from the EU). The authors thank the exchange students Lena Vollert and Peggy Chan for their assistance in the laboratory experiments. Hanna Runtti thanks Maa- ja Vesiteknikan tuki ry for financial support.

REFERENCES

- Abbas, M., Kaddour, S., & Trari, M. (2014). Kinetic and equilibrium studies of cobalt adsorption on apricot stone activated carbon. *Journal of Industrial and Engineering Chemistry*, 20, 745–751.
- Annadurai, G., Juang, R. S., & Lee, D. J. (2003). Adsorption of heavy metals from water using banana and orange peels. *Water Science and Technology*, 47, 185–190.
- Barrett, E. P., Joyner, L. G., & Halenda, P. P. (1951). The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical Society*, 73, 373–380.
- Bergna, D., Varila, T., Romar, H., & Lassi, U. (2018). Comparison of the properties of activated carbons produced in one-stage and two-stage processes. *C*, 4, 41.
- Bhatnagar, A., Kumar, E., & Sillanpää, M. (2010). Nitrate removal from water by nano-alumina: Characterization and sorption studies. *Chemical Engineering Journal*, 163, 317–323.
- Bouhamed, F., Elouear, Z., Bouzid, J., & Ouddane, B. (2016). Multi-component adsorption of copper, nickel and zinc from aqueous solutions onto activated carbon prepared from date stones. *Environmental Science and Pollution Research*, 23, 15801–15806.
- Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60, 309–319.
- Butler, J. A. V., & Ockrent, C. (1930). Studies in electrocapillarity. III. *Journal of Physical Chemistry*, 34, 2841–2859.
- Castellblaque, J., & Salimbeni, F. (2004). NF and RO membranes for the recovery and reuse of water and concentrated metallic salts from waste water produced in the electroplating process. *Desalination*, 167, 65–73.
- Chand Bansal, R., & Goyal, M. (2005). *Activated carbon adsorption*. CRC Press.
- Chen, J. P., & Wang, X. (2000). Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed-bed columns. *Separation and Purification Technology*, 19, 157–167.
- Cho, H., Oh, D., & Kim, K. (2005). A study on removal characteristics of heavy metals from aqueous solution by fly ash. *Journal of Hazardous Materials*, 127, 187–195.
- Demirbaş, E. (2003). Adsorption of cobalt(II) ions from aqueous solution onto activated carbon prepared from hazelnut shells. *Adsorption Science & Technology*, 21, 951–963.
- Depci, T., Kul, A. R., & Önal, Y. (2012). Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: Study in single- and multi-solute systems. *Chemical Engineering Journal*, 200–202, 224–236.
- Diagboya, P. N., & Dikio, E. D. (2018). Dynamics of mercury solid phase extraction using *Barbula lambarensis*. *Environmental Technology & Innovation*, 9, 275–284.
- Diagboya, P. N., Olu-Owolabi, B. I., Mtunzi, F. M., & Adebowale, K. O. (2020). Clay-carbonaceous material composites: Towards a new class of functional adsorbents for water treatment. *Surfaces and Interfaces*, 19, 100506.
- Digiano, F. A., Baldauf, G., Frick, B., & Sontheimer, H. (1978). A simplified competitive equilibrium adsorption model. *Chemical Engineering Science*, 33, 1667–1673.
- Dimitrova, S. V., & Mehanjiev, D. R. (2000). Interaction of blast-furnace slag with heavy metal ions in water solutions. *Water Research*, 34, 1957–1961.
- El-Ashtouky, E.-Z., Amin, N. K., & Abdelwahab, O. (2008). Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination*, 223, 162–173.
- Fernández, Y., Marañón, E., Castrillón, L., & Vázquez, I. (2005). Removal of Cd and Zn from inorganic industrial waste leachate by ion exchange. *Journal of Hazardous Materials*, 126, 169–175.
- Freundlich, H. (1906). Over the adsorption in solution. *The Journal of Physical Chemistry*, 57, 385–471.
- Gwenzi, W., Musarurwa, T., Nyamugafata, P., Chaukura, N., Chaparadza, A., & Mbera, S. (2014). Adsorption of Zn²⁺ and Ni²⁺ in a binary aqueous solution by biosorbents derived from sawdust and water hyacinth (*Eichhornia crassipes*). *Water Science and Technology*, 70, 1419–1427.
- Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, 34, 451–465.
- Hossain, M. A., Ngo, H. H., Guo, W. S., Nghiem, L. D., Hai, F. I., Vigneswaran, S., & Nguyen, T. V. (2014). Competitive adsorption of metals on cabbage waste from multi-metal solutions. *Bioresource Technology*, 160, 79–88.
- Hu, J., & Shipley, H. J. (2012). Evaluation of desorption of Pb (II), Cu (II) and Zn (II) from titanium dioxide nanoparticles. *Science of the Total Environment*, 431, 209–220.
- Iqbal, M., Saeed, A., & Akhtar, N. (2002). Petiolar felt-sheath of palm: a new biosorbent for the removal of heavy metals from contaminated water. *Bioresource Technology*, 81, 151–153.
- Jain, M., Garg, V. K., Kadirvelu, K., & Sillanpää, M. (2016). Adsorption of heavy metals from multi-metal aqueous solution by sunflower plant biomass-based carbons. *International Journal of Environmental Science and Technology*, 13, 493–500.
- Katal, R., Baei, M. S., Rahmati, H. T., & Esfandian, H. (2012). Kinetic, isotherm and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk. *Journal of Industrial and Engineering Chemistry*, 18, 295–302.
- Katsou, E., Malamis, S., Tzanoudaki, M., Haralambous, K. J., & Loizidou, M. (2011). Regeneration of natural zeolite polluted by lead and zinc in wastewater treatment systems. *Journal of Hazardous Materials*, 189, 773–786.
- Kurniawan, T. A., Chan, G. Y. S., Lo, W., & Babel, S. (2006). Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, 118, 83–98.
- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24, 1–39.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40, 1361–1403.
- Lataye, D. H., Mishra, I. M., & Mall, I. D. (2009). Adsorption of α -picoline onto rice husk ash and granular activated carbon from aqueous solution: Equilibrium and thermodynamic study. *Chemical Engineering Journal*, 147, 139–149.
- Mansoorian, H. J., Mahvi, A. H., & Jafari, A. J. (2014). Removal of lead and zinc from battery industry wastewater using electrocoagulation process: Influence of direct and alternating current by using iron and stainless steel rod electrodes. *Separation and Purification Technology*, 135, 165–175.
- Marsh, H., & Rodríguez-Reinoso, F. (2006). CHAPTER 5 – Activation processes (thermal or physical). In H. Marsh, & F. Rodríguez-Reinoso (Eds.), *Activated carbon* (pp. 243–321). Elsevier Science Ltd.
- Mohubedu, R. P., Diagboya, P. N. E., Abasi, C. Y., Dikio, E. D., & Mtunzi, F. (2019). Magnetic valorization of biomass and biochar of a typical plant nuisance for toxic metals contaminated water treatment. *Journal of Cleaner Production*, 209, 1016–1024.
- Motsi, T., Rowson, N. A., & Simmons, M. J. H. (2009). Adsorption of heavy metals from acid mine drainage by natural zeolite. *International Journal of Mineral Processing*, 92, 42–48.
- National Institute of Advanced Industrial Science and Technology Research Center for Deep Geological Environments Naoto TAKENO. (2005). *Atlas of Eh-pH diagrams intercomparison of thermodynamic databases*.
- O'Connell, D. W., Birkinshaw, C., & O'Dwyer, T. F. (2008). Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology*, 99, 6709–6724.
- Onundi, Y. B., Mamun, A. A., Khatib, M. F. A., & Ahmed, Y. M. (2010). Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon. *International Journal of Environmental Science & Technology*, 7, 751–758.
- Özacar, M., & Şengil, İ. A. (2005). Adsorption of metal complex dyes from aqueous solutions by pine sawdust. *Bioresource Technology*, 96, 791–795.
- Özçimen, D., & Ersoy-Meriçboyu, A. (2009). Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons. *Journal of Hazardous Materials*, 168, 1118–1125.
- Park, J., Ok, Y. S., Kim, S., Cho, J., Heo, J., DeLaune, R. D., & Seo, D. (2016). Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere*, 142, 77–83.
- Lahti, R., Bergna, D., Romar, H., Tuuttila, T., Hu, T., & Lassi, U. (2017). Physico-chemical properties and use of waste biomass-derived activated carbons. *Chemical Engineering Transactions*, 57, 43–48.
- Rule, K. L., Comber, S. D. W., Ross, D., Thornton, A., Makropoulos, C. K., & Rautiu, R. (2006). Diffuse sources of heavy metals entering an urban wastewater catchment. *Chemosphere*, 63, 64–72.
- Runtti, H., Tuomikoski, S., Kangas, T., Lassi, U., Kuokkanen, T., & Rämö, J. (2014). Chemically activated carbon residue from biomass gasification as a sorbent for iron(II), copper(II) and nickel(II) ions. *Journal of Water Process Engineering*, 4, 12–24.
- Saeed, A., Akhter, M. W., & Iqbal, M. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separation and Purification Technology*, 45, 25–31.
- Seo, D. C., Yu, K., & DeLaune, R. D. (2008). Comparison of monometal and multimetal adsorption in Mississippi River alluvial wetland sediment: Batch and column experiments. *Chemosphere*, 73, 1757–1764.
- Shukla, A., Zhang, Y., Dubey, P., Margrave, J. L., & Shukla, S. S. (2002). The role of sawdust in the removal of unwanted materials from water. *Journal of Hazardous Materials*, 95, 137–152.

- Ting, Y. P., & Teo, W. K. (1994). Uptake of cadmium and zinc by yeast: Effects of co-metal ion and physical/chemical treatments. *Bioresource Technology*, *50*, 113–117.
- Tzou, Y., Wang, S., Hsu, L., Chang, R., & Lin, C. (2007). Deintercalation of Li/Al LDH and its application to recover adsorbed chromate from used adsorbent. *Applied Clay Science*, *37*, 107–114.
- Weber, W. J., & Morris, J. C. (1963). Kinetics of adsorption on carbon from solutions. *Journal of the Sanitary Engineering Division, American Society of Civil Engineers*, *89*, 31–60.
- Worch, E. (2012). *Adsorption technology in water treatment*. De Gruyter.
- Xu, W., Li, L. Y., & Grace, J. R. (2012). Regeneration of natural Bear River clinoptilolite sorbents used to remove Zn from acid mine drainage in a slurry bubble column. *Applied Clay Science*, *55*, 83–87.
- Zeldowitsch, J. (1934). Über den mechanismus der katalytischen oxydation von CO an MnO_2 [About the mechanism of catalytic oxidation of CO over MnO_2]. *Acta Physicochim URSS*, *1*, 364–449.