Biosorption optimization and kinetic modeling of Ni^{2+} and Zn^{2+} removal from aqueous solution using calamansi (*Citrofortunella microcarpa*) and dalandan (*Citrus aurantium*) peels

Czar Nicholas B. Siangko[1], Patricia Jean DG. Escasinas[1], Hajami Angel Sofia D. Florida[1], Angela Claudine C. Gaudia[1], Jeffrey Vistan[1], Justine E. Regala[3], Jervee M. Punzalan[3], Cristian Ryan A. Argamino[2*]

[1] *De La Salle University; 2401 Taft Ave, Malate, Manila, 1004 Metro Manila*
[2] *De La Salle University Laguna Campus; LTI Spine Road, Biñan City, Laguna 4024*
[3] *Department of Physical Sciences and Mathematics, University of the Philippines Manila 1004*
**Corresponding Author: cristian.argamino@dlsu.edu.ph*

Abstract: Heavy metal presence in water bodies has become a matter of concern due to their impacts on human health and the environment. Crop-based waste materials for heavy metal removal from aqueous solutions have since been investigated to help address issues in both solid waste management and environmental pollution. In this study, calamansi (*Citrofortunella microcarpa*) and dalandan (*Citrus aurantium*) peels were investigated for their percent removals and adsorption capabilities under experimental parameters including pH level, sorbent mass (m), and contact time (CT) through batch adsorption studies. Based on the highest percent removal (%R) of metal ions for each parameter, optimum conditions were determined for the biosorption of Ni^{2+} (pH 4, 0.50 g, 60 mins) and Zn^{2+}(pH 6, 0.25 g, 120 mins) in calamansi peels. Biosorption in dalandan peels yielded the following optimum conditions: Ni^{2+} (pH 4, 0.50 g, 10 mins), and Zn^{2+}(pH 5, 0.25 g, 30 mins). Adsorption kinetics were observed to be in accordance with a pseudo-second order Lagergren model. In summary, the results show that calamansi and dalandan peels exhibit considerable potential as heavy metal biosorbents which merit future studies on their efficiency, and their application to actual environmental water samples.

Key Words: biosorption; calamansi; dalandan; atomic absorption spectroscopy; Lagergren model

1. INTRODUCTION

As modernization of agriculture occurred, the production of agricultural wastes and heavy metals such as nickel and zinc from the operations of the industries has increased over time (Barakat, 2011). As a result, the contamination of water bodies with heavy metals has become one of the major environmental challenges, especially in the urban setting (Mallampati, et al., 2015). With their high solubility in water bodies, these toxic metals may be ingested by aquatic organisms. Although the removal of metal pollutants present in aquatic systems using large-scale applications of conventional adsorbents is attainable, their high cost and decreasing efficiencies prompted the development of better removal schemes. The usage of agricultural waste in remediating heavy metal polluted water is one that became a trend (Gutha, et al., 2015). Studies on agricultural wastes were continuously performed in the past years due to their abundance, economic value, and lack of use. Calamansi (*Citrofortunella microcarpa*), a common green citrus fruit, is native and abundant in various Asian countries including the Philippines. The peel of calamansi has been found to contain different phenolic compounds such as phenolic acids, tannins, and flavonoids (Cheong et. al, 2012; Lou & Ho, 2017), which are said to be effective agents of biosorption. Meanwhile, dalandan (*Citrus aurantium)* is a variety of fruit that belongs in the species of sweet oranges of the citrus family and is native to the Philippines and most tropical warm countries. The peel of dalandan contains flavonoids such as aurantiamarin, auranetin, and hesperidin (Stuart, 2018), and pectin, which is proven to be an effective agent for heavy metal adsorption (Schiewer and Patil, 2008). Agricultural waste peels, such as vegetable and fruit peels, are mostly used for examining and testing their adsorption properties for heavy metal pollutants and water purification as these materials may also reduce pollution and avoid piling up wastes (Pathak, Mandavgane, & Kulkarni, 2015). The researchers considered the abundance of dalandan and calamansi fruits in the Philippines and aimed for the utilization of their peelings. With this, this study aimed to test the effectiveness of dalandan and calamansi peels as remediating agents in polluted water containing Ni^{2+} and Zn^{2+}. This study aims to evaluate the Ni^{2+} and Zn^{2+} biosorption properties of both dalandan and calamansi peels. It also aims to determine the optimum adsorption conditions in terms of contact time, sorbent mass, and pH.

2. METHODOLOGY

2.1 Preparation of Adsorbents

Calamansi and dalandan fruits (10 kg each) were obtained from Suki Market, Quezon City. The peels were washed with distilled water, cut, and oven-dried for 2-3 hours at 95°C. Dried peels were then crushed and pulverized using an osterizer. To ensure particle size uniformity, pulverized fruit peels were subjected to a 0.5 mm sieve.

2.2 Preparation of Standardized Metal Solutions

Concentrated stock solutions (1000 ppm) of nickel and zinc were obtained from the Chemistry Laboratory in St. Joseph Hall of De La Salle University for the preparation of standard solutions. Dilution was done for the following concentrations: 0.5, 1, 2, 4, 8, 16, 32, and 50 ppm using distilled water.

2.3 Batch Adsorption Studies

Batch adsorption experiments were conducted for the adsorption of nickel and zinc on calamansi and dalandan peels as a function of pH level, sorbent mass, and contact time. The ion percent removals and adsorption capacities were measured by putting powdered peel adsorbents into 50 ml of 50 mg/L of metal solutions in a 250 ml conical flask. Experiments were conducted in a mechanical shaker at a speed of 150 rpm and at room temperature (25 ± 1 °C). All experiments were done in triplicates. The solutions were filtered through Whatman filter paper (Grade 42). The filtrate was obtained and analyzed via the Shimadzu Atomic Absorption Spectrophotometer (AA-6300) to measure the concentrations of remaining nickel and zinc ions. The adsorption capacity or metal uptake of both dalandan and calamansi peels were determined by calculating the concentration of metal retained in the biosorbents (q_e, mg/g) using the following formula:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad \text{(Eq. 1)}$$

where:

C_0= initial metal ion concentration in solution (mg/L)

C_e= final (equilibrium) metal ion concentration in solution (mg/L)

V= solution volume (L)

m= sorbent mass(g)

Meanwhile, the percent removal (%R) known as biosorption efficiency for the metal was evaluated from the following equation:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \qquad \text{(Eq. 2)}$$

Since all experiments were done in triplicate conditions, mean values were obtained for percent removals and adsorption capacities.

2.3.1 Effect of pH level of solution, sorbent mass, contact time

For the varying pH level of the solutions, setups were set to different values, from 2 to 6 (2, 3, 4, 5, 6). 0.1 M of NaOH and HCl were used to adjust the pH to their appropriate levels. The sorbent mass was kept to 0.1 g and the contact time was kept at 120 minutes. After the agitation of solutions, the final pH level of each was measured using a pH meter. Meanwhile, for the varying sorbent mass, setups were adjusted to 0.1 g, 0.25 g, and 0.5 g. The pH level was kept at 5 and the contact time of the biosorbent in the solution was kept at 120 minutes. Lastly, for varying contact times, setups were done in time periods of 10, 20, 30, 60, and 120 minutes. The pH level was kept at 5, the sorbent mass was controlled to 0.1 g. The values of the parameters were acquired from the study of Abdel-Aty, et al. (2012). In all setups, the solutions were filtered in preparation for analysis through AAS.

2.4 Biosorption Kinetic Model

Due to their simplicity and good fit, two different Lagergren models were employed to determine a viable biosorption kinetic model. The pseudo-first order Lagergren model is expressed as the equation:

$$\frac{d(q)}{dt} = k_1(q_e - q) \qquad \text{(Eq. 3)}$$

where:

q = amount of adsorbed metal ions at time t (mg/L)
q_e = amount of adsorbed metal ion at equilibrium
k_1 = pseudo-first order rate constant (min^{-1})
t = contact time (min)

The general solution to this pseudo-first order model, yielding a linearized version, is given by:

$$\log\left(q_e - q\right) = \log q_e - \frac{k_1 t}{2.303} \tag{Eq. 4}$$

The pseudo-second order Lagergren model is given by the equation:

$$\frac{d(q)}{dt} = k_2(q_e - q)^2 \tag{Eq. 5}$$

where:

q = amount of adsorbed metal ions at time t (mg/L)
q_e = amount of adsorbed metal ion at equilibrium
k_2 = pseudo-second order rate constant (L mg^{-1} min^{-1})
t = contact time (min)

Linearization of this second-order differential equation yields:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{Eq. 6}$$

To evaluate the model fit of the two kinetic models, the average deviation between the predicted uptake and the experimental uptake was calculated as the root mean squared errors (RMSE):

$$RMSE = \sqrt{\frac{\sum_{1}^{p}(q - q_m)^2}{p}} \tag{Eq. 7}$$

where:

q = experimental metal uptake
q_m = model metal uptake
p = number of data points

3. RESULTS AND DISCUSSION

3.1 Effect of pH level of solution

Figure 1 shows the effect of pH level of metal solutions on the adsorption capacities of calamansi and dalandan peels. The pH level of the solution is a crucial factor in biosorption which affects the solubility of metal ions, surface charge, and availability of binding sites in the biosorbents. At very low pH levels, H$^+$ ions compete with the metal ions for biosorbent binding sites decreasing the chance for metal adsorption (Feng, et al., 2011). Dissociation of functional groups such as carboxyl on the surface of the biosorbent can also be attributed to the changes in pH. For nickel, higher percentage removal was observed at pH 4 while the zinc maximum uptake was observed at pH 4-5 (Table 1). In general, percent removal tends to decrease at higher pH. This observation is consistent with the study reported by Ajjabi and Chouba in 2009. At higher pH, the decrease in the amount of metal removed could be due to the lower polarity of metal ions and the formation of anionic hydroxide complexes (Ajabi and Chouba, 2009; Osasona, et al., 2013).

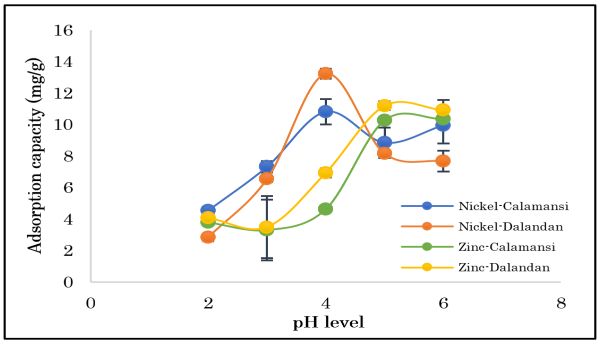


Fig. 1. Effect of pH level on nickel and zinc adsorption capacities of calamansi and dalandan peels

Table 1. Nickel and zinc percent removal of calamansi and dalandan peels. Figures in bold characters indicate the optimum conditions for each parameter.

	Percent removal (%R) ± SEM			
pH	Ni-Cal	Ni-Dal	Zn-Cal	Zn-Dal
2	18.18 ±0.26	11.39 ±0.26	15.15 ±0.06	16.28 ±0.39
3	29.27 ±0.35	26.18 ±0.21	13.22 ±1.93	13.93 ±1.97
4	**43.27 ±0.80**	**52.92 ±0.32**	18.52 ±0.09	27.74 ±0.29
5	35.39 ±0.97	32.68 ±0.19	41.08 ±0.05	**44.79 ±0.27**
6	39.81 ±1.15	30.68 ±0.66	**41.44 ±0.12**	43.69 ±0.63
Sorbent Mass	Ni-Cal	Ni-Dal	Zn-Cal	Zn-Dal
0.1	44.06 ±0.52	61.03 ±0.10	42.13 ±0.89	45.63 ±0.22
0.25	36.69 ±0.02	77.72 ±0.12	**57.30 ±1.06**	**70.10 ±0.11**
0.5	**46.63**	**87.19**	46.63	42.84

	±0.02	**±0.04**	±0.34	±0.02

Contact Time	Ni-Cal	Ni-Dal	Zn-Cal	Zn-Dal
10	33.24 ±0.54	**50.75** **±0.36**	39.56 ±0.38	39.66 ±0.88
20	24.33 ±0.49	40.77 ±0.79	38.87 ±0.15	40.05 ±0.19
30	40.10 ±1.13	50.13 ±0.07	40.95 ±0.19	**42.40** **±0.98**
60	**47.10** **±0.37**	44.79 ±0.48	**41.77** **±0.09**	41.38 ±0.18
120	53.97 ±0.77	37.88 ±0.48	42.74 ±0.19	41.93 ±0.19

3.2 Effect of sorbent mass

Figure 2 shows the effect of sorbent's mass on the adsorption capacity of both biosorbents. Based on Figure 2, it can be seen that adsorption capacity decreases with increasing sorbent mass for Ni-Cal, Ni-Dal, and Zn-Dal. This observation can also be seen in Zn-Dal for sorbent mass 0.25 g and above. Meanwhile %R from Table 1 tends to increase from 0.1 g to 0.25 g of sorbent mass for Ni-Dal, Zn-Cal, and Zn-Dal.

At a higher sorbent mass of 0.5 g, %R and adsorption capacity for Zn decreases. This can be attributed to adsorption site aggregation at higher sorbent mass resulting in a reduced surface area available for adsorption.

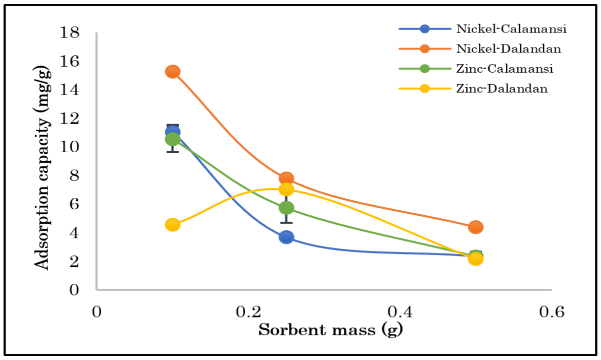


Fig. 2. Effect of sorbent mass on nickel and zinc adsorption capacities of calamansi and dalandan peels

3.3 Effect of contact time

Figure 3 illustrates the effect of contact time on the extent of adsorption of Zn^{2+} and Ni^{2+} by both biosorbents. The result shows high adsorption capacity within the 10 minutes of the adsorption process. The removal decreased for the next 10 minutes and increased within the 30 minute time interval reaching a plateau. This shows that a large number of adsorption sites are present at the beginning of the adsorption process. After some time, less adsorption sites are available that could be occupied by the metal ions. This also goes to show that the biosorption process occurs on the surface rather than being absorbed.

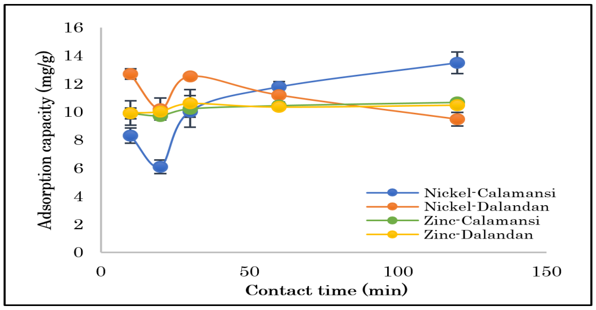


Fig. 3. Effect of contact time on nickel and zinc adsorption capacities of calamansi and dalandan peels

3.4 Optimum biosorption conditions

The optimum conditions described in Table 1 were chosen based on the highest %R exhibited on each parameter. Figure 4 below shows the comparison of %R among the parameters and treatment groups. It can be observed that the highest %R was obtained from the optimum sorbent mass (0.25 g) for the adsorption of Zn^{2+} in dalandan.

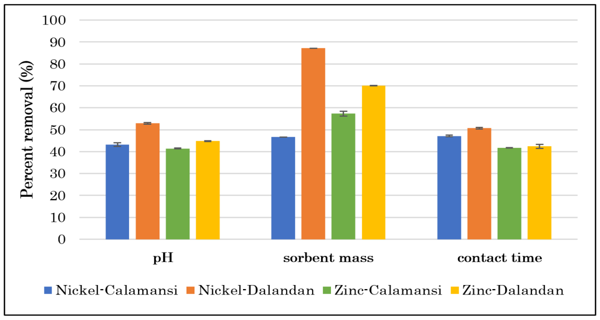
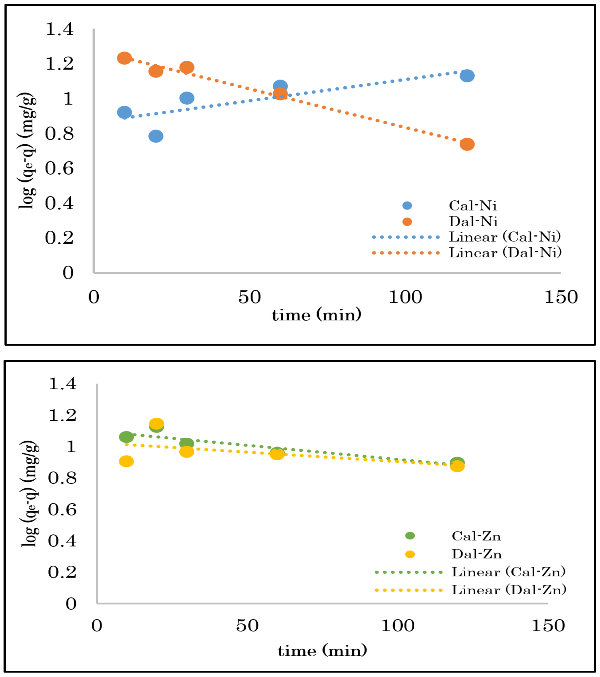


Figure 4. Optimum conditions for nickel and zinc biosorption of calamansi and dalandan peels

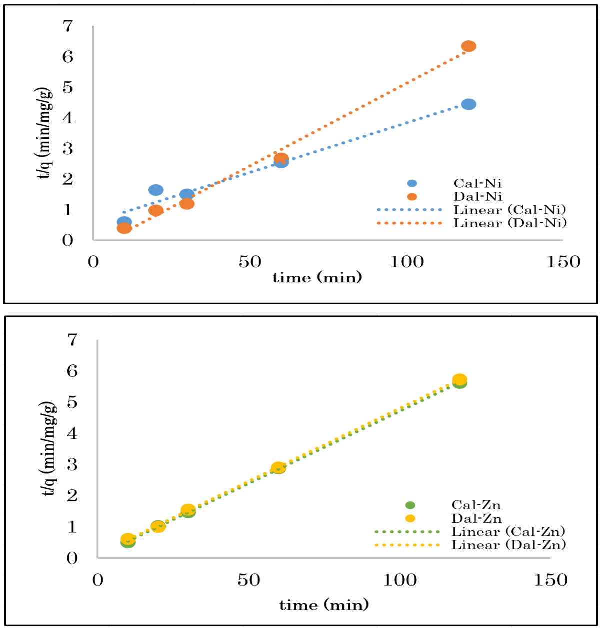
3.5 Kinetic biosorption model

The data for Ni^{2+} and Zn^{2+} were fitted to both pseudo-first-order and pseudo-second-order adsorption kinetic models (Figures 5 and 6). Based on Table 2, the correlation coefficient (R^2) values for the pseudo-first-order kinetic model range from 0.2585 to 0.9843, indicating that the adsorption process does not fit this kinetic model. On the other hand, the calculated R^2 values for pseudo-second order model range from 0.9685 to 0.9999 making it a more suitable model for describing Ni^{2+} and Zn^{2+} adsorption onto calamansi and dalandan peels.

The adsorption capacity q_e and reaction constants k_1 and k_2 for the pseudo-first and pseudo-second order models, respectively, were estimated from their corresponding linear plots, and are given in Table 3. It was found that the pseudo-second order model has a closer predicted q_e and q_m metal uptake values as indicated by its lower RMSE across all setups than that of the pseudo-first model (Table 3 & 4), further signifying that the pseudo-second order model is a better approximation of the adsorption phenomenon among the two models. Given that both biosorbents follow a pseudo-second order reaction mechanism, a 1:2 binding stoichiometry is thus indicated where one divalent metal binds to two monovalent binding sites. Despite displaying high linearity, the pseudo-second order model does not take into account the effect of metal concentration on reaction rate (Schiewer & Patil, 2008).



Figures. 5a and 5b. Linearization of the pseudo-first order model of nickel and zinc-binding kinetics, respectively



Figures. 6a and 6b. Linearization of the pseudo-second order model of nickel and zinc-binding kinetics, respectively

Table 3. Pseudo-first order kinetic parameters

	k_1	q_e	R^2	RMSE
Ni-Cal	$5.53 \cdot 10^{-3}$	$-6.37 \cdot 10^{-2}$	0.6450	30.5875
Ni-Dal	$4.15 \cdot 10^{-3}$	$1.07 \cdot 10^{-2}$	0.9843	35.4963
Zn-Cal	$1.01 \cdot 10^{-2}$	$4.02 \cdot 10^{-2}$	0.7892	30.7359
Zn-Dal	$2.76 \cdot 10^{-3}$	$1.09 \cdot 10^{-2}$	0.2585	28.8101

Table 4. Pseudo-second order kinetic parameters

	k_1	q_e	R^2	RMSE
Ni-Cal	$1.77 \cdot 10^{-3}$	30.86	0.9685	3.1366
Ni-Dal	$1.08 \cdot 10^{-2}$	18.59	0.9927	5.7477
Zn-Cal	$2.69 \cdot 10^{-2}$	21.65	0.9999	0.6269
Zn-Dal	$1.83 \cdot 10^{-2}$	21.41	0.9997	0.6068

4. CONCLUSIONS

This study has shown that both calamansi and dalandan peels exhibit promising potential as efficient heavy metal biosorbents for nickel and zinc. From the batch adsorption studies, the optimum conditions for nickel and zinc biosorption of calamansi peels were determined to be pH 4 and 6, both 0.1 g, and 60 and 30 minutes, respectively. On the other hand, the identified optimum conditions for the nickel and zinc biosorption of dalandan peels were pH 4 and 5, 0.1 g and 0.25 g, and 10 and 30 minutes, respectively. It was observed that the biosorption kinetics by the two fruit peels for both heavy metals more appropriately follow a pseudo-second order model than a pseudo-first order model.

Future researchers may analyze and examine the biosorbent capacities of said peels by modifying the parameters observed. It is also recommended that modification in peel biosorbents may be implemented, more biosorption factors may be introduced, and adsorption isotherm and thermodynamic studies involving calamansi and dalandan peels may be conducted in future studies.

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