

EFFICACY OF *EICHHORNIA CRASSIPES*, *PISTIA STRATIOTES* AND *NYMPHAEA LOTUS* IN THE BIOSORPTION OF NICKEL FROM REFINERY WASTEWATER

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Abstract. The invasive nature of *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* is worrisome because they tend to dominate the economic and ecological region of the aquatic environment, hence the need for their eco-friendly utilization. This research is aimed at assessing the efficacy of *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* as a low-cost absorbent for the biosorption of Nickel (Ni^{2+}) from refinery wastewater. Refinery wastewater was collected from the effluent point of Kaduna Refining and Petrochemical Company (KRPC). The selected macrophytes were characterized using Fourier transform infrared (FTIR) spectroscopy. Biosorption of Ni^{2+} from the wastewater and aqueous Ni^{2+} solution was performed under factors such as contact time, particle size, absorbent dosage, pH and Ni^{2+} concentration. The Langmuir equation and Freundlich isothermal were used in determining absorption equilibrium while pseudo-first and pseudo-second-order were used to determine adsorption kinetics. The result obtained shows that Ni^{2+} absorption by the selected macrophytes is greatly influenced by contact time, particle size, absorbent dosage, pH and Ni^{2+} concentration with high efficiency recorded in the removal of Ni^{2+} from refinery wastewater. Both Langmuir equation and Freundlich isothermal gives a nearly perfect fitting for adsorption of Ni^{2+} for all the selected macrophytes signifying favorable Ni^{2+} adsorption. Pseudo-second-order kinetic model gives nearly perfect fitting than the pseudo second-order kinetic model signifying that adsorption of Ni^{2+} by the selected macrophytes is due to the physical and chemical reaction. The selected macrophyte can be effectively utilized as low-cost biosorbents for the removal of Ni^{2+} from Refinery wastewater.

Keywords: Langmuir equation, adsorption kinetics, macrophytes, heavy metals, invasive species

Introduction

Aquatic macrophytes are plants that can survive in or around water bodies (Osti et al., 2018). They are classified into four major groups namely emergent macrophyte, floating leaves macrophyte, submerged macrophyte and free-floating macrophyte (Bordoloi et al., 2015; Galal and Farahat, 2015; Pulzatto et al., 2018). The ability of *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* to overtop ecological and economic zones of aquatic ecosystem is alarming due to the negative impact it causes on economic yield, human health and aquatic organisms (Lamb et al., 2016). These macrophytes hindered the penetration and flow of sunlight due to their ability to extend over water bodies (Ugya, 2015; Ma et al., 2019).

The control of *Eichhornia crassipes*, *Pistia stratiote* and *Nymphaea lotus* is necessary because of the macrophytes to interfere with water flow and sunlight penetration which is detrimental to flora and fauna inhabiting the habitat (Ugya et al., 2019a). Different control method has been used against these plants in the past but

recent research has focused on how to utilize the benefit associated with these plants (Lareo, 1981; Chen et al., 2012; Hanks et al., 2015).

The incessant discharge of heavy metal polluted water into the environment is worrisome due to their persistence nature and ability to accumulate in the food chain (Dudgeon et al., 2006; Lintern et al., 2016; Ugya and Imam, 2017; Liu et al., 2018). The menace associated with heavy metal pollution is endemic in developing countries where industries channel wastewater into nearby water bodies either untreated or not properly treated due to their proximity to these water bodies (Ugya et al., 2015; Desrosiers et al., 2019). The wastewater produced by oil refinery industries is rich in heavy metals particularly Ni^{2+} which pose serious toxicity at low-level exposure (Hughes et al., 2015; Ugya et al., 2019b). These heavy metal have been shown by many researchers to be associated with chronic and acute toxicological effects to man and detrimental to organisms such as algae, plants, micro-organisms and other vertebrate and invertebrate animals (Costa-Boeddeker et al., 2018; Wang et al., 2018; Xun et al., 2018; Ugya et al., 2019c). It is thereby paramount to treat wastewater before discharge (Zhang and Anadon, 2013; Tong and Elimelech, 2016).

A variety of techniques are available for the treatment of wastewater before discharging into water bodies, many of which have contributed in minimizing pollution resulting from chemical industries, but biosorption is gaining acceptance owing to the fact that most researchers have revealed the potentiality of some bio sorbents to effectively remediate wastewater with high heavy metal pollutants (Nahar et al., 2018; Ugya et al., 2019d). Biosorption is a remediation technology that depends on the mechanism of heavy metal accumulation by agricultural or biological adsorbents from an aqueous solution as a result of the binding site present on this bio sorbents (He and Chen, 2014; Ileri et al., 2014; Abdic et al., 2018). *Eichhornia crassipes*, *Pistia stratiote*, and *Nymphaea lotus* have been utilized by researchers such as in the biosorption of Cd, Pb, Cr, etc but little or no literature exists for the biosorption of Ni^{2+} from refinery wastewater. This study is aimed at assessing the efficacy of *Eichhornia crassipes*, *Pistia stratiote* and *Nymphaea lotus* as a low-cost absorbent for the biosorption of Ni^{2+} from refinery wastewater.

Materials and methods

Sample collection, authentication, and preparation

Eichhornia crassipes, *Pistia stratiote*, and *Nymphaea lotus* were collected at three different abandon pond of proximity located at Kinkinau, Ungwar Ma'azu, Kaduna South Local Government, Kaduna State, Nigeria. The macrophytes were handpicked with the aid of hand gloves, identified using relevant guides (Gusain and Suthar, 2017; Hanafiah et al., 2018) and authenticated in the herbarium of the Department of Botany, Ahmadu Bello University Zaria, Kaduna State, Nigeria and Department of Plant Biology, Bayero University Kano, Kano State, Nigeria (Table 1) (Ugya et al., 2019e). The macrophytes were cut into small pieces, washed twice with borehole water and once using distilled water and were dried in sunlight for 48 h. The macrophytes were grounded using a mechanical blender (Greenis, FGR-8840) and sieved accordingly to obtain Large (60 mm) and small (30 mm) particle sizes of *Eichhornia crassipes*, *Pistia stratiote*, and *Nymphaea lotus*. The macrophytes powders were stored separately in an airtight container before use. Refinery wastewater sample was collected from the effluent point of Kaduna Refining and Petrochemical Company (KRPC), which is in

Chikun Local Government, Kaduna State, Nigeria around latitude 10° 24' 36.18" N and longitude 7° 29' 17.37" E. The physicochemical and heavy metal characteristic of the wastewater was determined using standard method.

Table 1. Test plants used for biosorption

SN	Plants	Common name	Accession number
1	<i>Eichhornia crassipes</i>	Water Hyacinth	3268
2	<i>Pistia stratiotes</i>	Water Lettuce	1977
3	<i>Nymphaea lotus</i>	Water lily	BUKHAN0356

Sorbent characterization

The functional groups present in the treated and untreated *Eichhornia crassipes*, *Pistia stratiote* and *Nymphaea lotus* were determined using Fourier transform infrared (FTIR) spectroscopy (Rosales et al., 2016).

Effect of particle size and contact time on Ni²⁺ adsorption

The effect of contact time and particle size was determined by placing 2 g of *Eichhornia crassipes*, 0.5 g *Pistia stratiote* and 1 g *Nymphaea lotus* of two different particle sizes (30 mm (small size) and 60 mm (large size)) in separately in 250 ml containing 4.5 mg/l of Ni²⁺. The mixture was shaken at 150 rpm using a magnetic shaker at a constant temperature of 25 °C. Each set of flasks were agitated for 20, 30, 40, 50 and 60 min, respectively (Fig. 1). The sample was then filtered and Ni²⁺ concentrations of the solution were determined using AAS techniques. Biosorption capacity was thus calculated using the mass balance formula below (Amer et al., 2015):

$$q = \frac{v(C_i - C_e)}{m} \quad (\text{Eq.1})$$

where q (mg/g) is the adsorption capacity, C_i and C_e are the initial and final concentrations (mg/l) of Ni²⁺, respectively, v (l) is the volume of aqueous and m is the weight (mass) of adsorbent (g).

Percentage removal was calculated using the formula:

$$q\% \text{ uptake} = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (\text{Eq.2})$$

where C_0 and C_e are the initial and final concentrations (mg/l) of Ni²⁺ ions in the sample before and after shaking, respectively.

Effect of Ni²⁺ concentration on adsorption process

To 250 ml of solution containing 10 mg/l, 20 mg/l, 30 mg/l, 40 mg/l, and 50 mg/l of Ni, 1 g of dried *Eichhornia crassipes*, 0.5 g *Pistia stratiote*, and 1 g *Nymphaea lotus* were added separately and the mixture was shaken at 150 rpm using a magnetic shaker at a temperature of 25 °C for 1 h. The sample was then filtered and Ni²⁺ concentrations of the solution were measured using AAS techniques. Ni²⁺ percentage reduction of Ni²⁺ was thus calculated using Equation 2 (Kumar et al., 2018).



Figure 1. Experimental setup during culture

Effect of pH on Ni^{2+} adsorption process

The absorption ability of the macrophytes was compared at a pH of 2, 4, 6, 7, and 8 by placing 1 g of dried *Eichhornia crassipes*, 0.5 g *Pistia stratiote* and 1 g *Nymphaea lotus* in 250 ml each of the solution of Ni^{2+} at 4.5 mg/l and shaken at 150 rpm for 1 h using a magnetic stirrer at a constant temperature of 25 °C. The samples were filtered and the Ni^{2+} concentrations of the solution were determined using AAS technique. Ni^{2+} percentage removal was calculated using Equation 2 (Kumar et al., 2018). The pH of the solution was adjusted using 0.01 N NaOH and HNO_3 (Salim et al., 2016).

Effect of adsorbent dosage

The effect of adsorbent dosage was studied by placing 1 g, 2 g, 3 g, 4 g, and 5 g each of *Eichhornia crassipes*, 1 g, 2 g, 3 g, 4 g, and 5 g each *Nymphaea lotus* and 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1 g of *Pistia stratiotes* where placed in to a solution 250 ml of solution containing 4.5 mg/l of Ni^{2+} and shaken at 150 rpm using a magnetic stirrer for 1 h at a constant temperature of 25 °C. The samples were filtered and the Ni^{2+} concentrations of the solution were determined using AAS technique. Ni^{2+} Percentage removal was calculated using Equation 2 (Kumar et al., 2018).

Adsorption equilibrium study

Adsorption equilibrium study for Ni^{2+} using *Eichhornia crassipes*, *Pistia stratiote* and *Nymphaea lotus* was performed by placing 1g, 2g, 3g, 4g, and 5g of *Eichhornia crassipes*, 1 g, 2 g, 3 g, 4 g, and 5 g *Nymphaea lotus* and 0.2g, 0.4g, 0.6g, 0.8g and 1g of *Pistia stratiotes* in 5 mg/l, 10 mg/l, 15 mg/l, 20 mg/l and 25mg/l of Ni^{2+} and shake at using a magnetic stirrer at 150 rpm for 24 h at a constant temperature of 25 °C. The samples were filtered and the Ni^{2+} concentrations of the solution were determined using AAS technique. Langmuir and Freundlich isotherm models were thus determined using Equations 3 and 5 (Manikandan et al., 2016).

Langmuir equation is represented below:

$$\frac{1}{q_x} = \frac{1}{b_i q_f} \cdot T_e + \frac{1}{q_f} \quad (\text{Eq.3})$$

The equation above was adopted from Kumar et al. (2018), where T_e is equilibrium Ni^{2+} concentration in solution, q_f is maximum Ni^{2+} absorbed per unit weight of *Eichhornia crassipes*, *Pistia stratiote*, and *Nymphaea lotus*, b_i is affinity adsorbate. The value of q_f and b_i is determined from the slope and intercept. Z_l is the separation factor and is calculated using the formula below:

$$Z_l = \frac{1}{1 + b_i T_g} \quad (\text{Eq.4})$$

where T_g is the initial concentration of Cr^{3+} and Pb^{2+} in the solution.

Freundlich Isotherm is represented below:

$$\log(q_x) = \log(K_f) + \frac{1}{r \log T_e} \quad (\text{Eq.5})$$

The equation was adopted from Wang et al. (2010), where K_f is *Freundlich* constant r is *Freundlich* coefficient, and K_f and r are determined by plotting a graph of q_x against T (Wang et al., 2010).

Adsorption kinetics

Adsorption kinetics is fundamental in describing the character of an absorbent. To ascertain the mechanism involved in the adsorption of Ni^{2+} by *Eichhornia crassipes*, *Pistia stratiote*, and *Nymphaea lotus*. Pseudo first-order and the pseudo second-order reaction was used (Ho and McKay, 1998).

The pseudo first-order is represented below:

$$\log(q_i - q_t) = \log(q_i) - \frac{K_1 T}{2.303} \quad (\text{Eq.6})$$

The pseudo second order is represented below:

$$\frac{T}{q_t} = \frac{1}{K_2 q_2} + \frac{T}{q_2} \quad (\text{Eq.7})$$

Data treatment

Experiments were conducted in triplicate and data were analyzed statistically and presented as mean $\pm$ standard deviation as represented by error bar on figures. The Residual Sum of Squares (RSS) was determined for both adsorption kinetic and isotherm models to check error in model fittings. All analysis was done using BM SPSS statistics version 23

Results and discussion

Physicochemical and heavy metal characteristic of KRPC wastewater

The result represented in Table 2 shows the heavy metal and physicochemical status of KRPC wastewater. Most of the parameters determine such as total suspended solid (TSS), electrical conductivity (EC) and hardness were within the permissible limit for

wastewater except for total dissolve solid (TDS), alkalinity and turbidity which were above the permissible limit as such indicate pollution resulting from organic and inorganic pollutants. Cu^{2+} and Ni^{2+} were within the permissible limit whereas Cd^{2+} was above the permissible limit and could pose a threat to aquatic organisms. Although, it has been reported that Ni^{2+} is an essential element needed for different biochemical and physiological pathways in biological systems, excess amount of Ni^{2+} could lead to cellular and tissue damage leading to a variety of disease. The detectable amount of Ni^{2+} in the wastewater was within the permissible limit of wastewater by WHO but this could still pose a treat to man and other aquatic organisms because of the persistence's nature of Ni^{2+} and subsequent bioaccumulation in the food chain (Tchounwou et al., 2012).

Table 2. The physicochemical and heavy metal characteristic of KRPC wastewater

SN	Parameter	Mean $\pm$ SD	WHO limit (2004)
1	pH	7.2 ± 0.75	6-9
2	Turbidity	15.4 ± 5.02	5
3	EC	65.5 ± 13.42	50-500
4	TDS	1219.50 ± 680.70	500
5	TSS	8.40 ± 6.40	30
6	Alkalinity	98.95 ± 43.57	50
7	Hardness	30.96 ± 17.23	500
8	Nitrate	2.07 ± 0.50	-
9	Chloride	33.28 ± 7.94	-
10	Ni^{2+}	0.54 ± 0.08	3.0
11	Cd^{2+}	0.09 ± 0.06	0.003
12	Cu^{2+}	1.77 ± 0.27	2.0

Mean $\pm$ SD are expressed in mg/l except for pH (no unit)

Characterization of biosorbent

The result obtains for the surface characterization of biosorbent using FTIR spectrum analysis (Fig. 2) shows that the functional group changes occur in the profile of *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* following the absorption of Ni^{2+} . The peak at nearly 3500 cm^{-1} for untreated *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* represent the presence of OH-group, this OH-group has been stretched to Ni-OH bond in treated *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* as shown in Figure 2. The peak at nearly 1500 cm^{-1} shows the presence of CH_2 functional group in untreated *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus*, the stretching seen in the same peak for treated *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* is attributed to the absorption of Ni^{2+} . The peak at nearly 3000 cm^{-1} for untreated *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* shows the presences of C-H functional group which stretches in the treated *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* due to absorption of Ni^{2+} (Sujatha et al., 2013).

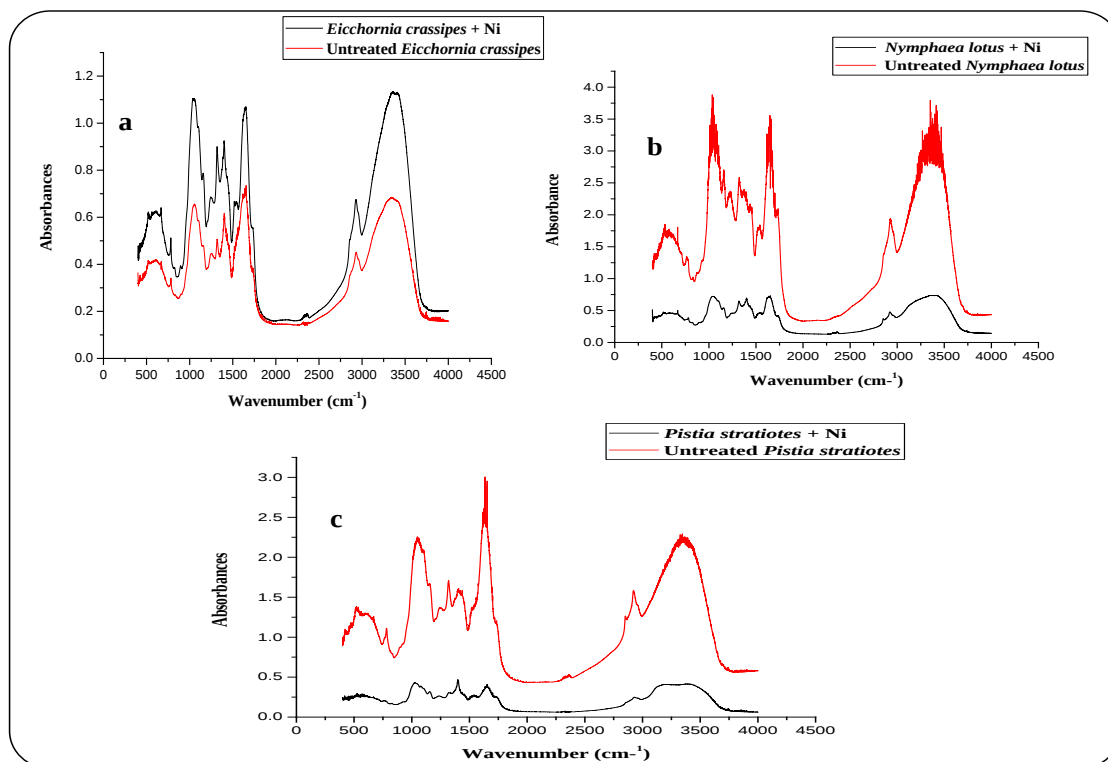


Figure 2. FTIR of (a) *Eichhornia crassipes* (b) *Nymphaea lotus* and (c) *Pistia stratiotes* before and after treatment

Effect of Ni^{2+} concentration and absorbent dosage on adsorption process

The result in Figure 3a shows that Ni^{2+} absorption by the macrophytes is strongly influenced by the change in Ni^{2+} concentration because significant difference exists between the absorption of Ni^{2+} by *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* at Ni^{2+} concentration of 10 mg/l if compared to 20 mg/l, 30 mg/l, 40 mg/l, and 50 mg/l. This enhanced absorption of Ni ion at a concentration of 10 mg/l by the 3 absorbents is attributed to the fact that at the concentration of 10 mg/l the 3 absorbents have available binding sites to bind Ni^{2+} but these binding sites become saturated as metal ion increase (Feng et al., 2011). The result in Figure 3b shows that a significant difference exists in Ni^{2+} absorption for various dosages of *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus*. These increasing trend of Ni^{2+} absorption with increasing dosage could be attributed to favorable pH of the solution and the fact that an increase in dosage of absorbent lead to increase of the maximum Ni^{2+} uptake due to availability of more binding site.

Effect of particle size, contact time and pH on Ni absorption

The result obtained shows higher reduction efficacy of Ni^{2+} from aqueous solution by biosorbent of larger size (60 mm) if compared to smaller sizes (30 mm) (Fig. 4). This significant differences could be attributed to the fact that the 60 mm biosorbent is porous as such have larger surfaces which permit increase Ni^{2+} absorption while 30 nm biosorbent is less porous as such have fewer surfaces whereas the absorption potential of a biosorbent depends on the number of surfaces of the biosorbent (Migahed et al.,

2017). The highest reduction efficacy of Ni^{2+} was recorded at a pH of 4 (Fig. 5a) this result could be attributed to the fact that the solubility of Ni is at pH 4 or the binding site of *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* were activated at pH of 4. The result obtained in (Fig. 5b) shows that Ni^{2+} was effectively adsorbed by *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* at all the contact time when exposed to refinery wastewater, this could be attributed to the fact that binding is available via out the period of adsorbent exposure to Ni^{2+} . The availability of binding site via out the period of adsorbent exposure could be due to the fact that the competition of binding sites by Ni^{2+} is minimal even though other metals such as Cd^{2+} , Pb^{2+} , Cr^{3+} , etc were presences but the concentration is too low to cause competition for binding by the co-ions present (Nor, 1994).

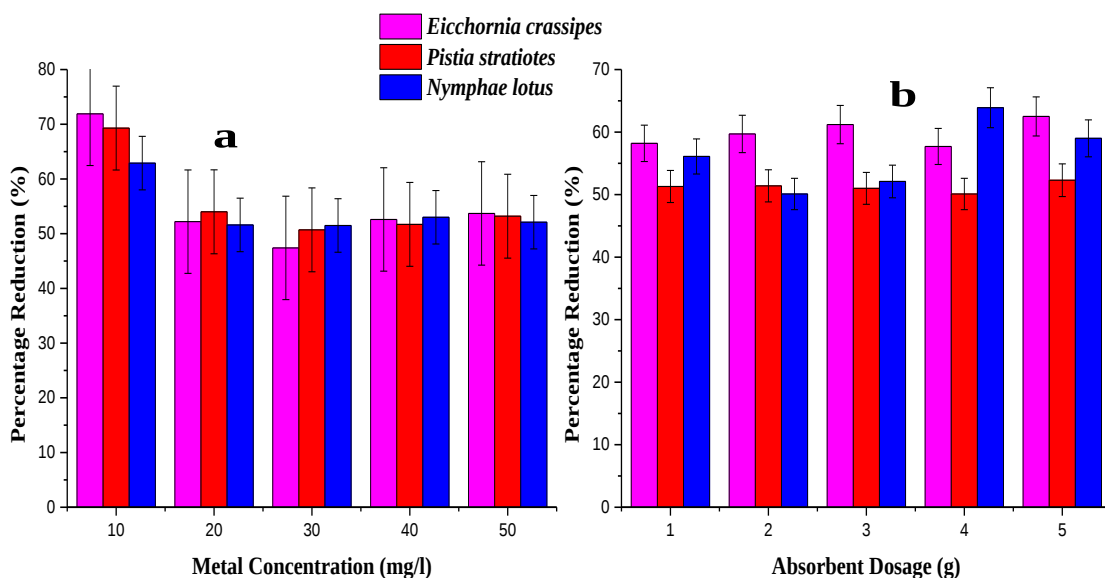


Figure 3. Effect of absorbent dosage (a), metal concentration (b) on Ni biosorption

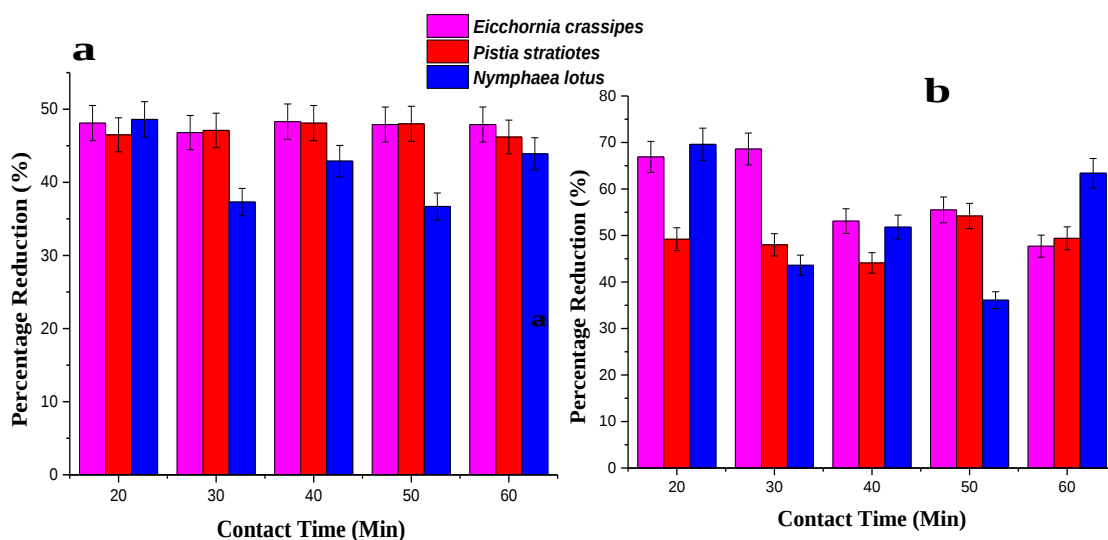


Figure 4. Effect of contact time and particle size (a) small size (b) large size on the absorption of Ni

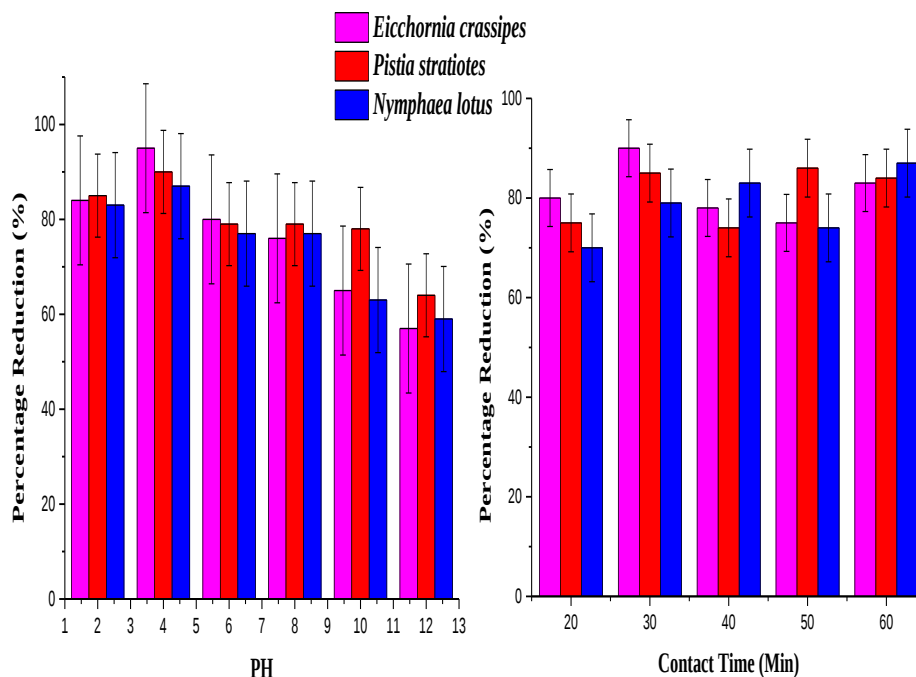


Figure 5. (a) Effect of PH on Ni absorption from aqueous solution. (b) Effect of contact time on the Ni absorption from refinery wastewater

Adsorption isotherms

The Langmuir model obtained gives a nearly perfect fitting for adsorption of Ni^{2+} for *Eichhornia crassipes* (0.9933) and *Pistia stratiotes* (0.9898) while poor-fitting was recorded for *Nymphaea lotus* (0.9311). Although it can be concluded that the adsorption of Ni^{2+} onto *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* correlated well with Langmuir equation with the relationship becoming more linear with R^2 value closer to 1 (Amer et al., 2015; Ugya et al., 2019c). The Freundlich model shows a nearly perfect fitting for absorption of Ni^{2+} for *Eichhornia crassipes* (0.9978), *Pistia stratiotes* (0.9885) and *Nymphaea lotus* (0.9753) with a high n value of (3.1) *Eichhornia crassipes*, (2.7) *Pistia stratiotes* and (2.3) *Nymphaea lotus* which are all within the range of 1-10 signifying favourable absorption of Ni^{2+} for *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* (Rosales et al., 2016; Poonam et al., 2018).

Adsorption kinetics

The biosorption of Ni^{2+} by *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* was determined at various initial concentration and time interval for the understanding of biosorption mechanism (Manikandan et al., 2016). The result obtained shows that the Pseudo Second-order kinetic model gives nearly perfect fitting for *Eichhornia crassipes* (0.9194) and *Pistia stratiotes* (0.9645) but poor fitting for *Nymphaea lotus* (0.7329). The correlation coefficient shows that the absorption of Ni by *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea lotus* follows the pseudo second-order kinetic model because poor fittings of (0.7501) *Eichhornia crassipes*, (0.5678) *Pistia stratiotes* and (0.5404) *Nymphaea lotus* was obtained for pseudo-first order model. This result obtained signifies that that the absorption of Ni^{2+} to *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* is due to chemical and physical reaction

of Ni^{2+} and the surface of *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* which leads to the formation of bond between the valence electron and the negative surface charge of *Eichhornia crassipes*, *Pistia stratiotes* and *Nymphaea lotus* to attain an equilibrium state (Low et al., 1994).

Conclusion

The petrochemical refining industry is the world largest contributor of Ni^{2+} particularly in developing countries like Nigeria where wastewater containing Ni^{2+} is discharged into nearby water bodies without proper treatment due to low technologic know-how. It is thereby paramount for petrochemical refineries to utilize the availability of aquatic macrophytes as low-cost absorbents for further treatment of its wastewater before discharge since most industries are unwilling to establish a costly convectional treatment plant.

The comparison of the present study and other research as shown in Table 3, shows that although *Eicchornia crassipes* have the highest Ni^{2+} reduction efficiency both *Pistia stratiotes* and *Nymphaea lotus* can also be used effectively as biosorbents for the removal of Ni^{2+} from refinery wastewater.

Table 3. Comparison of biosorption efficiency of Ni^{2+} by different macrophytes

SN	Macrophytes	Heavy metal	Percentage reduction (%)	References
1	<i>Eichhornia crassipes</i>	Ni^{2+}	90	Present study
2	<i>Pistia stratiotes</i>	Ni^{2+}	87	Present study
3	<i>Nymphaea lotus</i>	Ni^{2+}	86	Present study
4	<i>Lemna minor</i>	Ni^{2+}	82	Axtell et al. (2003)
5	<i>Hydrilla verticillata</i>	Ni^{2+}	92	Mishra et al. (2016)
6	<i>Salvinia sp</i>	Ni^{2+}	71.4	Dhir and Kumar (2010)

Further investigation is needed on how to increase the efficiency of these macrophytes for the uptake of Ni^{2+} . More research needs to be done using more macrophytes such as *Salvinia sp*, *Azolla sp*, *Ludwigia sp*, etc to discover more novel eco-friendly cheap biosorbent for Ni^{2+} removal from wastewater.

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