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Adsorptive behaviour, Isothermal and Kinetic modelling involved in removal of Ni (II) and Cu (II) ions using N, N-Dibenzylidene-ethane-1, 2-diamine Schiff base

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Abstract
In this study, a Schiff base N,N-Dibenzylidene-ethane-1,2-diamine derived from ethylenediamine and Benz aldehyde was successfully prepared and used as adsorbent for the removal of Cu(II) and Ni(II) ions from their aqueous solutions in batch mode. Batch optimization parameters were studied at the equilibrium time of 60 minutes for both Ni (II) and Cu (II). Residual metal ion concentration where determined using atomic absorption spectrometry. Effect of initial metal ion concentration showed that they give higher % removal at 200 mg/L. The adsorption kinetics revealed the metal ions were adsorbed satisfactorily obeying Pseudo second order model with R^2 values of 0.984 and 0.989 for Ni (II) and Cu (II) respectively. The optimum pH value obtained was 4 for both Cu (II) and Ni (II). Langmuir isotherm model fitted well with the experimental data showing the process is chemisorption. The calculated R_L values of the metal ions 0.0036 for Ni (II) and 0.0055 for Cu (II) revealed the adsorption process being favourable. The calculated heat of adsorption values of 106.0 J/mol for Ni (II) and 961.7 J/mol for Cu (II) also showed that the adsorption of the metal ions onto the synthesized Schiff base is a chemical process.

Keywords: adsorption, Schiff base, Langmuir, pseudo second order model, chemisorption

Introduction
The quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment. Heavy metals are non-biodegradable pollutants and they are very difficult to eliminate naturally from the environment (Abas *et al.*, 2013) [1].

The major sources of copper ion and its compounds are water pipes, copper water heaters, frozen greens and canned greens using copper to produce a ultra-green color, alcoholic beverages from copper brewery equipment etc. However, an excessive intake of copper (II) can lead to mental disorder, anemia, hypertension, nausea and vomiting, hyperactivity, insomnia, autism, stuttering, inflammation and enlargement of liver, heart problem and cystic fibrosis (Lakherwal, 2014) [15].

Nickel is widely distributed in the environment, and can be found in air, water, and soil. Natural sources of atmospheric nickel include dusts from volcanic emissions and the weathering of rocks and soils (Aleksandra and Urszula, 2008) [4]. Contact with nickel compounds can cause a variety of adverse effects on human health, such as nickel allergy in the form of contact dermatitis, lung fibrosis, cardiovascular and kidney diseases and cancer of the respiratory tract (Aleksandra and Urszula, 2008) [4].

There are several conventional methods by which heavy metals can be removed from aqueous solution of their compounds. These methods includes; Chemical precipitation, electro dialysis, coagulation/flocculation, ultrafiltration, reverse osmosis, and adsorption being very simple, economical, effective and versatile has become the most preferred method for removal of toxic contaminants from wastewater (Amer *et al*, 2014) [15].

Recently, one of the important chelating agents receiving an increased interest recently due to the presence of defined chelating group is Schiff bases. Schiff bases are obtained through the condensation of aldehydes or ketone with amines and contain multi dentate coordination sites such as –O and –N donor atoms which have high bonding affinity towards many heavy metal ions (Oo *et al*, 2013) [17]. Ajdari and Behzad (2016) [2] reported the synthesis of a schiff base (SBA-15) and functionalized with amine ($–NH_2$) and 3-methoxy salicylaldehyde (3-MS) to form a mesoporous silica with Schiff base modified surface (3-MS–SBA-15). Oo *et al.* (2013) [17] reported a Schiff base synthesized from 4-aminoantipyrine and 2-methoxybenzaldehyde which was evaluated for the first time in the removal of copper (II) ions from aqueous solution. Hassan *et al.* (2015) [10] prepared a chitosan-khellinone Schiff base and was utilized in the removal of Ni (II) and Fe (II) ions from their aqueous solutions. This research aimed at utilizing Schiff base as adsorbent and study the adsorption capacity toward Ni (II) and Cu (II) metal ions.

Materials and Methods
Preparation of Schiff base
The Schiff base derived from benzaldehyde and ethylenediamine was prepared through a procedure adopted from Muzammil *et al*. (2015) [16] in which 3.3 ml of ethylenediamine (0.05 mol, 3.0 g) was added into 10.1 ml of benzaldehyde (0.1 mol, 10.6 g) solution that was dissolved in

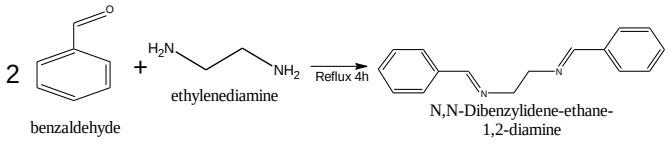
50 ml ethanol in the presence of 2 to 3 drops of 0.1 M NaOH. The mixture was refluxed for 4 hours. The resulting mixture was concentrated to half volume using water bath at 80 ºC and allowed to cool to room temperature (29 ºC). Yellow crystalline solid appeared upon cooling and were kept in a desiccator containing anhydrous calcium chloride ($CaCl_2$) for total dryness. The isolated Schiff base was stored in a container for use.

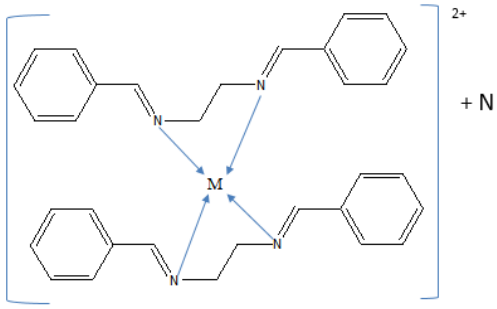
Batch Adsorption Process

The influence of variables such as contact time, initial metal ion concentration, pH and agitation speed (rpm) on the adsorptive removal of metal ions were all investigated in a batch system. For the preparation of stock solution, required amount of $NiCl_2.6H_2O$ (98 %, Merck) (4.0489 g) and $CuSO_4.5H_2O$ (98 %, Merck)(3.9291 g) were carefully and accurately weighed using analytical weighing balance (FA 2004) and then dissolved and made up to the mark in 1.0 L. The residual concentration of the metal ions after adsorption were determine using Atomic Absorption Spectrophotometer (BUCK SCIENTIFIC VGP 210) at a predetermined λ_{max} of each metal cathode lamp 232.0 nm and 324.7 nm for Ni(II) and Cu(II) ions respectively.

The obtained experimental data of the metal ions from effect of time, temperature, and concentration were used to evaluate some selected kinetic models and isotherm models respectively (El-sayed *et al.,* 2011).

Results and Discussion





M= Ni and Cu; N = SO_4^{2-} or $2Cl^-$

Fig 1: The Structure of N, N-Dibenzylidene-ethane-1, 2-diamine Schiff base

Effect of Contact Time on adsorption of the metal ions onto the Schiff base

Figure 2 shows the result obtained from the effect of contact time on metal ion removal. The adsorption process achieved equilibrium at 60 min with maximum percentage removal of 65.65% for Cu (II) ions. This result is in agreement with the result obtained by Yar-Khuhawar *et al*. (2009) [18] where they observed an optimized time of 60 minutes for Cu (II) ions using a resin. Ni (II) ion adsorption with increasing contact time is also presented in Fig. 2. The increase in contact time at 300 rpm stirring rate leads to increase in percentage removal of the metal ions. The adsorption process is a fast process, leading to 68.87% of the metal ion removal within the first 60 min, this may be attributed to the high affinity and interaction between adsorbent (Schiff base) and metal ion due to the availability of more active site on the Schiff base. Thus, the optimum time for Ni (II) ion removal is 60 min. This is in line with the result obtained by Khobragade and Pal (2015) [14] in the adsorptive removal of Cu (II) and Ni (II) from single-metal, binary-metal and industrial wastewater systems by surfactant modified alumina.

The difference in percentage removal of Ni (II) and Cu (II) ions may be attributed to the difference in their ionic sizes. The ionic sizes of Ni and Cu are 0.69Å and 0.73Å respectively. The smaller the ionic size the greater its affinity to reactive sites. The percentage removal trend observed was Ni > Cu, this trend of the adsorption is due to the fact that metal ion with smaller ionic radius diffuse faster in aqueous systems and compete better for exchange site than for those with larger sizes.

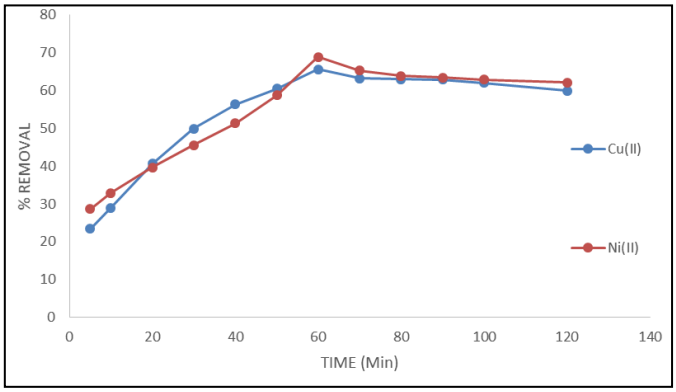


Fig 2: Effect of contact time on the metal ions onto the Schiff base

Pseudo First Order Kinetics

For the adsorption of Ni(II) and Cu(II) ions, the pseudo first order kinetic rate constant k_1, values of correlation coefficient R^2 and the values of calculated and experimental q_e of the respective metal ions are presented in Table 1. Disagreement occurs in which calculated q_e are not closer to the experimental q_e, indicating the inability of pseudo first order model to fit the kinetic data even if the plot has high correlation coefficient. The trend shows that the predicted q_e seems to be lower than the experimental values in all the metal ions. Also, low values of R^2 suggest that the adsorption process for all the metal ions do not follow pseudo first order kinetic model.

Pseudo Second Order Kinetics

Considering the adsorption of Ni (II) and Cu (II) ions, the values of rate constant k_2, correlation coefficient (R^2) and experimental and calculated q_e are also reported in Table 1. In almost all the adsorption process for the metal ions, the correlation coefficient (R^2) were all higher than 0.98. However, the calculated q_e values agreed very well with the experimental data. As such, in comparison to pseudo first order kinetic this model, pseudo second order is considered more appropriate to represent the kinetic data in all the metal

ions adsorption process. This tendency however comes as an indication that the rate limiting step in the adsorption of these metal ions is chemisorption involving valence force through complexation, coordination or chelation. This result agreed with that reported by Dadrasnia *et al.* (2015) [7], in which the same conclusion indicated that the pseudo second order model fitted well with the experimental data.

Elovich Kinetic Model

The calculated constant values of Elovich model and correlation coefficient of Ni (II), and Cu(II) ions are as presented in the Table 1. From the lower values of correlation coefficient R^2 is a clear indication that this model is not suitable for representing the experimental kinetic data of the respective metal ions adsorption onto the Schiff base.

Intraparticle Diffusion Model

The values of R^2 and k_{id} of Intraparticle diffusion model in the adsorption of Ni(II) and Cu(II) ions are presented in Table 1. From the nature of the values obtained for the R^2 it can be seem that higher values are obtained in all the process involving the metal ions, suggesting that apart from pseudo second order kinetic model, Intraparticle diffusion model can also be used to model the experimental data of the adsorption process for the respective metal ions. Moreover, higher values of k_{id} were observed for all the metal ions with a trend Ni (II) >Cu (II) indicating an enhancement in the rate of adsorption and also illustrating a better adsorption mechanism (improved bonding between the adsorbate and the substrate).

Table 1: Kinetic Models and Calculated Parameters on Adsorption of Ni and Cu.

Kinetic Models	Parameters	Ni	Cu
Pseudo First Order	**R^2**	**0.769**	**0.705**
$\ln(q_e - q_t) = \ln q_e - k_1 t$	$q_{e(exp)}$(mg/g)	6.887	6.565
	$q_{e(cal)}$(mg/g)	3.645	3.013
	k_1 (min^{-1})	0.020	0.023
Pseudo Second Order	**R^2**	**0.984**	**0.989**
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$q_{e(exp)}$(mg/g)	6.887	6.887
	$q_{e(cal)}$(mg/g)	7.062	6.863
	k_2 (min^{-1})	0.014	0.015
Elovich	**R^2**	**0.891**	**0.912**
$q_t = \frac{1}{\beta} In(\alpha\beta) + \frac{1}{\beta} Int$	β (g/mg)	0.754	0.712
	α(g/mg/min)	0.439	1.502
Intraparticle Diffusion	**R^2**	**0.926**	**0.912**
$logR = logk_{id} + alog(t)$	A	0.289	0.333
	k_{id} (min^{-1})	17.660	14.737

Effect of initial Metal ion Concentration

The effect of initial Metal ion concentration of Cu (II) and Ni (II) on their removal efficiency by Schiff base as adsorbent was investigated and studied by varying the metal ion concentration from 10-200 mg/L, and their respective results are shown in Figure 3. The percentage metal ions removal increase with increase of initial metal ion concentration, in which percentage removal increases up to the 200 mg/l studied with percentage removal of 96.75 and 94.94% for Ni(II) and Cu(II) respectively. The removal was found to be increasing up to the region of higher concentration and this can be due to the availability of active sites for saturation Ibrahim and Ibrahim (2018a) [11]. These results contradict the results obtained by Igberase *et al.* (2017) [13], where they observed that at lower initial concentration of 0.5 mmol/L the % R of Pb, Cu, Ni, Zn, and Cd were 99.9, 99.5, 98.6, 98, and 97.8%, respectively.

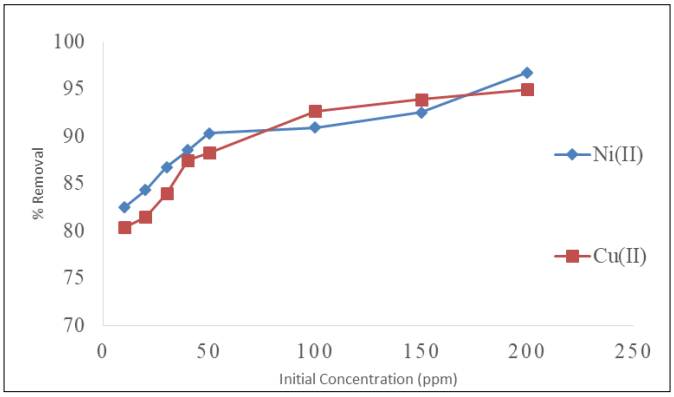


Fig 3: Effect of Initial Concentrations on the Removal of metal ions.

Effect of Solution pH

The effect of solution pH has great influence in adsorption process, so therefore, the pH of metal solution is an important parameter governing metal ion adsorption. This is because the pH of the metal solution affects the solubility of metal ion and surface charge of the adsorbent. In this study the pH was varied from 2 to 12. For Ni (II) and Cu(II) ions, maximum percentage removal of 89.29% and 73.75% respectively was achieved at pH 8. This is because at low pH, the removal of these metal ions was low due to the protonation of adsorbent surface which give rise to positively charge surface thereby creating an electrostatic repulsion between the positively charge adsorbent surface and the metal ions which subsequently compete with the H^+ present in the solution for the active sites of adsorption. Therefore, the optimum pH for removal of Cu (II) and Ni (II) ions was observed at pH 8.

These results are in accordance with the result obtained by Hassan *et al.* (2013), where they observed increase of percentage removal of Cu (II) as the pH of the solution increase and reach an optimum at pH 8. Hassan *et al.* (2015) [10] later reported an optimum adsorption for Ni (II) to be pH 8.

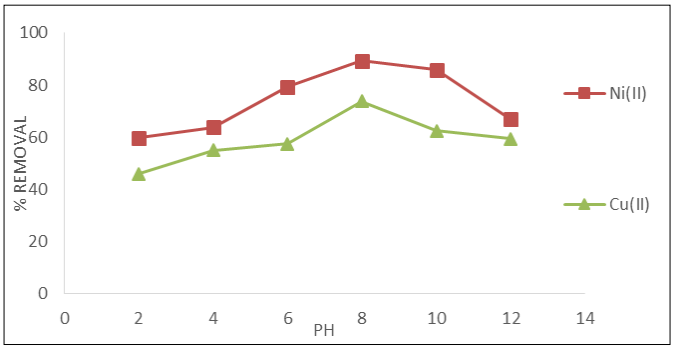


Fig 4: Effect of pH on the removal of metal ions.

Effect of Agitation Speed

Figure 5 shows the result of effect of agitation speed within the range of 100, 150, 200, 250 and 300 rpm for the three metal ions. The maximum percentage removal was obtained at moderate speeds of 150rpm for Cu (II) and Ni(II) ions with percentage removal of 90 and 95% respectively. This may be linked to the fact that at higher speed more than 150 rpm the metal ions get detached from the surface of the adsorbent leading to desorption of the metal ions back to the aqueous medium, which results in the decrease of the percentage removal. These results are in consistent with the results reported by Hassan *et al.* (2015) [10].

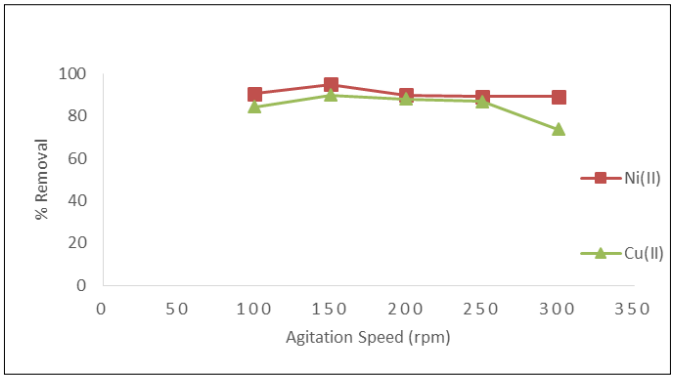


Fig 5: Effect of Agitation Speed on the adsorption of Ni (II) and Cu (II) ions.

Equilibrium Studies

Equilibrium studies provide the knowledge and relation between the concentration of adsorbate ions in bulk solution and adsorbed amount of them at equilibrium. In this work, experimental data were modelled using Langmuir, Freudlich, Temkin and Dubinin-Raduskevich isotherm models in order to investigate the characteristic of the adsorption process.

Langmuir Isotherm Model

The Langmuir (Ce/qe vs. Ce) plot for adsorption of Ni and Cu were depicted and the values of Q_m and K_L constants with the correlation coefficients (R^2) presented in Table 2. The maximum monolayer capacity (Q_m) obtained from the Langmuir model was 0.8140 mgg^{-1} for Ni (II) and 0.7580 mgg^{-1} for Cu (II) onto the Schiff base. This is an indication that the Schiff base has more affinity for Ni (II) than for Cu (II) metal ions. The correlation coefficients of the metal ions for Langmuir isotherm model were 0.9951 for Ni (II) and 0.9933 for Cu (II), indicating the linearity of the process. The calculated R_L values of the metal ions are 0.0036 for Ni(II) and 0.0055 for Cu (II) revealing the favourable nature of the adsorption process Ibrahim and Ibrahim (2018b) [12], thus, showing the feasibility of the process. This is consistent with the result obtained by Dada *et al*. (2012) [6].

Freundlich Isotherm Model

In Freundlich model, 1/n value is an important indicator for evaluating whether adsorption is favorable or not since, if 1/n = 1, it corresponds that adsorption is linear, 1/n < 1 suggest that adsorption is a physical adsorption and fits Freundlich model and finally if 1/n > 1, it means that adsorption is a chemical process. 1/n value also corresponds to the degree of adsorption heterogeneity, meaning the smaller 1/n values express higher heterogeneity (Akalin *et al.*, 2017) [3]. As shown in Table 2, the correlation coefficient (R^2) value of the metal ions for Freundlich model are 0.8723 for Ni (II) and 0.8847 for Cu (II) and 1/n values of 1.5314 for Ni (II) and 1.2514 for Cu (II) is a clear indication that the experimental data of all the metal ions are not in accordance with Freudlich isotherm model and suggesting that the adsorption process is chemical. This result is in agreement with the result obtained by El-Aila *et al*. (2016) [8].

Temkin Isotherm Model

The calculated Temkin isotherm model parameters are presented in Table 2 in which the equilibrium binding constant K_T values of the metal ions are 0.2402 for Ni (II) and 0.1286 for Cu (II). The order of the equilibrium binding constant among the metal ions is $Ni^{2+} > Cu^{2+}$. The R^2 values are 0.7294 for Ni (II) and 0.8863 for Cu (II). However, the calculated heat of adsorption values are 106.0 J/mol for Ni (II) and 961.7 J/mol for Cu (II) these values show that the adsorption of the metal ions onto the synthesized schiff base is a chemical process because the heat of adsorption i.e Temkin isotherm constant b was found to be higher than 8 J/mol. This is in line with the result of (Akalin *et al.*, 2017) [3].

Table 2: Isotherm Models and Calculated Parameters on Adsorption of Cr, Ni and Cu.

Isotherm Models	Parameters	Ni^{2+}	Cu^{2+}
Langmuir	**R^2**	**0.9951**	**0.9933**
$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{K_{LQ_m}}$	Q_m(mg/g)	0.8140	0.7580
	K_L(L/mg)	1.3799	0.8945
	R_L	0.0036	0.0055
Freundlich	**R^2**	**0.8723**	**0.8847**
$logq_e = logK_F + \frac{1}{n_F} logC_e$	K_f(mg/g)	1.6248	0.0308
	1/n_f	1.5314	1.2514
	n_f	0.9529	0.7991
Temkin	**R^2**	**0.7294**	**0.8863**
$q_e = B_T InK_T + B_T InC_e$	B_T(J/mol)	2362.5	2619.2
	K_T(L/g)	0.2402	0.1286
		106.00	961.70

Conclusion

This study shows that the N,N-Dibenzylidene-ethane-1,2-diamine Schiff base derived from ethylenediamine and Benz aldehyde was successfully used as adsorbent for the removal of Ni(II) and Cu(II) ions from their aqueous solutions in batch mode with high efficiency. The process was found to be pH dependent following pseudo second order kinetics, Langmuir isotherm model.

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