

Adsorption of Hg^{2+} and Ni^{2+} from aqueous solutions using unmodified and carboxymethylated granular activated carbon (GAC)

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Abstract: The use of unmodified and carboxymethylated granular activated carbon (GAC) for adsorption of Hg^{2+} and Ni^{2+} from aqueous solutions was assessed in this work. The effect of concentration and modification by carboxymethyl group on the adsorption of these metal ions was studied in batch process. The adsorption data were correlated with Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models. Results show that Freundlich model gave the best description for the adsorption process followed by the Langmuir model. Langmuir adsorption capacity corresponding to sites saturation was found to be 20.83 mg g^{-1} and 19.05 mg g^{-1} for adsorption of the Hg^{2+} and Ni^{2+} respectively onto the unmodified adsorbent and 19.72 mg g^{-1} and 17.01 mg g^{-1} for adsorption onto the carboxymethylated substrate. The apparent energy values obtained from the Dubinin-Radushkevich model further indicates that the forces of the adsorption follow physical mode. Modification by carboxymethyl group generally caused a decline in the adsorption capacity by the adsorbent. Results obtained generally showed that Hg (II) ions were better adsorbed onto both adsorbents as compared to Nickel (II).

Keywords: Adsorption, Granulated Activated Carbon, Heavy Metals, Isotherm Models, Metal Ions

1. Introduction

Industrial and municipal wastewaters frequently contain heavy metal ions. These heavy metals are considered a serious environmental problem due to their toxicity, long persistence, bioaccumulation and biomagnifications in food chain [1]. In fact, heavy metals are toxic to aquatic flora, animals and human beings even at relatively low concentrations [2]. Mercury and nickel are considered among the common toxic and hazardous metals found in wastewater of several industries. Once mercury enters the food chain, large accumulation of Mercury compounds takes place in humans and animals [3]. Mercury causes damage to the central nervous system, chromosomes, impairment of pulmonary function, kidney disorder, chest pain and dysphoea [4]. The US Environmental Protection Agency (EPA) has found that short-term and long-term exposure to mercury at levels in drinking water above the maximum

contaminant level (MCL) of 0.002 mg L^{-1} may cause kidney damage [5]. Nickel on the other hand, is one of the most mobile heavy metals in the aquatic environment. The exposure to nickel is known to cause asthma and is related to hard metal related respiratory diseases. Cancer of the lungs and nasal regions are associated with sulphide and oxide forms of nickel [6].

Current methods that have been used to remove heavy metal ions include precipitation, coagulation/flocculation, sedimentation, flotation, filtration, membrane process and electrochemical techniques. These unit processes may also be combined to achieve a better treatment, even though each method has its own merits and demerits in application, but suffice it to say that these methods are both costly and ineffective, particularly when there is a very low concentration of heavy metals [7, 8].

Adsorption has recently proven to be a well-established technique for efficient removal of heavy metal ions from aqueous solutions. Many research works involving low-cost, non-conventional adsorbents have been carried out for the removal of heavy metal ions from wastewater using adsorption process. These adsorbents include bacterial, algal ([9, 10], fungal biomass [11] as well as biopolymers [12]. Other adsorbents include sun flower stalks [13], Maize Cob and husk [14, 15], *Medicago sativa* (Alfalfa) [16], Shea butter seed husk [17, 18], cassava waste [19], white star apple [20], saw dust-carbon [21], Sago waste [22], rice husk [23], peanut hull carbon [24] and so on.

Nonetheless, activated carbon is the most efficient and popular adsorbent and has been used with great success for the removal of heavy metals [25]. In fact, the surface chemistry of activated carbons plays an important role in determining their adsorption performance in waste water treatment. The presence of several functional groups on carbon surface such as carboxylic, carbonyl, hydroxyl, ether, quinoline, lactone and anhydride, implies the presence of many types of pollutant-carbon interaction [26]. These functional groups on the carbon surface are activated and often times modified by different methods for enhanced separation and purification of substances from solutions.

In this present study, granular activated carbon was used as adsorbent for the removal of Hg (II) and Ni (II) ions from aqueous solutions. The effects of concentration and modification by carboxymethylation were investigated and the maximum adsorption capacities evaluated using different equilibrium isotherm models.

2. Materials and Methods

2.1. Adsorbent Preparation

The granular activated carbon (Xtrusorb-600) used as adsorbent in this study was obtained from Calgon Co, USA, and used without further purification. The activated carbon was ground with a manually operated blender and sieved with a test sieve shaker to obtain the final sample size of 250 μm . The particle size of 250 μm was used for the adsorption experiments. 100 g of the screened adsorbent was modified by carboxymethylation while another 100 g was left unmodified and labeled UGAC (unmodified granular activated carbon). The carboxymethylation was done using the method described elsewhere [27]. Specifically, 100 g of the adsorbent was added to a mixture of 650 mL ethyl alcohol and 554 mL toluene. Thereafter, 33 mL of a 50 % solution of sodium hydroxide was added in 1 min and followed by gradual addition of 25 g of monochloroacetic acid. The reaction mixture was kept at 65 °C for 70 min with agitation and left overnight. The excess sodium hydroxide solution was neutralized with glacial acetic acid. The carboxymethylated adsorbent was filtered, washed with ethyl alcohol, dried under oven at a temperature of 105°C for 1 h and labeled carboxymethylated granular activated carbon (CGAC).

2.2. Adsorption Experiments

All reagents used were of analytical grade and were used as purchased without further purification. Double distilled and deionized water was used in the sample preparation. 1000 mg L⁻¹ stock solutions of HgCl₂ and Ni(NO₃)₂·6H₂O were prepared at a pH 5.0 and temperature of 30°C. From the stock solutions, working concentrations of 5 – 60mg L⁻¹ of each of the metal ions was obtained by dilution. The effect of concentration on the adsorption of the metal ions was studied by transferring 100ml of the different concentrations of the metal ions into various 250 ml conical flasks while maintaining the pH of the solutions at 5.0. Sequentially, 0.4 g of each of the adsorbents was weighed into the flasks, corked and labeled. The flasks were placed in a rotary shaker and agitated for 1h to attain equilibrium. At the end of the adsorption process, the content of each flask was filtered, centrifuged and the residual metal ion concentrations (C_e) analyzed using a buck scientific flame Atomic Absorption spectrophotometer (AAS) model 200A. The concentrations of the metal ions adsorbed at the different concentrations were calculated by difference. The amount of metal ions adsorbed was calculated using the formula:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

Where q_e is the amount of metal ion adsorbed (mg g⁻¹), C₀ and C_e are the initial and equilibrium concentrations of the solution, V = volume of the adsorbate solution in dm³ and m is the dry mass of the adsorbent in gram.

3. Results and Discussion

The physical properties of the Xtrusorb-600 granular activated carbon are shown in Table 1. The physical parameters of the activated carbon listed here are bulk density (kg m⁻³), BET surface area (m²g⁻¹), micropore area (m²g⁻¹), micropore volume (cm³kg⁻¹), pore distribution (%) and average pore diameter (Å). The values reported in Table 1 are in consonance with those reported in the literature [28].

Table 1. Physical Properties of a granular Activated Carbon (Xtrusorb-600) by Calgon Co. USA.

Property	Value
Bulk density, kg m ⁻³	400
BET Surface area, m ² g ⁻¹	1058
Micropore area m ² g ⁻¹	937
Micropore volume cm ³ kg ⁻¹	390
Pore distribution, %< 50Å	72.1
50 – 500 Å	23.2
500 Å	4.7
Average pore diameter Å	34.83

3.1. Influence of Metal ion Concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of the adsorbates between the aqueous and solid phases. Hence a higher initial concentration of the metal ions will be expected

to enhance the adsorption process. Such an effect is demonstrated in Figs. 1 and 2, which show the plots of the adsorption capacity against initial concentration of the metal ions for the adsorption process. It can be observed from the figures, that the amount of the metal ions adsorbed by both adsorbents (UGAC and CGAC) increased with increase in the initial concentration of the metal ions. The adsorbents however, showed better removal for Hg²⁺ than Ni²⁺. Comparison of the adsorption capacities by both adsorbents indicates that modification by carboxymethylation caused a decline in the adsorption capacity by the carboxymethylated GAC. This reduction in the amount of the metal ions adsorbed by the carboxymethylated granular activated carbon (CGAC) reveals that the carboxymethyl groups (-COCH₃) may have blocked some of the micropores of the activated carbon, hence making it difficult for the metal ions to anchor onto the adsorption sites, and this subsequently reduced adsorption of the metal ions by the CGAC. A similar conclusion was given in Igwe *et al.*, [29] on the sorption kinetics and intraparticle diffusivities of Cd, Pb and Zn ions on maize cob.

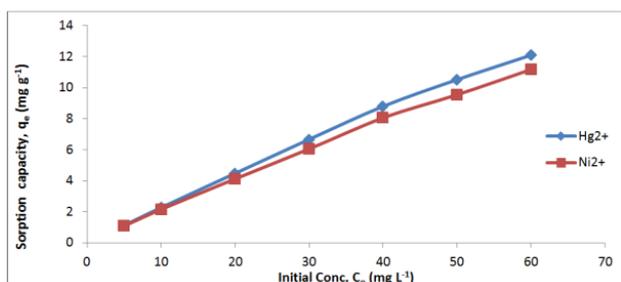


Fig 1. Plot of the amount adsorbed vs initial conc. for adsorption of the metal ions onto the unmodified GAC

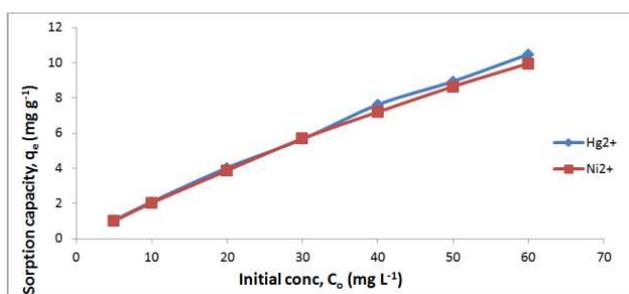


Fig 2. Plot of the amount adsorbed vs initial conc. for adsorption of the metal ions onto the carboxymethylated GAC

4. Adsorption Isotherms

The equilibrium established between adsorbed metal ions on the adsorbents and unadsorbed metal ions in solution is represented by adsorption isotherms. Four isotherm equations have been tested in the present study, namely, the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin [30-34].

The chemical Langmuir isotherm equation allows for the evaluation of the maximum adsorption capacity (q_{max}) corresponding to monolayer coverage and the Langmuir

constant K_L of the adsorption process and is given as:

$$C_e/q_e = 1/q_{max}K_L + C_e/q_{max} \tag{2}$$

Where C_e is the residual (equilibrium) metal ion concentration left in solution after adsorption, q_e is the amount of metal ions bound to per gram of the dried substrate at equilibrium, q_{max} is the maximum amount of metal ions per unit mass of the adsorbent to form a complete monolayer on the surface bound at high C_e while K_L is a constant related to the affinity of the binding sites. q_{max} and K_L were determined from the slope and intercept of the linear plots of C_e/q_e Vs C_e as shown in Figs. 3 and 4. The R² values obtained from the plots show that the adsorption process followed the Langmuir adsorption model. The Langmuir constants and R² values are all shown in Table 2. The Langmuir maximum adsorption capacity corresponding to monolayer coverage, q_{max} is normally used to compare the efficiencies of adsorbents with other substrates which have been tested for the adsorption of the metal ions. Inspection of the q_{max} values obtained for the metal ions on the two surfaces showed that Hg²⁺ was better adsorbed on the unmodified GAC than the carboxymethylated granular activated carbon (CGAC).

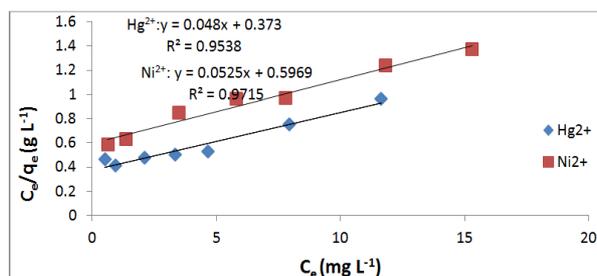


Fig 3. Langmuir isotherm plot of Ce vs Ce/qe for adsorption of the metal ions on the unmodified GAC

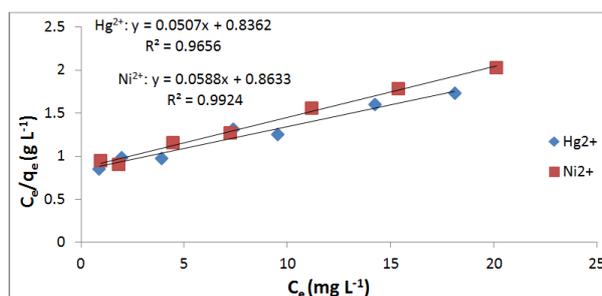


Fig 4. Langmuir isotherm plot of Ce vs Ce/qe for adsorption of the metal ions on the carboxymethylated GAC

Table 2. Langmuir Isotherm Constants

Adsorbents	q _{max} (mg g ⁻¹)	K _L (L mg ⁻¹)	R _L	R ²
Hg ²⁺				
UGAC	20.83	12.90 x 10 ⁻²	0.08	0.9538
CGAC	19.72	6.06 X 10 ⁻²	0.22	0.9656
Ni ²⁺				
UGAC	19.05	92.26 x 10 ⁻²	0.012	0.9715
CGAC	17.01	6.81 X 10 ⁻²	0.20	0.9924

On the other hand, the adsorption coefficient (i.e., ratio of adsorption and desorption rate) K_L , which is related to the apparent energy of adsorption showed that the two metal ions, Hg²⁺ and Ni²⁺ were better adsorbed onto the unmodified GAC than the carboxymethylated GAC. The high correlation coefficients (R^2 values) of the metal ions, which ranged between 0.9656 and 0.9924, showed that the experimental data fitted the Langmuir adsorption isotherm. The essential characteristics of the Langmuir Isotherm are assessed in terms of a dimensionless equilibrium parameter, R_L , which is expressed as [35]:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (3)$$

Where C_0 is the initial metal ion concentration and K_L is the Langmuir constant. The separation factor or equilibrium parameter, R_L , explains the nature of the adsorption isotherm to be either favourable if $0 < R_L < 1$, unfavourable if $R_L > 1$, linear if $R_L = 1$ or reversible if $R_L = 0$.

The values of R_L obtained for the two metal ions, Hg²⁺ and Ni²⁺ on both adsorbents at initial concentration of 60 mg L⁻¹ are all greater than 0 but less than unity indicating that the isotherm was favourable under the condition of our study.

The empirical Freundlich equation is usually suitable for adsorption on a heterogeneous surface as well adsorption isotherm in which a plateau is lacking, indicating a multilayer formation. This isotherm was employed in our study to assess the adsorption intensity of the metal ions towards the adsorbents and is given by Equation [4]

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

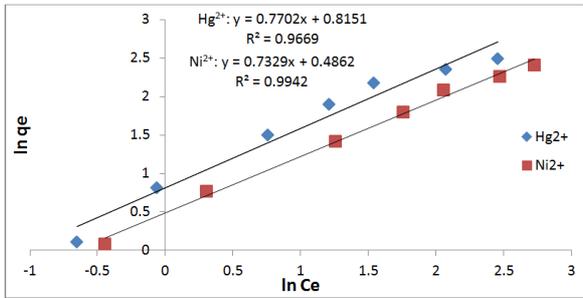


Fig 5. Freundlich isotherm plot of $\ln q_e$ vs $\ln C_e$ for adsorption of the metal ions on the unmodified GAC.

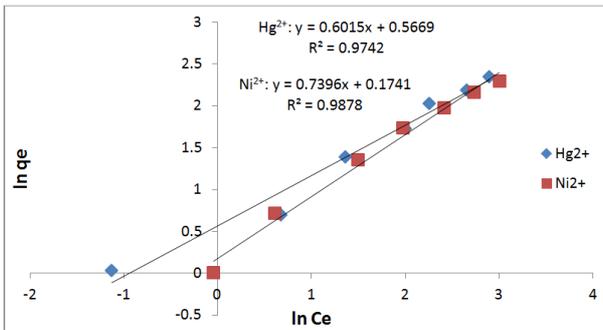


Fig 6. Freundlich isotherm plot of $\ln q_e$ vs $\ln C_e$ for adsorption of the metal ions on the carboxymethylated GAC.

K_F and n are Freundlich constants incorporating all parameters affecting the adsorption process such as adsorption intensity and the capacity. These constants, n and K_F were evaluated from the slope and intercept of the linear Freundlich plots of $\ln q_e$ vs $\ln C_e$ as shown in Figs. 5 and 6. The values of these constants, K_F and n and the R^2 values are presented in Table 3. The K_F indicates the ease of adsorption and separation of the heavy metals from aqueous solutions. The value of the constant n , which explains how the bonded metal ions are distributed on the adsorbent surface, gives an indication of the favourability and capacity of the adsorbent/adsorbate system. The K_F values obtained from the study showed that more metal ions were bonded to the unmodified (GAC) surface than the carboxymethylated surface. The higher K_F values obtained for Hg²⁺ ions suggest that Hg²⁺ has a greater affinity towards the adsorbents than Ni²⁺. This shows that the higher the K_F values, the greater the adsorption intensity. It is also worthy to note that n values between 1 and 10 represent favourable adsorption conditions [36]. From the n values obtained in this study (Table 3), the range of the exponent was $1.29 < n < 1.67$ indicating beneficial adsorption for the system. The R^2 values for the Freundlich isotherm are all higher than those obtained from Langmuir isotherm, indicating a better fit of the isotherm for the adsorption data and further show that the forces of the adsorption in this study are mostly governed by physisorption.

Table 3. Freundlich Isotherm Constants

Adsorbents	K_F	n	R^2
Hg ²⁺			
UGAC	2.26	1.30	0.9669
CGAC	1.76	1.66	0.9742
Ni ²⁺			
UGAC	1.63	1.36	0.9942
CGAC	1.19	1.35	0.9878

The Dubinin-Radushkevich isotherm was also employed in this study to determine if adsorption had occurred by physical or chemical process. The linearized Dubinin-Radushkevich adsorption isotherm is represented as [37]

$$\ln q_e = q_D - B_D \left[RT \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (5)$$

Where q_D is the Dubinin-Radushkevich isotherm constant, which is related to the degree of metal ions adsorption by the adsorbent surface and B_D is a constant related to the mean energy of adsorption per mole of the adsorbate as it is transferred to the surface of the adsorbent from the infinite distance in the solution, R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The linear plots of $\ln q_e$ vs $[RT(1+1/C_e)]^2$ confirm Dubinin-Radushkevich isotherm as shown in Figs. 7 and 8. The constants q_D and B_D were calculated from the intercepts and slopes of the linear plots respectively and are presented in Table 4. The apparent energy E (kJ mol^{-1}) of adsorption from the Dubinin-Radushkevich isotherm was calculated using equation [5]

and it is presented in Table 4.

$$E = 1/(2B_D)^{1/2} \tag{6}$$

From Table 4, it could be seen that q_D values (i.e., the theoretical saturation capacity or the amount of metal ions adsorbed upon complete saturation of the adsorbent surface) were higher for UGAC than CGAC indicating that the unmodified adsorbent (UGAC) exhibited a higher adsorption capacity than the carboxymethylated adsorbent (CGAC).

Again, the magnitude of E_D gives an information on the nature of the adsorption process, that is whether it is chemical or physical adsorption and with values in the range, $E_D = 1-8 \text{ kJ mol}^{-1}$ showing physical adsorption and in the range $9-16 \text{ kJ mol}^{-1}$ for chemisorptions [36]. From Table 4, the calculated E_D values were all found to be less than 8 kJ mol^{-1} , indicating that the adsorption process followed physical adsorption.

Table 4. Dubinin-Radushkevich Isotherm Constants

Adsorbents	q_D	B_D	$E \text{ (kJ mol}^{-1}\text{)}$	R^2
Hg^{2+}				
UGAC	8.718	3.08×10^{-7}	1.274	0.8976
CGAC	6.820	5.73×10^{-7}	0.934	0.8062
Ni^{2+}				
UGAC	7.301	3.74×10^{-7}	1.157	0.8232
CGAC	6.782	6.48×10^{-7}	0.879	0.8525

However, the high R^2 values obtained for Dubinin-Radushkevich isotherm model further confirm its good fit for the experimental adsorption data.

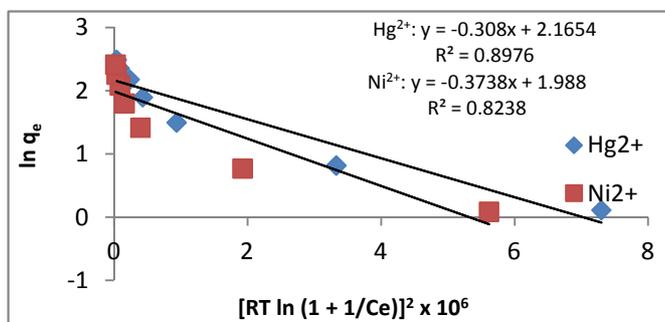


Fig 7. Dubinin-Radushkevich isotherm plot of $\ln q_e$ vs $[RT \ln (1+1/C_e)]^2$ for adsorption of the metal ions on the unmodified GAC

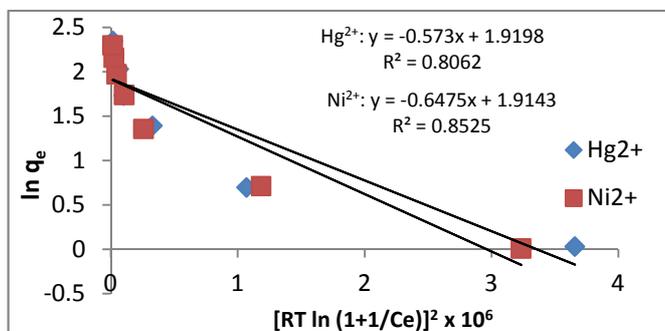


Fig 8. Dubinin-Radushkevich isotherm plot of $\ln q_e$ vs $[RT \ln (1+1/C_e)]^2$ for adsorption of the metal ions on the carboxymethylated GAC

The Temkin isotherm was also applied to the experimental data to explore the interactions between the adsorbent and adsorbates (metal ions) based on the assumption that the free energy of adsorption is simply a function of surface coverage [38] It is a useful tool to estimate the heat of adsorption. The linear Temkin isotherm model equation is given as:

$$q_e = \frac{RT}{b_T} \ln k_T + \frac{RT}{b_T} \ln C_e \tag{7}$$

The expression RT/b_T is related to the heat of adsorption, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is absolute temperature in Kelvin, $b_T \text{ (J mol}^{-1}\text{)}$ is the Temkin isotherm constant, which expresses the variation of adsorption energy and k_T is the equilibrium binding constant corresponding to the maximum binding energy. Both k_T and b_T were calculated from the slope and the intercept of the linear plots of q_e vs $\ln C_e$ as shown in Figs. 9 and 10. The Temkin constants and the coefficients of correlation (R^2 values) are presented in Table 5.

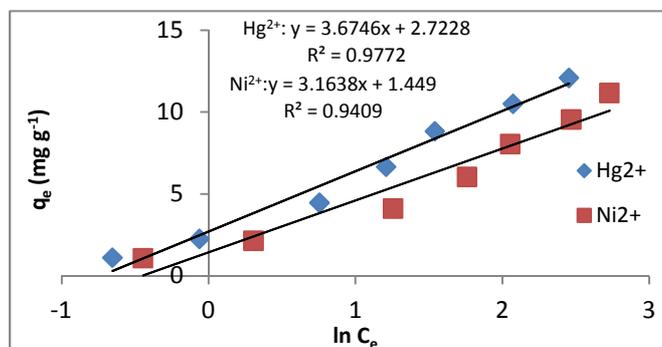


Fig 9. Temkin isotherm plot of q_e vs $\ln C_e$ for adsorption of the metal ions on the unmodified GAC

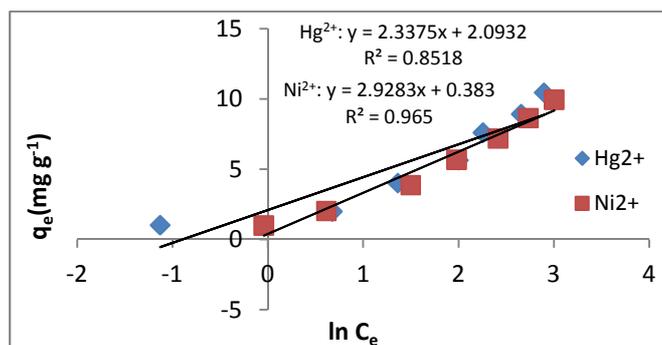


Fig 10. Temkin isotherm plot of q_e vs $\ln C_e$ for adsorption of the metal ions on the carboxymethylated GAC

Table 5. Temkin Isotherm Constants

Adsorbents	K_T	b_T	R^2
Hg^{2+}			
UGAC	2.098	685.6	0.9772
CGAC	2.449	1078	0.8518
Ni^{2+}			
UGAC	1.581	796.2	0.9409
CGAC	1.140	860.3	0.9650

5. Conclusion

This study indicates that the adsorbents, unmodified Granular activated carbon (UGAC) and Carboxymethylated Granular activated carbon (CGAC) can adsorb mercury (II) and Nickel (II) ions from aqueous solutions. The influence of metal ion concentration on the adsorption of the metal ions was reported and results obtained showed an increase in adsorption capacity with increase in metal ion concentrations. The carboxymethylated GAC showed a decline in the adsorption capacity due to blockage of the micropores of the granular activated carbon by carboxymethyl groups (-COCH₃). The analysis of the experimental data using four different isotherm models viz: the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models shows that Freundlich model gave the best description for the adsorption process followed by Langmuir model then Temkin and lastly Dubinin-Radushkevich model. The R² values were all high. The adsorption process was found to be a physisorption process as seen from the apparent energy of adsorption calculated from the Dubinin-Radushkevich model. Maximum adsorption capacities corresponding to monolayer coverage, q_{max} (mg g⁻¹) obtained from the Langmuir plots were 20.83 and 19.05 for Hg (II) and Ni (II) onto the UGAC and 19.72 and 17.01 respectively for adsorption onto CGAC. Results obtained showed that mercury (II) was better adsorbed than Nickel (II) on both adsorbents. The conclusion from this study is that both adsorbents could be good substrates for the removal of these two heavy metal ions from aqueous solutions as can be observed from the high q_{max} values.

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