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Research Article

A STUDY ON THE ADSORPTION OF Ni(II) IONS FROM WASTEWATER USING ACID ACTIVATED *ANISOMELES MALABARICA* LEAVES

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ABSTRACT

In the present investigation, the efficiency of activated carbon prepared from *Anisomeles malabarica* leaves (AMC) as an adsorbent for the removal of Ni (II) ion was investigated. *Anisomeles malabarica* leaves were treated with sulphuric acid before adsorption. The influence of various operating conditions such as adsorbent dosage, initial concentration of adsorbate, contact time, pH and temperature were explored in a Batch adsorption technique. The Langmuir, Freundlich and Tempkin isotherm models were used to compute the experimental outcomes. Freundlich Isotherm model were fitted well than that of other two isotherm models. The maximum adsorption capacity was obtained as q_m =361.73 mg/g with the optimum conditions of adsorbent dosage 25mg, temperature 30°C, initial adsorbate concentration 30mg/L, contact time 30min and pH 6.5.

Keywords: Adsorption, *Anisomeles malabarica,* Activated carbon, Ni (II) ion, Isotherms.

1. INTRODUCTION

Among the most noticeable and recurrent adverse effects of industrial activity that causes water contamination is the release of heavy metals and other harmful contaminants into waterways [1, 2]. Nickel was picked as an adsorbate as its compounds have extensive usage in various industrial activities, including electroplating, batteries manufacturing, mineral processing, non-ferrous metal, paint formulation, porcelain enameling and copper sulfate manufacture leading to elevated concentrations in the aquatic ecosystem [3, 4]. Also, Nickel is a toxic non-biodegradable metal that can be detected in both wastewater and solid waste [5]. Ni(II) ion is a micronutrient for plants, animals and humans. However, the chronic toxicity of nickel to humans and the environment is well known and high nickel concentration can induce skin allergies, pulmonary fibrosis, lung cancer, bone disorders, cyanonosis, sever fatigue, headache, dry cough and shortness of breath [6-11]. The acceptable limit of nickel in drinking water is 0.01mg/L and for discharge of industrial wastewater is 2.0mg/L [12, 13]. Different conventional physico-chemical treatment methods for nickel removal, such as chemical precipitation, ion exchange, membrane filtration and electrochemical, have been typically used in recent decades [14, 15]. These techniques, however, has significant drawbacks like inadequate elimination, expensive and a secondary contamination issues, that limit their usage and implementation of nickel-contaminated wastewater treatment [16]. Adsorption technology has gained the most attention than any other techniques because it is versatile and cost-effective for eliminating trace amounts of heavy metals. Even when commercial activated carbon is a well-known adsorbent for the elimination of toxic metals from wastewater, its high cost prevents it from being used in developing countries. Recently, much attention has been devoted to study the different types of low-cost sorbents [17, 18]. The current study focused on the use of activated carbon made from *Anisomeles malabarica* leaves to remove Ni(II) ions from aqueous media in a batch mode. The effects of pH, temperature, contact time, adsorbent dose, initial Ni(II) ions concentration and ionic strength were investigated. Desorption experiments and Isothermal models, such as Freundlich, Langmuir and Tempkin were investigated.

2. MATERIAL AND METHODS

2.1. Chemicals

Analar grade reagents and chemicals were used. A stock solution of nickel (1000 mg/L) was prepared by dissolving accurately weighed 4.4786g of nickel sulphate in 1000 ml distilled water. The stock solution was diluted to the appropriate concentration for all experimental solutions. Before mixing the adsorbent, the pH of each experimental solution was adjusted to the desired initial pH value with dilute HCl (or) NaOH. The concentration of residual Ni(II) ions was determined with atomic absorption spectrophotometer (Perkin Elemer 2380).

2.2. Preparation of adsorbent

Anisomeles malabarica leaves were collected from various areas of Tiruchirappalli District, Tamil Nadu, India (Fig.1). The dried content was charred using an excess amount (w/v) of concentrated sulphuric acid and keeping at 120°C for 10h. The carbon was then washed with surplus amount of distilled water and dried at 110°C for 1h and the resultant material was soaked in 5% sodium bicarbonate solution and allowed to stand overnight to eliminate any residual acid. The content was thoroughly washed with hot distilled water until the washings were almost neutral. The carbonized product was treated at 1100°C for 8h in a muffle furnace and the resulting carbon was activated in the presence of activating agent carbon dioxide at 800°C to 1000°C.

Fig. 1: *Anisomeles malabarica* leaves

2.3. Batch experiments

The Batch adsorption tests were performed in 250mL Erlenmeyer flask with 50mL solutions of standard Ni (II) ions and agitated in a temperature-controlled shaker. A series of batch adsorption experiments were carried out under different operating conditions related to activated AMC dose (10, 25, 50, 100, 200 and 250 mg/50mL), contact time (10, 20, 30, 40, 50 and 60 min), initial solution pH (3, 4, 5, 6, 6.5, 7, 8 and 9), initial Ni(II) ions concentration (10, 20, 30, 40 and 50 mg/L) and temperature (30, 40, 50 and 60°C), at a constant agitation speed (150 rpm). The solution pH of the initial Ni(II) ions was adjusted to optimum values using 0.1 M NaOH or 0.1 M HCl. The pH of the solution was measured with a systronics digital pH meter. Afterwards, the sample was centrifuged at 250rpm for 10min. The initial and the residual concentration of Ni(II) ions were measured using a spectrophotometer. By implementing the following equations, the percentage removal and amount of Ni(II) ions taken up by the activated AMC were calculated.

$$\% \text{ Removal} = \frac{C_i - C_t}{C_i} \times 100 \qquad (1)$$

$$q_t = \frac{(C_i - C_t)}{m} V \qquad (2)$$

where, ‘C_i’ and ‘C_t’ are the initial and liquid phase concentrations of Ni(II) ions at time ‘t’ (mg/ L); ‘q_t’ is the amount of Ni(II) ions adsorbed on the activated AMC at any time (mg/g); ‘m’ is the mass of the activated AMC and ‘V’ is the volume of the Ni(II) ions (L).

3. RESULTS AND DISCUSSION

3.1. Effect of initial Ni(II) ions concentration and contact time

The effect of initial concentration and contact time of the Ni (II) ions on activated AMC was assessed at various concentrations (10, 20, 30, 40 and 50mg/L) with contact time (10, 20, 30, 40, 50 and 60 min), while maintaining pH 6.5, temperature, 30°C and 25 mg/L of activated AMC dose, constant. Fig. 1 depicts the outcome of the experiment and the equilibrium contact time was found to be 30 minutes. The equilibrium concentration did not shift significantly as contact time was increased, suggesting that the adsorption system reached equilibrium [19]. 81% of Ni (II) ions were eliminated from the solution at equilibrium. As shown in the figure, an initial concentration of 30mg/L registered maximum adsorption among the various concentrations studied (fig. 2). The gradual removal of initial Ni(II) ions is likely due to the wide availability of active sites on the activated AMC surface, where a contact time of 30 minutes offered optimum adsorption, after which the system reached equilibrium. It could also be described as the presence of sufficient external surface area on the activated AMC boosted the adsorption rate in the initial stages, followed by a slower internal diffusion process, which could be the rate determining step [20, 21]. As a result, the optimized conditions for all experiments are set to an initial concentration of 30 mg/L and 30 minutes time intervals are preset.

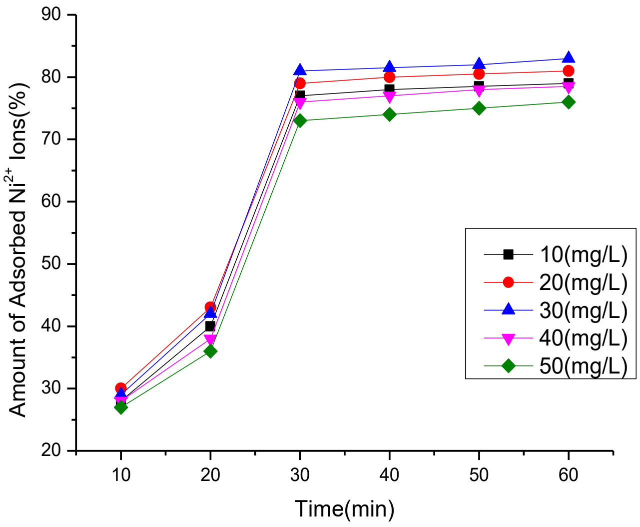

Fig. 2: Effect of initial concentration and contact time

3.2. Effect of activated AMC dose

The Ni(II) ions removal percentage on activated AMC was probed at various activated AMC dosages (10, 25, 50, 100, 200 and 250 mg), while maintaining pH 6.5, temperature 30°C, 30 min contact time and 30 mg/L initial adsorbate concentration, constant. Fig. 3 showed that the Ni (II) ions percentage removal increased with an increase in the activated AMC dosage and reached a constant value after a particular activated AMC dose. The increase in the Ni (II) ions adsorption percentage with activated AMC dose may be due to an increase in adsorbent surface area and availability of more adsorption sites [22-24]. Further increment inactivated AMC dosage, the results showed no further appreciable increase in adsorption. This may be due to overlapping of adsorption sites due to overcrowding of adsorbent particles [25, 26].

3.3. Effect of pH

The impact of pH on Ni(II) ions removal from wastewater was explored over a pH range of 3-9 while holding other variables constant, *viz.*, 30 mg/L initial Ni(II) ions concentration, 25mg/50mL activated AMC dosage, 30°C temperature and 30 min contact time. The removal efficiency of Ni(II) ions increased rapidly with increasing pH of the solution initially with pH 6.5 being the optimum pH (Fig. 4). The adsorption of most of the heavy metal ions on activated carbon increased with increasing pH in common [27]. It was driven by the fact that at low pH, the protonation of active sites at the carbon surface was boosted, preventing the formation of links between cationic metals and protonated active sites [28]. Further increase of pH makes the percentage removal decrease drastically. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent which ultimately leads to the reduction in adsorption capacity [29].

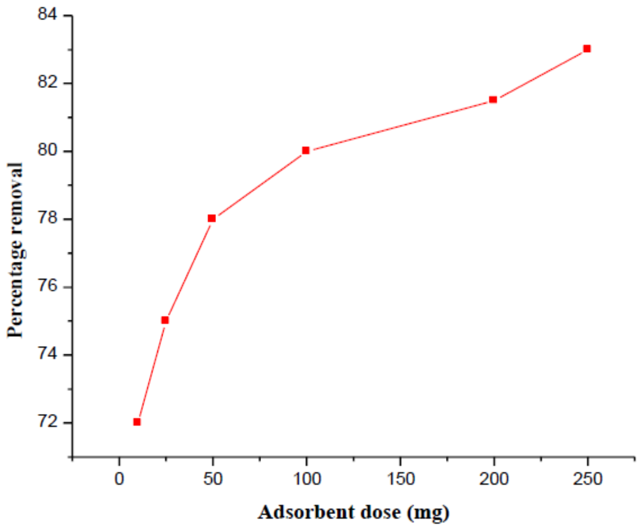

Fig. 3: Effect of activated AMC dose

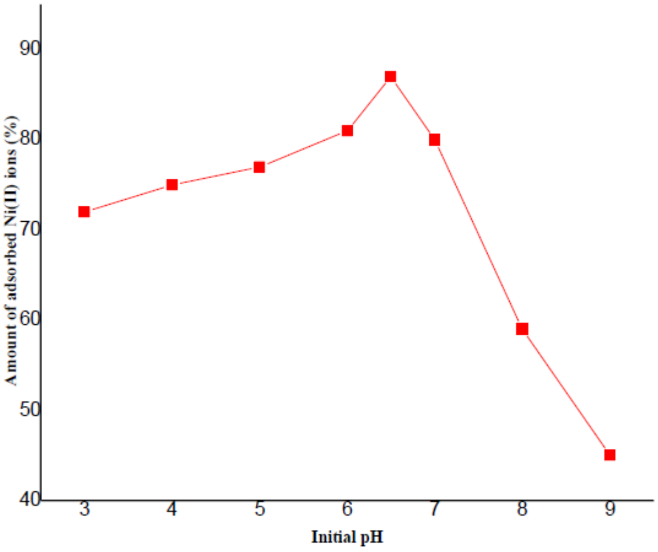

Fig. 4: Effect of pH

3.4. Effect of ionic strength

Several environmental features can influence the adsorption of heavy metals by activated carbon. NaCl was used as a competitive ion in this study. The impact of NaCl on Ni (II) ions adsorption on activated AMC is shown in the fig. 5. In a low concentration of the solution, NaCl had little effect on the adsorption efficiency. Due to partial neutralization of the positive charge on the activated AMC surface and subsequent compression of the electrical double layer by the Cl^- ion, the sorption of Ni (II) ions will be increased at higher ionic strength [30].

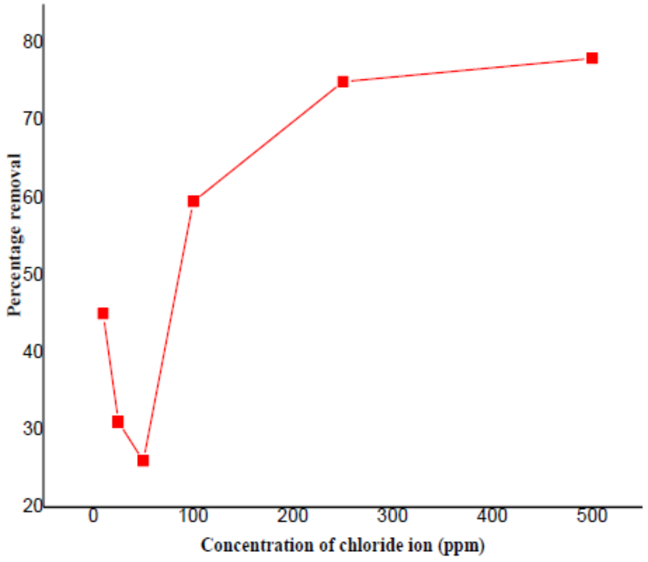

Fig. 5: Effect of ionic strength

3.5. Effect of temperature

Fig. 6 shows that the data pertaining to varied temperature environments. A steady increase in the percentage removal is evident with temperature, which reflects the mobility of surface active sties and reduction in the boundary layer thickness, in turn restricting the mass transfer resistance of Ni(II) ions [31].

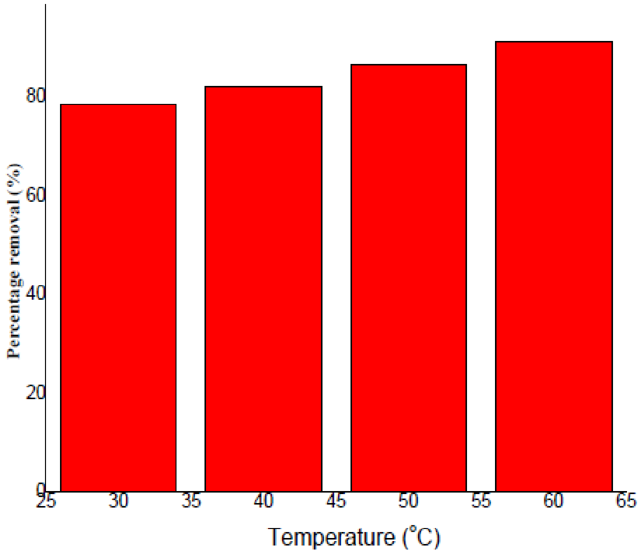

Fig. 6: Effect of temperature

3.6. Desorption studies

Desorption of Ni(II) ions-loaded from the surface of activated AMC with HCl as an eluent was observed (Table 1) to vary linearly with the concentration of the hydrochloric acid (0.02, 0.04, 0.06, 0.08 and 0.10 M) and shows a trend of maximum desorption at 0.10M (eluent). The results of desorption experiments imply a maximum of 79.95% using regenerated activated AMC for Ni (II) ions [32].

Table 1: Desorption data

HCl Concentration (M)	Percentage removal (%)
0.02	68.53
0.04	70.67
0.06	73.54
0.08	76.23
0.10	79.95

3.7. Adsorption Isotherms

An adsorption isotherm is a set of constant values that express the adsorbent's surface characteristics and affinity. It can be used to assess the adsorbent's adsorption potential for different pollutants [33]. The data obtained was used to establish the mechanism of Ni (II) ions adsorption on activated AMC using Langmuir, Freundlich, and Temkin isotherms. For this adsorption system, the constant variables of the isotherm equations were derived using regression and a linear form of the isotherm equations. Table 2 lists the constant variables as well as correlation coefficient (R^2).

3.7.1. Freundlich adsorption isotherm

The Freundlich isotherm is an empirical principle that states a non-uniform heat distribution on the adsorbent surface, resulting in a heterogeneous adsorption [34]. This isotherm is generated from the hypothesis that the adsorption sites are distributed exponentially in terms of heat of adsorption. The adsorption isotherm is expressed by the equation:

$$q_e = K_F C_e^{1/n_F} \quad (3)$$

which, can be linearized as

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

where, 'q_e' is the quantity of Ni(II) ions adsorbed at equilibrium (mg/g); 'C_e' is the Ni(II) ions concentration in the aqueous media at equilibrium (mg/L); 'K_F' (L/g) and '$1/n_F$' are the Freundlich constants associated to adsorption capacity and adsorption intensity, respectively. The slope and intercept of the '$\ln q_e$' versus 'ln C_e' plot was used to determine the Freundlich constants, 'K_F' and '$1/n_F$'. To be regarded as favourable adsorption, the Freundlich exponent, 'n_F', should have values between 1 and 10 (i.e., $1/n_F < 1$) [35]. The 'n_F' values greater than unity suggests that the adsorption system is favourable [36]. Freundlich adsorption isotherm model which has the highest regression (R^2) coefficient, was found to be the best fit with the experimental evidence among the three models (Langmuir, Freundlich and Temkin).

Table 2: Isothermal constants data

Model	Constant	Temp., ˚C			
		30	40	50	60
Freundlich	K_F (mg/g) (L/mg)$^{1/n}$	1.7603	1.7743	1.6440	1.8278
	N	2.5411	2.4949	1.6932	2.4673
	R^2	0.9991	0.9997	0.9998	0.9992
Langmuir	q_m (mg/g)	361.73	373.39	574.08	395.68
	K_L (L/mg)	0.0703	0.0753	0.0464	0.0940
	R^2	0.9977	0.9985	0.9537	0.9993
Temkin	b_T (J/mol)	279.65	358.74	317.65	381.92
	K_T (L/mg)	1.0054	1.0428	1.0302	1.0402
	R^2	0.9975	0.9992	0.9506	0.09989

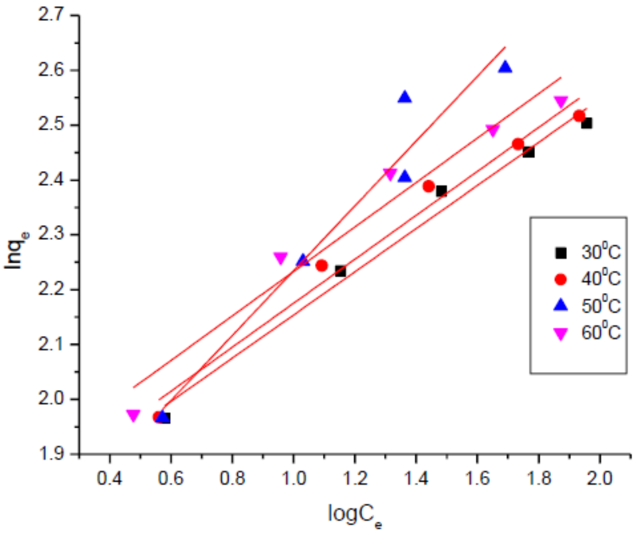

Fig. 7: Freundlich isotherm plot

3.7.2. Langmuir adsorption isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface [37]. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved. The Langmuir isotherm in a linear form is represented by [38]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (5)$$

where, 'q_e' is the amount of Ni(II) ions adsorbed at equilibrium (mg/g), 'C_e' is the concentration of Ni(II) ions in the aqueous phase at equilibrium (mg/L), 'q_m' is the maximum Ni(II) ions uptake (mg/g) and 'K_L' is the Langmuir constant related to adsorption capacity and the adsorption energy (L/mg). The linear plot (Fig. 8) of specific adsorption 'C_e/q_e' against the equilibrium concentration 'C_e' was employed to determine the value of 'q_m' (slope) and 'K_L' (intercept). A high 'K_L' value indicates a high adsorption affinity. The vital characteristics of Langmuir adsorption isotherm parameter can be used to predict the affinity between the adsorbate and adsorbent using a dimensionless constant called separation factor or equilibrium parameter (R_L), which is expressed by the following relationship [39]:

$$R_L = \frac{1}{1 + K_L C_i} \qquad (6)$$

where, 'C_i' is the initial Ni(II) ions or concentration (mg/L) and 'K_L' is the Langmuir constant (L/mg). 'R_L' value indicates the type of Langmuir isotherm to be irreversible ($R_L = 0$), linear ($R_L = 1$), unfavorable ($R_L > 1$), or favorable ($0 < R_L > 1$) [40]. The dimensionless separation factor (R_L) values for Ni (II) ions removal were calculated at different initial concentrations and temperatures (Table 3). The determined 'R_L' values (Table 3) for the Ni(II) ions at different concentrations fall within the range of 'zero to one' suggesting a favorable adsorption system [32].

Table 3: Dimensionless separation factor (R_L)

[Ni (II)] (mg/L)	Temperature (°C)			
	30	40	50	60
10	0.2214	0.2096	0.3011	0.1753
20	0.1244	0.1171	0.1772	0.0960
30	0.0865	0.0812	0.1256	0.0661
40	0.0663	0.0621	0.0972	0.0504
50	0.0538	0.0503	0.0793	0.0407

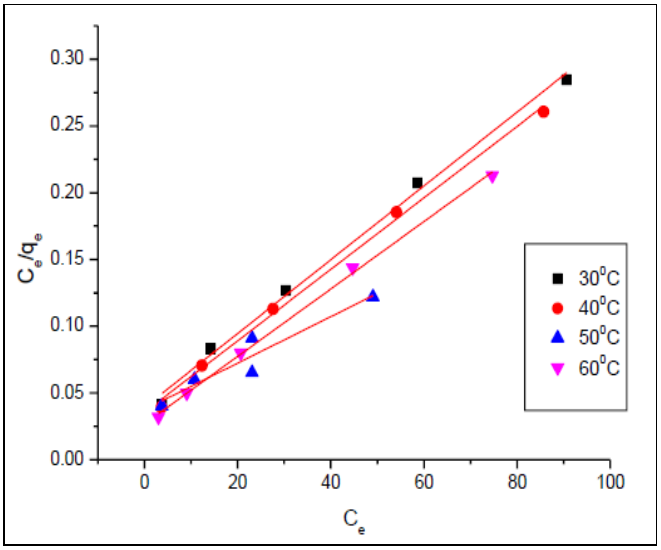

Fig. 8: Langmuir isotherm plot

3.7.3. Temkin adsorption isotherm

The Temkin isotherm model accounts for the effects of indirect adsorbent-adsorbate interactions on the adsorption system, as well the heat of adsorption (ΔH_{ads}) of all molecules in the layer will decrease linearly due to increased surface coverage [41]. The following is the linear version of Temkin isotherm model [42]:

$$q_e = \left(\frac{RT}{b_T}\right)\ln K_T + \left(\frac{RT}{b_T}\right)\ln C_e \qquad (7)$$

where, 'K_T' (L/g) is the Temkin isotherm constant which is related to the adsorption capacity, 'b_T' (J/mol) is Temkin constant which is related to heat of adsorption, 'R' is the ideal gas constant (8.314 J/mol/K), and 'T' is the absolute temperature (K).

The Temkin constants, 'K_T' and 'b_T' are calculated from a linear plot of 'q_e' versus '$\ln C_e$' for the Temkin isotherm model which clearly indicates that all points are scattered on straight lines with no proper fitting. The weak adsorption pattern is easily comprehended by the lower binding constant (K_T) and heat of adsorption (b_T) parameters determined from the plots (Fig. 9). Hence the adsorbent-adsorbate interaction does not favour for this adsorption system.

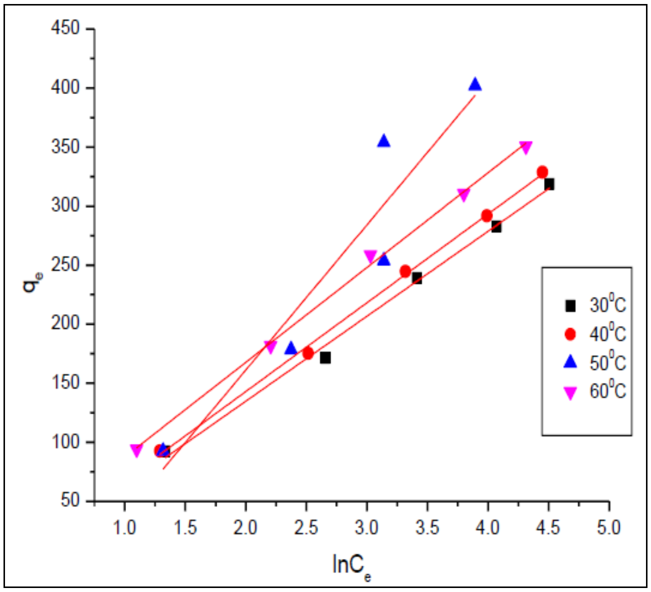

Fig. 9: Temkin isotherm plot

4. CONCLUSION

Anisomeles malabarica leaves can be successfully used as a raw material for the production of activated carbon. The adsorption rate and equilibrium conditions of the Ni^{2+}-activated AMC system was investigated using Batch technique that includes activated AMC dosage, contact time, initial Ni(II) ions concentration, pH, ionic strength and temperature. Langmuir, Freundlich and Temkin isothermal parameters were explored. Based on Regression coefficient (R^2) values, Freundlich isotherm model has been found to be the best fit. The desorption results demonstrated that after the desorption process, the activated AMC can be regenerated. The results suggests that the activated carbon prepared from *Anisomeles malabarica* leaves can be used as a cost-effective favorable adsorbent for the removal of Ni(II) ions from aqueous phase.

5. REFERENCES

1. Basu M, Guha AK, Ray L. *Int J Environ Sci Technol,* 2019; 16:237-248.
2. Celebi H, Gok G, Gok O. *Sci Rep,* 2020; 10:17570.
3. Bhatnagar A, Minocha AK. *Colloid Surface B,* 2010; 76:544-548.
4. El-Sadaawy M, Abdelwahab O. *Alex Eng J*, 2014; 53:399-408.
5. Demirbas E, Kobya M, Oncel S, Sencan S. *Bioresour Technol*, 2002; 84:291-293.
6. Hernandez-Rodriguez M, Yperman J, Carleerb R, Maggen J, Dadi D, Gryglewicz G, et al. *J Env Chem Eng,* 2018; 6:1161-1170.

7. Jia, YF, Xiao B, Thomas, KM. *Langmuir,* 2002; **18(2)**:470-478.
8. Aman T, Kazi AA, Sabri MU, Bano Q. *Colloids Surf, B*, 2008; **63**:116-121.
9. Erdogan S, Onal, Y, Akmil-Basar C, Bilmez-Erdemoglu S, Sarici-Ozdemir C, Koseoglu E, et al. *Appl Surf Sci*, 2005; **252**:1324-331.
10. Fonseca-Correa RA, Giraldo L, Moreno-Pirajan JC. *Heliyon*, 2019; **5**:e01789.
11. Kasprzak KS, Sunderman FW, Salnikow K. *Mutat Res Fund Mol M*, 2003; **533**:67-97.
12. Norseth T, vol. II: *Specific Metals*, 2nd edn. L.Friberg, G.Nordberg and V. Vouk, Eds., Elsevier Science Publishers, Amsterdam: 1986.
13. Ahmed AMM, Ali AE, Ghazy AH. *Adv J Chem A*, 2019; **2(1)**:79-93.
14. Shahnaz K, Amirabbas Z, Mohammad P, Hossein F, Majid A, Mohammad I. *Chem Eng J*, 2018; **337**:169-182.
15. Rani P, Johar R, Jassal PS, *Water Sci Technol*, 2020; **82(10)**: 2193-2202.
16. Karidakis T, Agatzini-Leonardou S Neou-Syngouna P. *Hydrometallurgy*, 2005; **76(1-2)**:105-114.
17. Babel S, Kurniawan, TA. *J Hazard Mater*, 2003; **97**:219-243.
18. Katal R, Hasani E, Farnam M, Baei MS, Ghayyem MA. *J Chem Eng Data*, 2012; **57**:374-383.
19. Desta MB. *J Thermodyn,* 2013; **2013**:1-6.
20. Li W, Zhang L, Peng J, Li N, Zhang S, Guo S. *Ind Crop Prod*, 2008; **28(3)**: 294-302.
21. Moyo M, Chikazaza L, Nyamunda BC, Guyo U. *J Chem*, 2013; **2013**:1-8.
22. Yao S, Sun S, Wang S, Shi Z. *Indian J Chem Technol*, 2016; **23**:146-152.
23. Garg UK, Kaur MP, Garg VK, Sud D. *J Hazard Mater*, 2007; **140(1-2)**:60-68.
24. Al-Qahtani KM. *J Taibah Univ Sci*, 2016; **10 (5)**:700-708.
25. Najua DT, Luqman CA, Zawani Z, Suraya AR. *J Eng Sci Tech*, 2008; **3(2)**:180-189.
26. Onundi YB, Mamun AA, Al Khatib MF, Ahmed YM. *Int J Environ Sci Tech*, 2010; **7(4)**:751-758.
27. Kumar P, Dara SS. *Indian J Environ Health*, 1980; **22:**196-202.
28. Abudaia JA, Sulyman MO, Elazaby KY, Ben-Ali SM. *Int J Environ Sci Develop*, 2013; **4(2)**:191-195.
29. Baral SS, Das SN, Rath P. *Biochem Eng J*, 2006; **31(3)**:216-222.
30. Zhu B, Fan T, Zhang D. *J Hazard Mater*, 2008; **153**:300-308.
31. Nassar MN. *J Hazard Mater*, 2010; **184**:538-546.
32. Akpomie KG, Dawodu FA. Adebowale AO, *Alex Eng J*, 2015; **54**:757-767.
33. Moniruzzaman M, Rahman MA, Aktar S, Khan M. *Int J Waste Resour*, 2017; **7(4)**:301-306.
34. Freundlich H, Heller, W. *J Am Chem Soc*, 1939; **61**:2228-2230.
35. Vistuba JP Nagel-Hassemer ME, Lapolli FR, Recio MAL. *Environ Technol*, 2013; **34(2)**:275-282.
36. Kataria N, Garg VK. *J Mol Liq*, 2018; **271**:228-239.
37. Langmuir I. *J Am Chem Soc*, 1918; **40**:1361-1403.
38. Dabrowski A. *Adv Colloid Interface Sci*, 2001; **93(1-3)**:135-224.
39. Webber TW, Chakkravorti RK. *AlChE J*, 1974; **20**:228-238.
40. McKay G. Blair HS, Gardner JR. *J Appl Polym Sci*, 1982; **27(8)**:3043-3057.
41. Tempkin MJ, Pyzhev V. *Acta Physicochim*, URSS, 1940; **12**:217-222.
42. Vijayaraghavan K, Padmesh TVN, Palanivelu K, Velan M. *J Hazard Mater*, 2006; **133(1-3)**:304-308.