

REMOVAL OF Ni²⁺ FROM AQUEOUS SOLUTION BY ADSORPTION ONTO TEA WASTE-DERIVED ACTIVATED CARBON

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ABSTRACT

Activated carbon from a locally available and widespread tea waste source was fabricated, characterized and used as an efficient adsorbent for the removal of Ni²⁺ from aqueous solutions. The response surface methodology (RSM) and central composite design (CCD) were used to investigate the effect of the essential variables including initial concentration, adsorbent dosage and pH solution on the absorption of Ni²⁺. The order polynomial regression equations-based model has been developed and found to be statistically significant by values of the coefficients of determination (R²) closer than 1.0 and the P-values < 0.0001 from analysis of variance (ANOVA). Based on the predicted optimum conditions, actual experiment was employed to obtain the maximum percentage of Ni²⁺ removal efficiency (96.6 %). There is no doubt that the use of tea waste as abundant raw material for the preparation of activated carbon to remove Ni²⁺ from aqueous solutions by five times with negligible change is a promising way.

Keywords: removal of Ni²⁺, tea waste, response surface methodology, activated carbon.

1. INTRODUCTION

Activated carbon (AC) is a microcrystalline and non-graphitic material, which possesses several emergent properties such as large surface area, good adsorption capacity, highly micro-porous structure [1]. Hence, it has also been recognized as a promising adsorbent for the elimination of heavy metal from groundwater pollution. However, the costly commercial activated carbon produced from traditional coal and wood has prohibited its potential applications [2]. The agricultural by-products have recently played a crucial role for the fabrication of activated carbon because they are locally available and renewable raw materials. Green tea is a well-known and widespread beverage all over the world [3]. Tea is massively

cultivated in some tropical countries due to it has been proven to contain several valuable natural compounds, for example, anti-oxidant and anti-carcinogenic substances. According to previous publications, main components of the tea leave waste are cellulose (37 %), hemicelluloses and lignin (14 %) and polyphenol (25 %) and tannins [4]. However, tea waste is often discharged from manufacturing process after the extraction of polyphenol, caffeine, and polysaccharide. The discard of residues without pre-treatment can lead some problems harmful for the living environment [5]. Thus, taking advantage of tea waste resource for the synthesis of activated carbon has been paid much attention of many environmental scientists and organizations.

Nickel contamination of pristine water is considered as one of the environmentally serious issues because of its toxicological influences on human health [6 – 8]. The presence of exceeding a concentration of Ni^{2+} in micro-organisms is responsible for the vulnerable diseases consisting of vomiting, chest pain, and rapid respiration [9]. According to the reports of World Health Organization (WHO), the critical concentration of nickel in drinking water is recommended to be 0.02 ppm. To remove the Ni^{2+} ions from aqueous solutions, some traditional methods were widely used including ion exchange, chemical precipitation, ultra filtration, electrochemical deposition, and adsorption [10]. However, adsorption technique is recognized as a significant means of treatment because of its great advantages such as metal recovery and cost effectiveness [11]. The present work aims to investigate influential factors of the removal of Ni^{2+} by adsorption onto tea waste-derived activated carbons using the response surface methodology (RSM). The RSM-based two-order polynomial regression equations were used to assess the mathematical interaction of several variables including initial Ni^{2+} concentration, the dosage of activated carbon and pH of the solution. Otherwise, the predicted optimum conditions for the maximum percentage of Ni^{2+} removal was also calculated by the statistical program Design – Expert 9.

2. MATERIALS AND METHODS

2.1. Chemicals and instruments

All chemicals for this study were commercially purchased from Merck and used as received without any further purification unless otherwise noted. All activated carbon samples were pretreated by heating at 105 °C for 3 hours. The scanning electron microscope (SEM) was recorded by instrument Hitachi S4800, Japan and used an accelerating voltage source of 10 kV with a magnification of 7000. The FT-IR spectra were recorded by using the Nicolet 6700 spectrophotometer instrument.

2.2. Production of activated carbon

The tea waste was placed in a heat-resistant glass vessel connected to an electric furnace. The sample was then heated from room temperature to 500 °C (10 °C/min) under a nitrogen atmosphere (400 cm³/min) and maintained the final temperature during 60 min. The carbonization system was gradually cooled down to room temperature overnight. The residual char was soaked with KOH solution (char : KOH = 1:1 by weight) for 1 day before heated to 800 °C using the same given system during 60 min. The sample was repeatedly washed with deionized water until filtered water obtained a neutral solution. Finally, the synthesized AC was slowly dried at 105 °C, and then smoothly ground for storage (33 % of AC yields).

2.3. Adsorption batch

The adsorbent (0.8 g/L – 9.2 g/L) was poured in an Erlenmeyer flask containing 50 mL of Ni²⁺ aqueous solution (8 ppm – 92 ppm). After adsorption equilibrium obtained, the adsorbent was removed from the mixture. The residual concentrations were confirmed by AAS and Ni²⁺ removal was calculated by the following equation:

$$\text{Ni}^{2+} \text{ removal (\%)} = \frac{C_o - C_e}{C_o} \cdot 100 \quad (1)$$

where, C_o and C_e are the Ni²⁺ initial and equilibrium concentrations (ppm), respectively.

2.4. Experimental design with RSM

Herein, RSM technique is used to optimize experimental results through second order polynomial regression equations. Central composite design (CCD) is used to establish given 20 experiments (Table 1) with five levels including the low (encoded -1), high (encoded +1) and rotatable (encoded ±1.68).

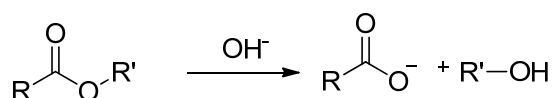
Table 1. Independent variables matrix and their encoded levels

No	Independent factors	Code	Levels				
			-1.68	-1	0	+1	+1.68
1	Initial concentration (ppm)	x ₁	8	25	50	75	92
2	Adsorbent dosage (g/L)	x ₂	0.8	2.5	5	7.5	9.2
3	pH of solution (-)	x ₃	0.6	2	4	6	7.4

3. RESULTS AND DISCUSSION

3.1. Textural characterization of activated carbon

The structure of activation carbon was chemically characterized by a means of Fourier transform infrared spectroscopy. According to the recorded profiles in Figure 1a, the sample was generally possessed complex surface with various kinds of functional groups. The strong absorption band around 3450 cm⁻¹ was attributable to the -OH stretching vibrations. The presence of the peak positioned around 2900 cm⁻¹ was correspondent to C-H vibrations in aliphatic groups. Unsaturated carbon bonds (C=C) in aromatic rings was also confirmed by stretching band at 1640 cm⁻¹, while the presence of the O-N asymmetric and C≡C bonding vibrations was attributable to the peak positions at 1541 cm⁻¹ and 2353 cm⁻¹ [10]. KOH activation was ascribed to increase the oxygen-containing group species such as phenolic hydroxyls, enolates, and esters, for an example as follows:



Thus, Ni²⁺ adsorption on the adsorbent surface by mechanisms like ion-exchange between

metal ions and functional groups can occur due to van der Waals forces or electrostatic attraction between active sites with metal ions [12]. The SEM micrographs in Figure 1b at a magnification of 60000 revealed the surface morphology of the as-synthesized activated carbon. Obviously, the structure of activates carbon was observed to be more highly porous and rich-defective.

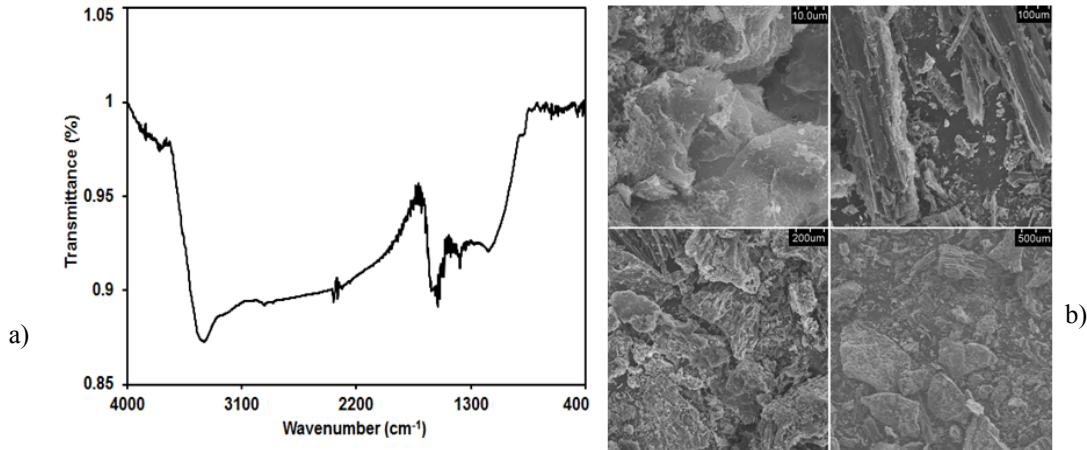


Figure 2. FT-IR spectra (a) and SEM micrograph (b) of the activated carbon

3.2. Assessment of experimental results with Design-Expert

The actual and predicted results of the percentage of Ni²⁺ removal efficiency were presented in Table 2. The ranges of investigation parameter were designed as follows: initial concentration (x_1) from 8 ppm to 92 ppm, an adsorbent dosage (x_2) from 0.8 g/L to 9.2 g/L and pH of the solution (x_3) from 0.6 to 7.4. The correlation between the responses and variables was described by the following quadratic equations:

$$Ni(II) \text{ removal } (\%) = 93.8 - 3.72x_1 + 9.34x_2 + 26.19x_3 + 8.5x_1x_2 + 0.38x_1x_3 - 2.08x_2x_3 - 4.23x_1^2 - 14.19x_2^2 - 17.19x_3^2 \quad (2)$$

The results of the ANOVA for response surface were used to assess the significance of quadratic model through correlation coefficients (R^2) and P-values. According to Table 3, the P-values were found to be less than 0.0001 and respective R^2 was closer 1.0 indicated the proposed models were statistically significant at 95 % confidence level. Moreover, the high fitness of model was also proved by the adequate precision (AP) ratio, which value was greater than 4.0 and by plots of predicted values versus actual values, which almost points positioned to the straight line (Figure 2a). Otherwise, lack of fit (LOF) value was statistically insignificant and hence indicated the model fitted data well.

Table 2. Matrix of observed and predicted values

No	Variables			Response (Ni ²⁺ removal)	
	x_1 (C _i , ppm)	x_2 (dosage, g/L)	x_3 (pH)	Actual (%)	Predicted (%)
1	25	2.5	2	30.5	33.2
2	75	2.5	2	7.2	8.0
3	25	7.5	2	34.6	39.0

4	75	7.5	2	45.4	47.8
5	25	2.5	6	87.6	88.9
6	75	2.5	6	65.9	65.2
7	25	7.5	6	83.5	86.5
8	75	7.5	6	95.7	96.8
9	8	5	4	93	88.1
10	92	5	4	75.9	75.6
11	50	0.8	4	38.6	38.0
12	50	9.2	4	74	69.4
13	50	5	0.6	5.4	1.1
14	50	5	7.4	90.2	89.2
15	50	5	4	95.3	93.8
16	50	5	4	96.1	93.8
17	50	5	4	94.7	93.8
18	50	5	4	93.1	93.8
19	50	5	4	92.4	93.8
20	50	5	4	90.2	93.8

Table 3. ANOVA for response surface quadratic models

Response	Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob. > F	Comment
Ni ²⁺ removal (%)	Model	17913.33	9	1990.37	148.06	< 0.0001 ^s	Mean = 69.47
	x ₁	188.66	1	188.66	14.03	0.0038 ^s	CV = 5.28
	x ₂	1191.00	1	1191.00	88.59	< 0.0001 ^s	R ² = 0.9926
	x ₃	9364.47	1	9364.47	696.59	< 0.0001 ^s	R ² _(adj.) = 0.9858
	x ₁ x ₂	578.00	1	578.00	43.00	< 0.0001 ^s	AP = 36.987
	x ₁ x ₃	1.13	1	1.13	0.084	0.7783 ⁿ	
	x ₂ x ₃	34.44	1	34.44	2.56	0.1405 ⁿ	
	x ₁ ²	258.46	1	258.46	19.23	0.0014 ^s	
	x ₂ ²	2900.77	1	2900.77	215.78	< 0.0001 ^s	
	x ₃ ²	4259.81	1	4259.81	316.87	< 0.0001 ^s	
	Residuals	134.43	10	13.44			
	LOF	110.84	5	22.17	4.70	0.0574	
	PR	23.59	5	4.72			

Note: ^s significant at p < 0.05 and ⁿ not significant at p > 0.05, LOF (lack of fit), PR (pure error).

3.3. Effect of independent variables on the removal of Ni²⁺

Referring to Table 3, the initial concentration, adsorbent dosage and pH of the solution were found to be strong effects on the percentage of Ni²⁺ removal because P-values of x_3 , x_1x_3 and x_2x_3 were statistically significant. Herein, the response surface was plotted with a variation of two parameters while the other parameter maintained at zero level (Figure 2).

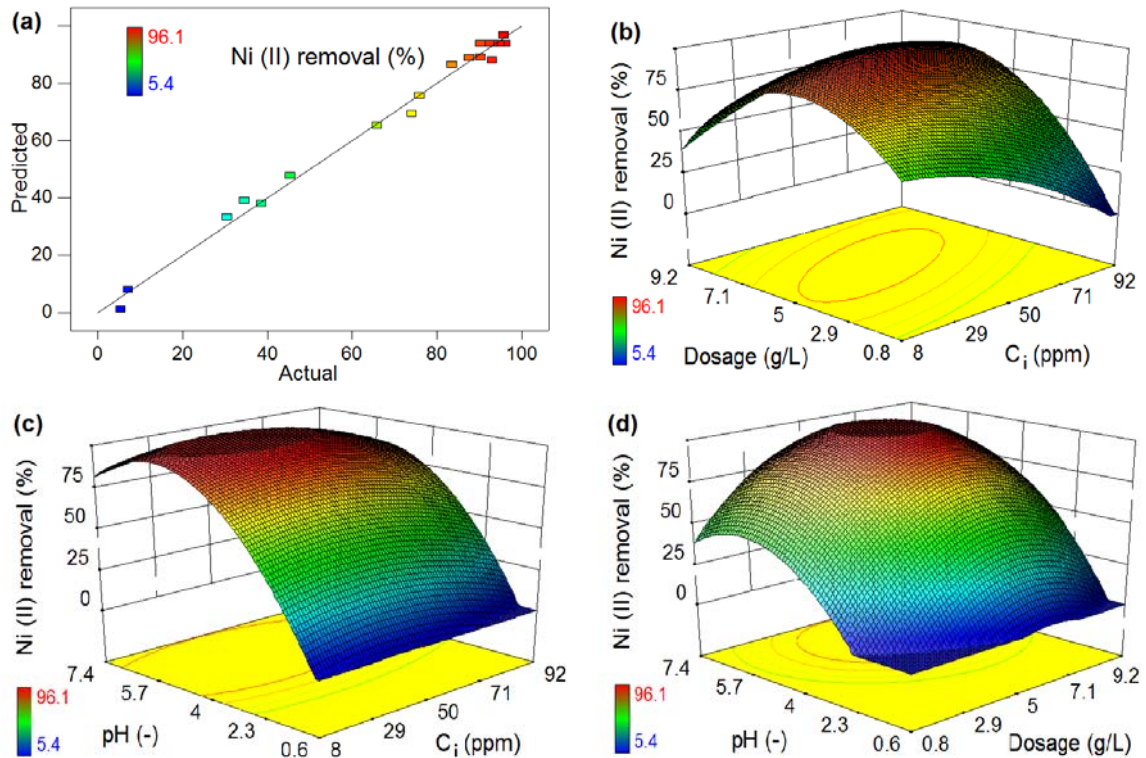


Figure 2. Actual versus predicted plot (a) and response surfaces (b–d) for regression model of the percentage of Ni²⁺ removal

According to three-dimensional response surface plots in Figures 2b–d, the Ni²⁺ removal efficiency was generally dependent on various kinds of initial concentration, adsorbent dosage, and pH of the solution. At a low value of adsorbent dosage, Ni²⁺ removal efficiency would increase by decreasing the initial concentration of nickel ions (Figure 2b). The removal of Ni²⁺ obtained the optimum range of value at a higher amount of activated carbon (around 5 g/L) and then the variation of percentage of Ni²⁺ removal was deducted. Figure 2c showed the effect of initial concentration and pH of the solution on the percentage of Ni²⁺ removal. It was obvious that initial concentration of Ni²⁺ influenced insignificantly on the removal efficiency while the variation of pH-values led the considerable change of Ni²⁺ removal efficiency. When the solution reached the strongly acidic environment (pH < 2), the adsorption of Ni²⁺ onto the activated carbon was negligible. In contrast, Ni²⁺ adsorption process could be improved clearly when the solution reached a neutral nature. In this case, the range of optimum pH for the 100 % of Ni²⁺ removal was found to be 4.5 – 6.5. Finally, the effect of AC dosage and pH on the removal of Ni²⁺ was observed in Figure 2d. A wide range for the value of pH (4.5 – 6.5) and dosage (3–8 g/L) was favorable for the adsorption of Ni²⁺. The predicted optimal conditions

based model experiment was further conducted to verify the suitability of the proposed models: C_i = 74.3 ppm, dosage = 5.5 g/L and pH = 5.1 (Table 4). Thereby, the test for the percentage of Ni²⁺ removal was obtained 96.6 % which is nearly closed to the predicted values of 98.4 %. These results demonstrate the high compatibility of the proposed models with the experimental data.

Table 4. Model confirmation for the removal of Ni²⁺ by tea waste-derived activated carbon (TWAC)

Sample	C _i (ppm)	Dosage (g/L)	pH (-)	Desirability	Ni ²⁺ removal (%)	
					Predict	Test
TWAC	74.3	5.5	5.1	1.00	98.4	96.6

3.4. Isotherm modelling and adsorbent recyclability

Table 5. Isotherm parameters for the adsorption of Ni²⁺ by TWAC

Isotherm	Equation	Parameters	Value of parameters
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m}$	K _L (L/mg)	0.1384
		q _m (mg/g)	20.75
		R _L	0.0728
		R ²	0.9995
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	K _F	2.6010
		[(mg/g).(L/mg)] ^{1/n}	0.6175
		1/n	0.9481
		R ²	
Temkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$	K _T (L/mg)	3.5885
		B ₁	2.3636
		R ²	0.9855

Table 6. Comparison of the textural properties of chemical-ACs and Ni²⁺ treatment

Source	Properties of AC			Ni ²⁺ treatment				Ref
	Chemical agent	Activation temp.	S _{BET} (m ² /g)	C _o (ppm)	Dosage (g/L)	pH	q _m (mg/g)	
Almond husk	H ₂ SO ₄	700	–	25	5	5	4.87	[4]
Apricot	K ₂ CO ₃	400	4.27	10	7	5.0	17.04	[5]
Palm shell	–	–	513	0.8	1	5	0.13	[6]
Glucose	H ₃ PO ₄	450	698	60	0.6	7	48.5	[7]
Sucrose			460				42.4	
Starch			12				41.1	
Sugarcane fiber	NH ₄ Cl	500	836	147	10	7	10.3	[8]
Seed coat	H ₃ PO ₄	300	–	40	5	7	13.51	[9]
Tea waste	KOH	700	–	75	5.5	5.0	20.75	<i>This work</i>

Adsorption models are essential to study the interaction between adsorbate and adsorbent. Herein, we showed three various adsorption isotherms including Langmuir, Freundlich and Tempkin and their results revealing the linear regression correlation and constant values were represented in Table 5. For the Langmuir isotherm, a plot of C_e against C_e/q_e produced a straight line with the R^2 value of 0.9995 for adsorption model of Ni^{2+} . Moreover, the value of R_L was found to be less than 1.0 and revealed that Langmuir adsorption was more dominant. For the other models, lower values of R^2 corresponding to 0.9481 and 0.9855 for Freundlich and Tempkin indicated to the data fitness in the following order: Langmuir > Tempkin > Freundlich. Therefore, Langmuir model illustrated the best description of the Ni^{2+} adsorption behavior onto the surface of activated carbon and consolidated that the Ni^{2+} adsorption process is mainly monolayer adsorption. With the maximum adsorption value from the model Langmuir (20.75 mg/g), the present study showed the higher capacity than activated carbon fabricated from the other wastes (Table 6). The recycling test was undertaken to recognize the reuse of activated carbon after the first batch experiment. The HCl (1.4 M) was used to deprotonate Ni^{2+} from adsorbent [12]. The removal percentage of Ni^{2+} of the fifth recycled TWAC was decreased from 96.6 % to 78.2 %. Therefore, TWAC can be used for the removal of Ni^{2+} several times without a considerable decrease of adsorption capacity. The present results for adsorption of Ni^{2+} onto activated carbon from tea waste revealed the potential use of tea waste as a raw material source (Table 6).

4. CONCLUSIONS

The porous activated carbon fabricated from cheap and abundant tea waste source was found to be an effective adsorbent for removal of Ni^{2+} ions from aqueous solution. The RSM involving CCD was successfully applied to assess the influence of independent parameters, including Ni^{2+} initial concentration, pH and AC dosage on the removal of Ni^{2+} and to optimize the adsorption conditions. The developed quadratic models for the adsorption were statistically significant. Under optimal conditions $C_i = 74.3$ ppm, dosage = 5.5 g/L and pH = 5.1, the excellent result was obtained up to 96.6 % of Ni^{2+} removal. Moreover, adsorption isotherm was satisfactory represented by the Langmuir equation with high capacity of monolayer adsorption (20.75 mg/g). The recycling results up to five times proved a great potential for application of low-cost tea waste-derived activated carbon for removal of environmental pollutants.

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