

Utilization of Tea Waste Biomass -Al₂SiO₃ Nanocomposite for the Removal of Ni(II) from Aqueous Solution: Isotherm and Kinetic Studies

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Abstract—Degradation in water quality is accelerating day by day owing to the rapid industrialization and urbanization. Heavy metals are among the most significant pollutants found in wastewater. They pose serious threat to both human health and ecosystem as they are non-biodegradable. Present work explored the adsorption efficiency of Tea waste biomass- Al₂SiO₃ nanocomposite for the removal of Ni(II) from aqueous solution. Tea waste biomass is an agricultural waste. Thus using a nanocomposite derived from it as adsorbent provides two fold advantage, one managing solid waste and the other is treating waste water at low cost. The adsorbent was characterized using FTIR and surface morphology was also studied using SEM. It showed excellent removal efficiency of 98% for Ni(II). Various physico-chemical parameters like effect of contact time, pH and temperature were studied using batch process to optimize conditions for maximum adsorption. The optimum pH for Pb(II) was found to be 4. Kinetic data showed that pseudo-second order model was well obeyed over wide range of concentrations. Equilibrium isotherm data fitted well to Langmuir and freundlich isotherm models.

Keywords: *Asparagus racemosus*, carbon, isotherm, thermodynamics

1. INTRODUCTION

Amongst the various important human activities batteries, paints and pigments, metal smelting, electroplating, gas exhausts, energy and fuel production, down wash from power lines, intensive agriculture and sludge dumping are contributing to a large extent in contaminating the water with high level of heavy metals. These toxic heavy metals such as Pb(II), Cd(II), Hg(II), Cu(II) and Ni(II) are detrimental and pose a serious threat to environment because of their non-biodegradability and selective toxicity even at low concentrations. Amongst these Cd(II) is one of the toxic heavy metal which severely affects kidney, placenta, lungs, brain, gastrointestinal system and bones.

The permissible limit of nickel in drinking water as prescribed by WHO is 0.07mgL⁻¹. Due to the high toxicity of nickel, there has been increasing emphasis on the development of techniques for its removal.

Therefore, various techniques have been employed for elimination of these heavy metals from wastewater, including chemical coagulation, reverse osmosis, adsorption, electrolysis, ion exchange, ultra filtration, nanofiltration etc.

Among these, adsorption has gained attention of the researchers, due to its high removal efficiency, simplicity, economical viability and technical feasibility. Many readily available and low-cost materials have been reported in literature to produce activated carbon for the removal of heavy metals from water such as coconut shell [1], waste slurry generated from fertilizer plant [2], peanut hull [3] and rice husk [4] for the removal of heavy metals from water and waste water.

In the present work, adsorption properties of Tea waste biomass -Al₂SiO₃ nanocomposite, a novel adsorbent has been explored for the removal of Ni(II) from aqueous solution. Tea is an aromatic beverage commonly prepared by pouring hot or boiling water over cured leaves of the *Camellia sinensis*, an evergreen shrub native to Asia [5]. After water, it is the most widely consumed drink in the world [6]. There are many different types of tea; some teas, like Darjeeling and Chinese greens, have a cooling, slightly bitter, and astringent flavour, while others have vastly different profiles that include sweet, nutty, floral or grassy notes. Tea originated in Southwest China, where it was used as a medicinal drink. Alumina is one of the most widely used ceramics due to its high specific surface area, very good thermal stability and amphoteric properties. Due to these characteristics porous alumina is generally a very good candidate as a catalyst carrier as well as an adsorbent.

To evaluate the feasibility of the adsorbent, isotherm, kinetic and thermodynamic studies at 303, 313, 323 K, effect of pH, contact time, concentration with respect to temperature and point of zero charge studies were carried using batch adsorption studies. Further, characterization analyses were examined using SEM and TEM. Fig. 1 represents the graphical abstract of cleaning of water loaded with impurities

using Tea waste biomass -Al₂SiO₃ produced in the present study for the removal of nickel.

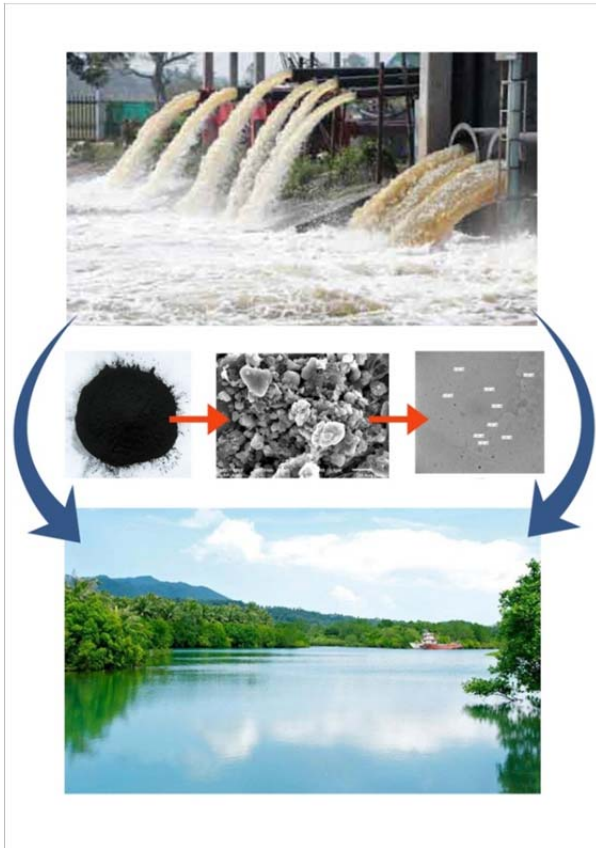


Fig. 1. Graphical Abstract

I. Experimental Procedure

All the chemicals used were analytical grade. The adsorbent was collected locally from Aligarh city, India. The adsorbent was washed several times with double distilled water (DDW) before use to remove any dirt, dust or colour and dried at 80°C. The solid obtained was then impregnated over 24h by activated alumina solution. It was then washed several times with DDW till the obtention of neutral pH and dried. The Tea waste biomass (TWB) -Al₂SiO₃ nanocomposite was obtained.

In batch experiments, 0.1g TWB-Al₂SiO₃ was added to a series of flasks containing 10 mL of Ni(II) solution of different concentrations at various temperatures and pH for different time intervals. The solution was centrifuged after predetermined time and concentration of metal ion was determined using Atomic adsorption spectroscopy.

The adsorption efficiency (%) and capacity of adsorbent were calculated using the following equation:

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

$$q_e = \frac{(C_o - C_e)}{M} \times V \tag{2}$$

Where, Co & Ce (mgL⁻¹) are the initial and final Ni(II) concentration respectively; V (L) is the volume of the solution and M (g) is the mass of adsorbent.

2. RESULTS AND DISCUSSION

A. Characterization

The morphology of the adsorbent surface was characterized using Scanning electron microscope (SEM). The morphology revealed irregular, porous and non homogeneous structure of the adsorbent. After adsorption image shows white patches of Ni(II) loaded on the adsorbent (Fig 2).

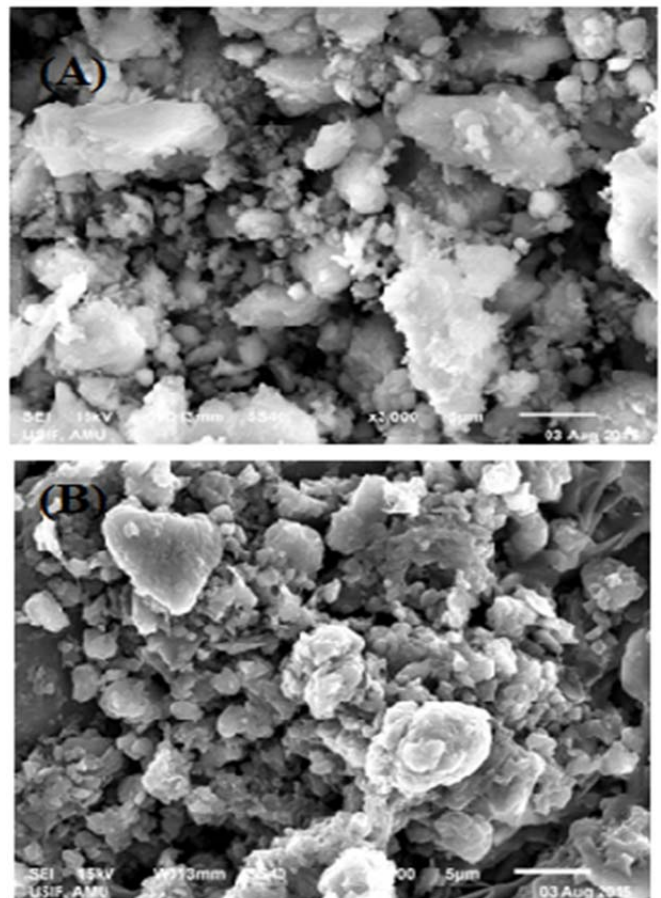


Fig. 2: SEM micrograph of (a) before and (b) after adsorption of Ni(II) (Magnification: 3000 X in both case)

TEM image revealed the size of the nanocomposite in the nanometer range.

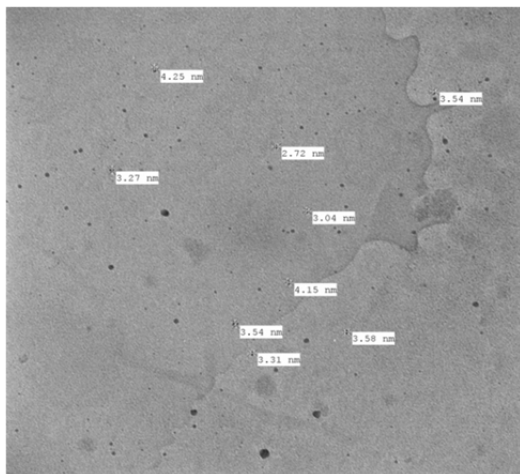


Fig. 3: TEM image of TWB- Al_2O_3 nanocomposite

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

The effect of initial concentration of Ni(II) was studied in the concentration range of 10-100 mgL^{-1} . To evaluate the effect of reaction time for the adsorption of Ni(II) on to TWB- Al_2O_3 nanocomposite, the exposure time was varied between 1 and 180 min, at 30 $^\circ\text{C}$, and an initial Ni^{2+} ion concentration of 50 mg/L . A usual phenomenon of increase in adsorption capacity with increase in initial Ni(II) concentration was observed which may be attributed to the increased concentration gradient between the bulk solution and adsorbent surface thereby lowering the resistance to mass transfer of Ni(II) from aqueous to solid phase [7]. The maximum adsorption capacity was found to be 0.95, 1.85, 4.76, 7.68, 9.37 mgg^{-1} at 10, 20, 50, 80 and 100 mgL^{-1} concentration of metal ion respectively. The contact time required to reach equilibrium was found to be dependent on initial Ni(II) concentration and the equilibrium time of 60 min was investigated as optimum time to carry out further experiments.

C. Effect of pH

The effect of pH on Ni(II) adsorption onto TWB- Al_2O_3 was investigated at pH 1 - 10, 30 $^\circ\text{C}$, and an initial Ni^{2+} ion concentration of 50 mg/L . It was observed that the metal uptake capacity increases with an increase in pH from 1 to 6. The Ni(II) ion exhibit maximum adsorption capacity at pH 6. Below pH 6, the dominant species of metal are Ni^{2+} and $\text{Ni}(\text{OH})^+$. Above pH6, precipitation of metal hydroxide $\text{Ni}(\text{OH})_2$ is likely to occur hence pH_f decreased due to excess H^+ ions remaining in the solution.



At low pH, there is large amount of H^+ ions which effectively competes with Ni^{2+} ions for adsorption sites through ion exchange mechanism, decreasing the metal uptake capacity. The change in metal uptake capacity with pH can be explained by considering the point of zero charge of TWB- Al_2O_3

nanocomposite (pH_{PZC}). The point of zero charge was found to be 4. At pH above the point of zero charge, the surface is negatively charged. The electrostatic forces of attraction allow the negatively charged functional groups present in adsorbent to capture the Ni^{2+} through surface complexation, forming chelate complexes. At pH below the point of zero charge, there is a net positive charge on the adsorbent which enhance the repulsion forces that exist between the positively charged metal ions and the adsorption sites, therefore decreasing the adsorption [8].

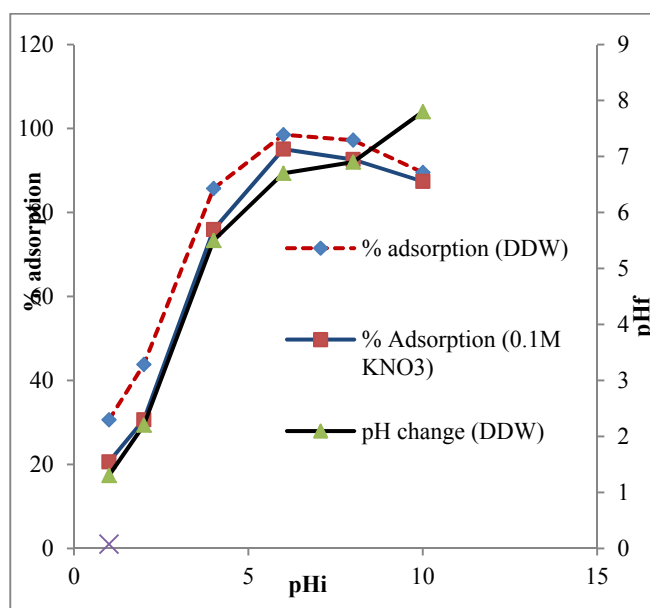


Fig. 4: Effect of pH and electrolyte on the adsorption of Cd(II) onto TWB- Al_2O_3 nanocomposite

3. ADSORPTION ISOTHERM

The Langmuir and Freundlich isotherm models were used to fit the experimental data for the adsorption of Ni(II) at 30, 40 and 50 $^\circ\text{C}$, to examine the relationship between the concentration of metal ion at equilibrium (C_e) and metal loading capacity (q_e). The linear forms of these isotherm models respectively are given as [9]:

$$\frac{1}{q_e} = \frac{1}{q_m} \times \frac{1}{b} \times \frac{1}{C_e} + \frac{1}{q_m} \quad (5)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

Where, C_e is the equilibrium concentration of Ni(II) (mgL^{-1}), q_e (mgg^{-1}) is the adsorption capacity at equilibrium, q_m (mgg^{-1}) and b (L mg^{-1}) are the Langmuir constants, K_f is the Freundlich isotherm constant and n represents capacity and intensity of adsorption. The values of b and q_m for Langmuir isotherm model were calculated from the slope and intercept of the linear plots of $1/q_e$ versus $1/C_e$ (fig. 5) at different temperatures The data fitted well in Langmuir isotherm model

with R² value 0.98 at all temperatures quantitatively describing the formation of monolayer on the surface of the adsorbent.

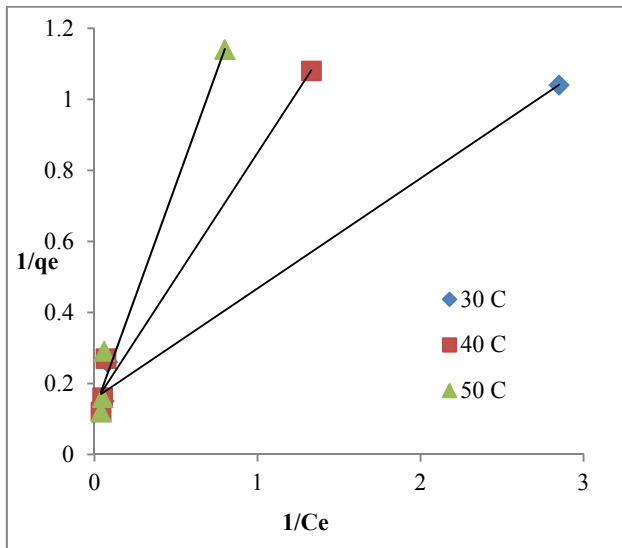


Fig. 5: Langmuir isotherm model

Table I: Adsorption Isotherm parameters for Cd(II)

Model Parameters			
Temperature (K)	303	313	323
Langmuir			
qm(mg/g)	10.291	9.770	7.787
b (L/mg)	0.630	0.417	0.230
R ²	0.982	0.983	0.981
Freundlich			
K _F (mg/g)	1.479	0.853	0.571
n	2.044	1.647	1.420
R ²	0.946	0.799	0.765

4. KINETIC STUDIES

To assess the rate and mechanism of adsorption, pseudo-first order and pseudo-second order models were used. The linear equations for pseudo-first-order and second order kinetic model can be expressed as [9]:

$$\log (q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303} \right) \times t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e} \right) \times t \quad (8)$$

Where q_e and q_t are the amounts of metal adsorbed (mgg⁻¹) at equilibrium and at time t, respectively and K₁ is the pseudo-first order adsorption rate constant (min⁻¹) and K₂ is pseudo-

second-order adsorption rate constant (gmg⁻¹min⁻¹). The values of pseudo first and second order constants are given in table 2 as obtained from the plot of t versus t/qt (fig. 6). The data fitted well in pseudo second order kinetic model with R² value 1.

Table II. Kinetic Parameters for the adsorption of Cd(II)

Kinetic models	parameters	Concentration (mg L ⁻¹)				
		10	20	50	80	100
Pseudo-first order	q _e (exp)	0.95	1.85	4.76	7.68	9.37
	q _e (cal)	0.27	0.32	1.12	1.00	1.48
	R ²	0.61	0.64	0.91	0.97	0.97
Pseudo-second order	q _e (exp)	0.95	1.85	4.76	7.68	9.37
	q _e (cal)	0.95	1.85	4.83	7.81	9.52
	K ₂	6.89	6.17	0.31	0.11	0.16
	R ²	0.99	0.99	0.99	0.99	1

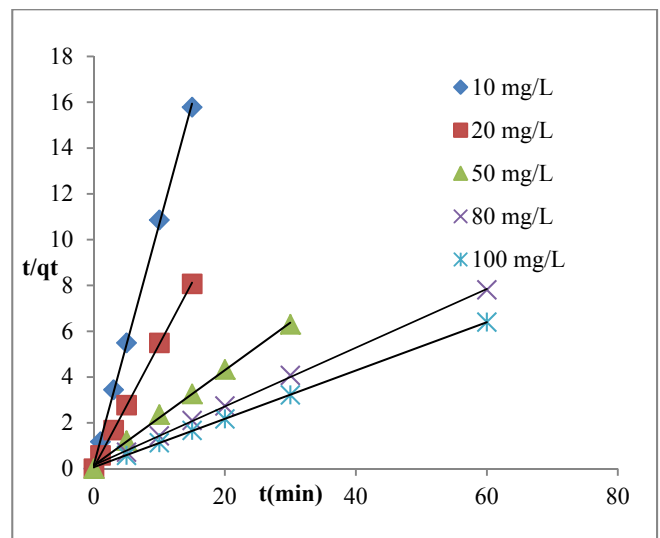


Fig. 6. Pseudo-second order kinetic model

5. THERMODYNAMIC STUDIES

The effect of temperature on the adsorption of Ni(II) was studied in the temperature ranging from 30-50°C. Langmuir adsorption capacity (mgg⁻¹) decreases with the increases in temperature (table 1). Decreased adsorption capacity at high temperature indicated exothermic nature of adsorption. Thermodynamic parameters such as standard free energy (ΔG⁰, kJmol⁻¹), enthalpy change (ΔH⁰, kJmol⁻¹), entropy change (ΔS⁰, Jmol⁻¹K⁻¹) were calculated using the following equations:

$$K_c = \frac{C_0 - C_e}{C_e} \quad (9)$$

$$\Delta G^0 = -RT \ln K_c \quad (10)$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (11)$$

Where, C_o and C_e are the initial and equilibrium concentration (mgL^{-1}), R is the universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), K_c is the distribution coefficient, T is the temperature of the solution in Kelvin. ΔH^0 and ΔS^0 can be calculated from a plot of $\log K_c$ versus $1/T$. Negative values of ΔG^0 (-2.99, -2.54, -1.91 KJ/mol) indicate the adsorption process was spontaneous, and the degree of spontaneity of the reaction decreased with increasing temperature [10]. Negative value of ΔH^0 (-19.91 KJ/mol) indicated the exothermic nature of adsorption as observed from the results obtained from Langmuir isotherm model and the negative value of ΔS^0 (-0.055 KJ/mol) indicated decreased randomness at solid-liquid interface.

6. CONCLUSION

The efficiency of *Asparagus racemosus* activated carbon was successfully determined in the present work. The adsorbent was characterized using SEM and TEM analysis. Maximum adsorption was attained at pH 6 in 60 min. The adsorption capacity decreased with increasing temperature. Langmuir isotherm with R^2 value 0.98 and pseudo-second order kinetic model was obtained as the most suitable models for describing Cd(II) removal. Therefore, AARC can be viable for designing a economical treatment plant for the removal of toxic Cd(II) from wastewaters.

7. ACKNOWLEDGEMENT

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