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Preparation, Characterization and Evaluation of the Adsorptive Potential of Activated Carbon Derived from Waste Tealeaves

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Abstract

Production of activated carbon from conventional sources poses substantial economic and fiscal challenges due to the considerably high cost of the precursor material. The following ongoing study aims to overcome the challenges by producing activated carbon from waste tea leaves using a combination of microwave assisted $ZnCl_2$ *activation and chemical modification. Initial characterization studies revealed a Methylene Blue Number of 467.2 mg/g and a* pH_{zpc} *of 6.45. Batch adsorption tests determined that equilibrium adsorption was highest when 0.25g of adsorbent was added to 100ml of synthetic copper solution and maximum net copper ion removal efficiency of 94.2%. Langmuir isotherm demonstrated highest correlation to the experimental data whilst the thermodynamic studies determined the value of Gibbs free energy* (ΔG^O) *and enthalpy* (ΔH^O) *to be negative and positively respectively; proving the adsorption as spontaneous and endothermic in nature*

Keywords: *Activated carbon, wastewater remediation, waste tea, microwave energy*

1. Introduction

The benefits of the rise of industrialization around the world have been overshadowed by several detrimental consequences that can be directly attributed to its unchecked and reckless growth. The natural resources have faced the direct brunt of these consequences as we find unimaginable levels of pollution, particularly in the hydrosphere. Water bodies around the world are being increasingly contaminated with industrial effluents including heavy metals such as lead and chromium alongside a host of other toxic compounds such as phenols and dyes. Despite the fact that several remediation techniques such as membrane perevaporation[1], breakdown using catalytic wet air oxidation[2], reverse osmosis[3] and ion-ion exchange exist, these technologies have proven to be far more expensive and uneconomical in many cases. In light of such circumstances, the need of the hour is the determination of a water treatment technique that is effective yet economical in nature.

Adsorption has often been considered to be a cost-efficient method and furthermore, its efficiency and versatility in the wastewater treatment have been the driving force behind its growing and extensive usage. The variable surface characteristics and the high degree of surface reactivity allows activated carbons to be highly effective in the remediation from wastewater. The popularity of the usage of activated carbon (AC) for wastewater treatment purposes is reinforced by the fact that about 275000 tons of it are consumed worldwide[3].

However, the production of commercially available activated carbon does entail several challenges; one of them being the high manufacturing costs[4]–[6]. The precursor material used for the synthesis of activated carbon entails the usage of coal and lignocellulosic material from biomass such as coconut shells[7]. These materials are expensive to procure and often need to be imported. As a result, there has been a growing interest wherein the feasibility of using alternative lignocellulosic biomass such as date seeds[8], giant reeds[9], bamboo shoots[10], cotton stalks[11], macadamia nutshells[12] and rice husks[13] for synthesis of activated carbon. Amongst these potentially viable sources of precursor material for the production of AC, waste tea has shown increasing promise because of its comparatively easier availability. This is reinforced by the fact that between 18 to 20 billion cups of tea are drunk worldwide in a day[14] and such a remarkable level of consumption does result in issues regarding the safe disposal of waste tea leaves. The problem is exacerbated by the generation of tea factory wastes during the manufacturing process. In India, the annual production of over 875,000 tons of tea resulted in the generation of close to 190,000 tons of tea factory wastes[15]. Despite the growing concerns regarding their safe disposal and the lack of sustainable waste management practices, it is quite evident that the net amount of waste tealeaves and tea factory waste can suffice to meet the worldwide demand for the activated carbon. The classification of the above wastes as carbonaceous adsorbents along with their favourable physiochemical characteristics such as large surface capacity and fast kinetics of adsorption make it a suitable low-cost precursor for the synthesis of activated carbon.

This research aims to produce high quality activated carbon from waste tealeaves using microwave assisted chemical activation followed by chemical modification. Zinc Chloride was chosen in for the chemical activation with mineral salts stage because it increases the carbon yield as it does not react with the carbon, hence restricting the tar formation and being a dehydrating agent it greatly enhances the decomposition of carbonaceous material during pyrolysis; thus the resultant AC has greater porosity and higher surface areas compared to other activating agents[12], [16]. Microwave treatment prior to the pyrolysis was chosen as it has been proven to considerably minimize the treatment time and energy requirements[17]. The conversion of the absorbed microwave energy into heat by dipole rotation and ionic conduction allows a uniform heating of the precursor material. Furthermore, the heating process itself is internal and volumetric, thereby allowing the reactions to proceed at an effective and heightened pace at low temperatures[3]. The resultant AC would then undergo characterization tests to determine its properties as well as an evaluation of its adsorptive properties. The adsorptive properties would be evaluated by conducting batch adsorption experiments where the changes in the adsorbent loading and pH on the removal of copper ions from synthetic wastewater would be tested.

2. Methodology

2.1 Pretreatment, pyrolysis and activation

Waste tea leaves required for the synthesis of the AC were sourced from the cafeteria in college. The precursor material was treated numerous times with boiling hot water until all the soluble polysaccharides and proteins and other contaminants like milk were removed after which it was dried in an oven at a temperature of 221°F for 12 hours. The tea leaves were then ground into a size range of 100-125µm using a domestic grinder. Zinc chloride was added to the ground tea leaves at an activating agent to precursor material ratio of 1:1 and 150ml of distilled water was added for every 20g of tea leaves. The impregnation ratio was chosen in order to maintain a balance between the micropores and the mesopores [7].This mixture was allowed to stand for 2 days before being activated in a domestic microwave for 5 minutes at a constant input power of 900W and frequency of 2450Mhz. The precursor material was then carbonized by placing the samples in a muffle furnace. The heating rate for the process was about 43°F/ min and the samples were kept at 662°F for 1 hour. Chemical modification of the activated carbon was done by treating the carbonized samples with 1M nitric acid. The chemically modified AC's were then dried at 221°F for four hours. [7], [18]

2.2 Characterization studies

The characterization of the activated carbon was done using three techniques primarily; Boehm Titration, pH and pH zero point charge and Methylene Blue Number. The quantification of the lactonic, phenolic and carboxylic acidic functional groups on the surface of the adsorbents and the methylene blue number were determined by using the procedure detailed by Gondogdu et al. In order to determine the pH zero point charge, the procedure adopted by Noh & Schwarz[19] was used wherein 0.1g of adsorbent was added to a series of 0.1M NaCl solutions whose pH ranged from 2-10 and the mixtures were agitated for 24 hour. The adsorbent and the solutions were separated after agitation and the equilibrium pH values of the filtrates were then determined [20].

2.3 Batch adsorption tests

The adsorptive potential of the activated carbon was evaluated by conducting batch adsorption tests were performed where specified amounts of the adsorbents are added to synthetic wastewater having a copper ion concentration of 500ppm. The batch adsorption tests evaluated the effects of contact time (30-3600s), adsorbent loading (0.25g – 1.00g) and pH (4.5 – 7.5)on the uptake of copper ions. The final concentration of the solutions post adsorption was measured using a Flame Atomic Absorption Spectrophotometer. The amount of copper adsorbed onto the activated carbon was calculated in mg g^{-1} from the relationship:

$$Qt = \frac{(Co-Ct)}{w}V \qquad [21]$$

The sorption efficiency was calculated by:

$$Sorption\ Efficiency\ (\%) = \frac{(Co-Ct)}{Ct} \times 100 \qquad [21]$$

Where Q_t is the amount of copper adsorbed at any time t(s), C_o and C_t are the initial and instantaneous copper concentration (mg/L), w and V are the weights of the adsorbent in grams and volume of the solution in liters respectively.

2.4 Equilibrium modeling

The sorption systems were designed by using sorption isotherm models in order to derive a relationship between the amount of Cu(II) adsorbed on the activated carbon and the concentration of Cu (II) in the solution at equilibrium. The adsorption of Cu (II) on the waste tea based AC were studied by Tempkin, Langmuir and Freundlich isotherm models. Freundlich isotherm, commonly used for the representation of non-ideal sorption on heterogeneous surfaces is mathematically denoted as:

$$lnq_e = lnK_f + \frac{1}{n}lnC_e \qquad [22]$$

Where q_e (mg/g) refers to the amount of adsorbate that gets adsorbed by 1g of the absorbent at equilibrium and Ce is the amount of adsorbate that is left unadsorbed in the solution after equilibrium is reached whilst n is an empirical factor denoting the intensity of adsorption. The Langmuir model on the other hand, has been developed for the representation of monolayer adsorption on a homogenous surface and can be denoted as shown below:

$$\frac{C_e}{q_e} = \frac{C_e}{S_m} + \frac{1}{K_l S_m} \qquad [23]$$

S_m and K_L are the Langmuir adsorption constants and correspond to the bonding strength (L mg^{-1}) and maximum capacity (L g^{-1}). On the other hand, the Tempkin adsorption model considers the species-sorbate interactions and makes the assumption that the sorption can be characterized by a uniform distribution of binding energies. Mathematically, the Tempkin isotherm is expressed as follows

$$q_e = B ln(k_T C_e) \qquad [24]$$

Here, the adsorption enthalpy is represented by B, q_e is the experimental adsorption capacity, k_T the equilibrium binding constant and C_e the concentration of the adsorbate at equilibrium.

2.7 Thermodynamic Evaluations

Thermodynamic data and parameters for the adsorption of Cu(II) were determined using the set of equations as shown below

$$\Delta G^0 = -RT \ln K_d \qquad [21],$$

$$\Delta H^o = -R\left\{\frac{T_2 T_1}{(T_2 - T_1)}\right\} ln \frac{K_{l2}}{K_{l1}} \qquad [25]$$

$$\Delta S^O = -\frac{(\Delta G^O - \Delta H^O)}{T}$$

here K, K_{L1}, K_{L2} are the equilibrium constants at temperatures T, T_1 and T_2 respectively that are derived from the Tempkin and Langmuir adsorption models developed earlier

3. Results and Discussions

3.1 Characterization Results

The procedure adopted for the synthesis of activated carbon resulted in an AC yield of 84%. It has to be noted that due to the very fine nature of the precursor material and the AC itself, small portions of it were lost in the process. The history of carbon treatment specifies the amount of oxygen functional groups. The results of the Boehm Titration have been summarized in Table 1

Table 1: Results of the Boehm Titration

Surface Acidic Functional Groups (mmol g^{-1})	
Total Acidic Groups	2.49
Carboxylic Groups	1.56
Phenolic Groups	0.4815
Lactonic Groups	0.512

The pH zero point charge is the pH value at the point where the net surface charge is zero and it was found out that the pH_{zpc} of the derived activated carbon was found out to be 6.38 and the pH value was 6.72. The slightly acidic nature of the adsorbent and the value of pH_{zpc} being < 7 asserts the dominance of acidic surface groups over the basic groups. This observation is further verified by the results of the Boehm Titration.[26] The Methylene Blue was found out to be 467.2 mg.g^{-1} hence indicating to the presence of a highly developed mesoporic structure. A separate test revealed that 0.5g of the adsorbent was able to completely decolorize to 50ml of methylene blue solution whose concentration was maintained at 50ppm.

3.2 Batch adsorption tests

The batch adsorption tests determined that the adsorption of Cu(II) ions onto the activated carbon was rapid at the initial stages and reached an equilibrium after 60 minutes. Increasing the adsorbent dosage of 0.25g to 1.00 g did increase the sorption efficiency from 60 to 94.2% but reduced the uptake of copper at equilibrium from 121.79 mg g^{-1} to 63.408 mg g^{-1} as shown in the table. This could be ascribed by the fact that the number of adsorption sites were far greater than the number of copper ions present in the solution. [27]. Whilst the amount of sorption revealed an increasing tendency as the contact time is increased, it is quite evident that the uptake of copper ions is quite rapid within the first 60 seconds of contact after which the adsorption of the copper ions shows a more gradual increase until equilibrium is reached after 60 minutes. Such behavior has been observed in other literature pertaining to the adsorption of metal ions onto activated carbon. [27], [28]

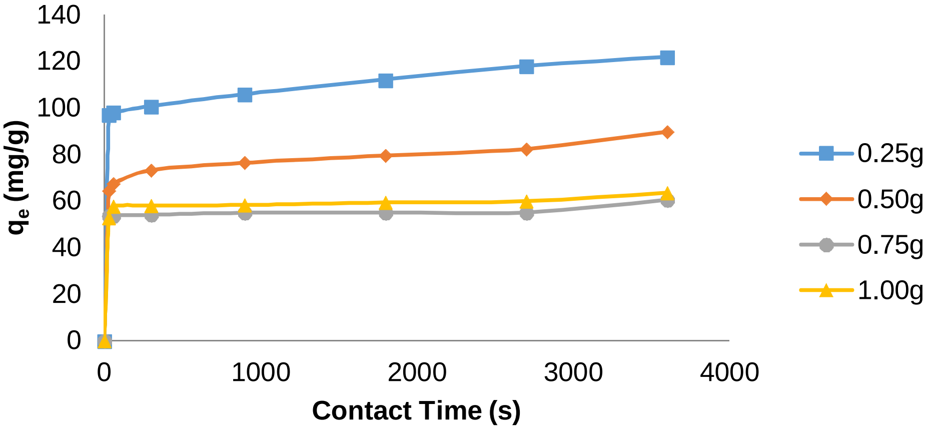

Figure 1: Effect of adsorbent loading on the adsorption of copper ions from aqueous solution

Elevating the pH of the stock copper sulphate solution from 4.5 to 7.5 was marked by a decrease in the amount of Cu(II) ions adsorbed from 155.353 mg/g to 96.96 mg/g. The decrease could be as a result of the precipitation of copper when the pH is raised beyond 6.5. Furthermore at elevated pH, $Cu[OH]^+$and $Cu(OH)_2$ are found predominantly in the solution, thereby resulting in the retardation of copper ion adsorption due the comparatively weaker interaction between the complex forms of copper and the surface functional groups[29]

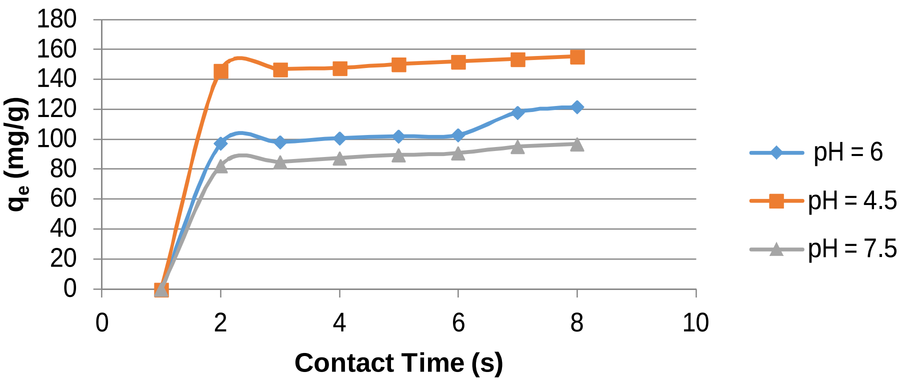

Figure 2: Effect of pH on the adsorption of copper ions from aqueous solution

3.3 Adsorption Isotherms

Upon comparing the experimental data as shown in Table against three isotherm models and using the criteria of high R^2, the adsorption of copper ions onto waste tea derived activated carbon could be best fit the Langmuir Adsorption Isotherm

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Table 3: Equilibrium model constants at different adsorbent loadings and pH

Isotherm		**Adsorbent Loading**				**pH**		
		0.25g	**0.50g**	**0.75g**	**1.00g**	**4.5**	**6**	**7.5**
Langmuir	R^2	0.998	0.9893	0.9992	0.9949	0.9998	0.998	0.9976
	S_M (mg/g)	59.5238	57.1428	48.7805	50	113.6363	59.5238	40.1606
	K_L (l/mg)	0.0099	0.03944	0.10616	0.1299	0.03274	0.0099	0.00659
Freundlich	R^2	0.9978	0.9394	0.9925	0.9068	0.999	0.9978	0.998
	1/n	0.8215	0.2679	0.1599	0.1186	0.3275	0.8215	1.2252
	Kf (L/g)	52.9633	11.3328	7.76246	7.2044	17.5035	52.96334	140.09
Tempkin	R^2	0.9994	0.9615	0.9948	0.9264	0.9994	0.9994	0.9996
	B (J/mol)	89.831	20.557	9.1302	6.931	49.301	89.831	109.97
	K_T (L/g)	0.00131	0.00022	0.00003	0.000004	0.000382	0.001314	0.001605

3.2 Thermodynamics

The thermodynamic parameters pertaining to the adsorption of copper ions on the prepared activated carbon at varying temperatures were calculated and are presented in Table

Table 4: Results of the thermodynamic evaluations

Temperature (K)	ΔG (J/mol)	ΔS (kJ/mol-K)	ΔH (J/mol)
298.15	-47.1695	0.9007	266.225
308.15	-973.847		

318.15	-1390.28		
328.15	-1968.54		

The negative values of the Gibbs free energy at each temperature pointed towards the spontaneous and feasible nature of the adsorption process. The affinity of copper ions towards the activated carbon was asserted by the positive value of ΔS^O. Furthermore, the positive value of ΔH suggested the adsorption to be endothermic [30]. This is reinforced by the fact that the increase in the temperature from 298K to 328K was marked by an increase in the equilibrium uptake of copper ions from 121.69 mg/g to 167.448 mg/g. A similar pattern pertaining to the thermodynamics of adsorption was reported by Malakahmad, Tan, and Yavari. [31]

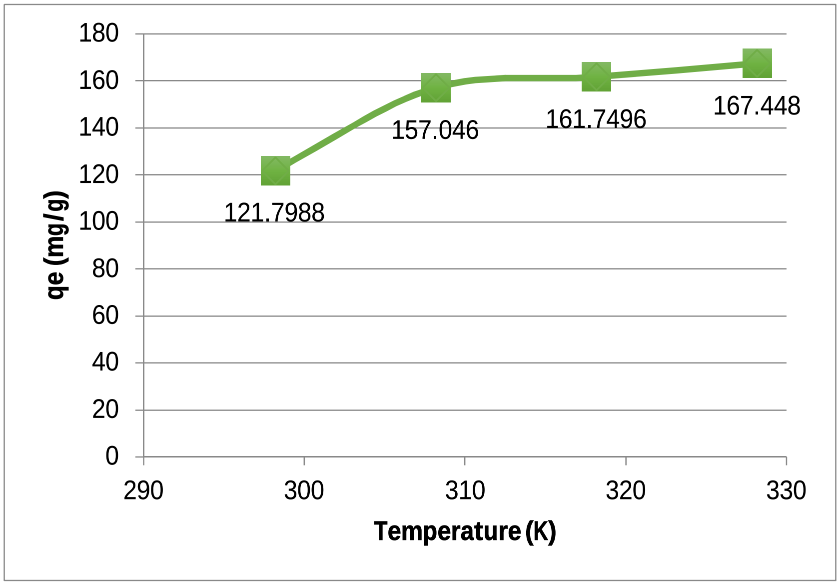

Figure 3: Effect of variation in temperature on equilibrium uptake of copper ions

5. Conclusion

The study could conclude that high quality granular activated carbon can be produced from waste tealeaves by combining microwave activation along with the use of appropriate chemical activating agents. Appropriate chemical modification of the adsorbent post-pyrolysis improves the surface characteristics of the adsorbent. The results of the characterization studies; notably the methylene blue number indicated that the derived activated carbon was quite efficacious in the removal of large molecules hinting to a more developed mesopore structure. The derived activated carbon demonstrated a copper ion removal adsorption capacity of 121.79 $mg.g^{-1}$ and a maximum sorption capacity of 95.1%. This result predominantly illustrates that an agricultural and household waste like waste tea leaves that are of no use and possesses the potential to be the root of damage to the environment can be turned into a beneficial material. It is quite evident that there exists a scope for expanding this research by means of improved characterization studies using BET (Branauer-Emmet-Teller) analysis and incorporation of Response Surface Methodology in order to determine the ideal production parameters and testing the potential of the activated carbon derived in the above-mentioned procedure for the removal of various other effluents

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