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REMOVAL OF NICKEL, MANGANESE AND ZINC FROM INDUSTRIAL EFFLUENT USING EUCALYPTUS CAMALDULENSIS AND CAMELLIA SINENSIS ADSORBENT

Jenisha M A[1], Arun Prasad J[2],FathimaDarrasGracy A[3]

[1]PG Scholar, Department of Civil Engineering, Erode Sengunthar Engineering College, Erode- 638057.
[2,3]Assistant Professor, Department of Civil Engineering, Erode Sengunthar Engineering College, Erode - 638057

ABSTRACT

Heavy metals are major toxic pollutants present in dyeing, paper, and paint industrial effluent and would cause severe health effect on humans. They are released into the environment from industries. Nickel, Manganese and zinc are the most toxic metals of widespread use in textile industry. Heaving metals contribute to a variety of adverse health effects due to their high toxicity, having the possibility to get mix with food chain through air, water and soil pollution it leads to bio accumulation. Conventional treatment method of metal removal is often limited by their cost and ineffectiveness. Adsorption, the use of activated biomass as adsorbents offers an attractive potential alternate for the removal of heavy metals from industrial wastewater. Eucalyptus camaldulensis and Camellia sinensis are naturally occurring and abundant biomass can offer an economical solution for heavy metals removal.

In my project I have used natural adsorbent for the removal of heavy metals Nickel, Manganese, Zinc. The treatment process would provide the better solution in conservation of health and environment.

Keywords**:** *Adsorption, Bio accumulation, Camellia sinensis, Eucalyptus camaldulensis, Heavy metals removal.*

I. INTRODUCTION

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a solid phase. In principle adsorption can occur at any solid fluid interface. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic,covalentor metallic) of the constituent atomsof the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbents. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption(characteristic of weak vanderWaals forces) or chemisorption(characteristic of covalent bonding). It may also occur due to electrostatic attraction.

II. EXPERIMENTAL INVESTIGATION

Adsorption occurs when an adsorbate adheres to the surface of an adsorbent. Due to reversibility and desorption capabilities, adsorption is regarded the most effective and economically viable option for the removal of metals from aqueous solution. Although efficient, adsorption is not effective with very concentrated solution as the adsorbent easily gets saturated with the adsorbent. It is only feasible for very dilute solutions, is labour intensive because it requires frequent regeneration and it is not selective in terms of metal attenuation. Adsorption is therefore not applied in a large scale of metal remediation.

Water is a universal solvent and is known as “tonic of life”. Water is one of the most Important elements on earth. Every living being needs water for its survival. Water is a transparent, tasteless, odorless, and nearly colorless chemical substance, which is the main constituent of Earth's streams, lakes, and oceans, and the fluids of most living organisms. It is vital for all known forms of life, even though it provides no calories or organic nutrients. Its chemical formula is H_2O, meaning that each of its molecules contains one oxygen and two hydrogen atoms, connected by covalent bonds.

Water is the name of the liquid state of H_2O at standard ambient temperature and pressure. It forms precipitation in the form of rain and aerosols in the form of fog. Clouds are formed from suspended droplets of water and ice, its solid state. When finely divided, crystalline ice may precipitate in the form of snow. The gaseous state of water is steam or water vapor. Water moves continually through the water cycle of evaporation, transpiration (evapotranspiration), condensation, precipitation, and runoff, usually reaching the sea. Water plays an important role in the world economy. Approximately 70% of the freshwater used by humans goes to agriculture.

2.1 Material Collection

2.1 Camellia Sinensis

2.2 Activated Carbon

The waste water was collected from a tannery industry. At the collection point, containers were rinsed with samples thrice and then filled with sample, corked tightly and taken to the laboratory for treatment and analysis. The eucalyptus adsorbent derived from various waste sources of tea estate was cleanly shaved to remove all the fibers on its surface. They were cut into small pieces, washed with distilled water to remove the dirt. The method of analysis was consistent with the standard methods (APHA, 1985). The pH of the sample was measured on the site and other parameters were measured in the laboratory.

2.2. Reagents

All the chemicals used in this work were of analyticalreagentgrade purchased from nearby area of college. All the glassware used was washed and rinsed several times.Nickelzinc and manganese solutions and standards were prepared by using analytical gradenickel chloride($NiCl_2.6H_2O$), Zinc chloride ($Zncl_2$) and Manganese chloride(Mncl2) withdistilled water. The solutions of Ni, Zn and Mn were prepared from stock solutions containing 1000 mg/L of Ni, Zn and Mn, respectively.

2.3. Preparation of Adsorbent Material

Camellia materials collected nearby area of kothagiri, ooty district, Tamil naduIt is cleaned and washed thoroughly and sun dried for 7 days. The dried plantain peels were then crushed into smaller particles in a mortar and sieved with 150 µm sieve until a reasonable quantity of that particle size is obtained, followed by repeated washing to eliminate dust and other impurities. It was then dried in an oven at 25 °C for about 48 h after which it was stored in sterilized closed glass bottles prior to use as anadsorbent. The powdered plantain peels were then modified by immersing in 5% solution of NaOH and autoclaved at 121 °C for 15 minat 10 psi. After keeping at 25 °C for 48 h, it was filtered and washed many times with distilled water until clear water withneutral pHwas obtained. Then, the modified plantain peel (MPP) was dried at 25 °C for 48 h. The MPP was applied for all the adsorption experiments.

The wood material washed repeatedly to remove dust and soluble impurities. The barks were then dried in sunlight and ground to a fine powder with 250 µm mesh. For modification process, the bark powder was treated with 37 % formaldehyde and 0.1 M NaOH at 50 °C for 2 h. The barks were filtered out, washed with distilled water until the washings were approximately at pH 4, and oven dried. The modified bark (MBB) was kept in an airtight container for further use.

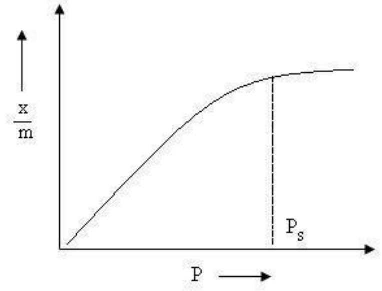
III. ADSORPTION ISOTHERMS

Adsorption isotherm is a graph or a relation between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at a constant temperature.

Different adsorption isotherm was studied by different scientists.

3.1 Freundlich Adsorption Isotherms

Freundlich proposed an empirical relationship between amount of gas adsorbed by unit mass of adsorbent and pressure at a particular temperature. Following equation was proposed for Freundlich adsorption isotherm- $\mathbf{x/m = k.\ p^{1/n}\ (n > 1)}$

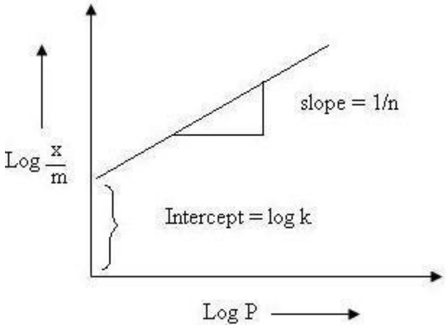


Adsorption isotherm

x is the mass of the gas adsorbed m is the mass of the adsorbent p is the pressure *k* and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. Taking log of the above equation, the following equation will be observed

$$\log x/m = \log k + 1/n \log p$$

x/m is plotted on y axis and log p is on x axis. If straight line is observed than only Freundlich isotherm is verified.



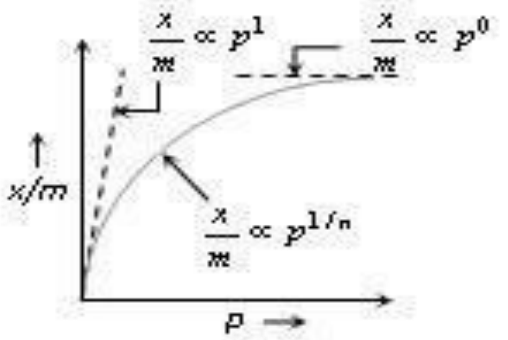
Slope gives 1/n and intercept gives log k. The value of 1/n varies from 0 to 1.

If 1/n is 0, adsorption is independent of pressure.

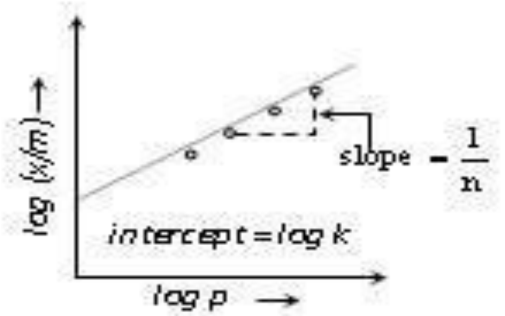
If 1/n is 1, adsorption changes with pressure.

3.2 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is the relation between pressure and extent of adsorption in chemical adsorption.



Freundlich adsorption isotherm: plot of x/m against



Plot of log x/m against log p for the adsorption of a gas on a solid

It explains the chemical Adsorption on the basis of kinetic theory of gases and also overcomes the drawbacks of Freundlich adsorption isotherm as

1. It gives reason why the extent of adsorption gets saturated at high pressure range
2. How and why the extent of adsorption depends on the surface area of adsorbent.

3.3 Metal Ions Adsorption Experiments

In order to study and evaluate the significance of variables on the percentage removal of Ni $^{2+}$, Zn and Mn, the adsorption experiments were conducted batch wise. A weighed amount of adsorbents and 50 mL of aqueous solution containing the metal ion was shaken on an orbital shaker at room temperature. The effect of the initial pH on heavy metal ion removal was studied by performing equilibrium adsorption tests at different pH values. The adsorption isotherms of Ni^{2+}, Mn^{2+} and Zn^{2+} ions on the adsorbent were studied at concentration 10 – 100 mg L^{-1}. The adsorption kinetic studies were carried out under optimized conditions from 2 to 180 min. The mixture was filtered and the concentration of the remaining metal ion in the filtrate was determined by the atomic absorption spectrophotometer.

Amount of metal ion uptake by 1 g of the adsorbent was calculated from the following mass balance equation:

$$qe = (Co-Ce)\ V/M$$

whereqe (mg g^{-1}) is the amount of metal ion uptake,

Ce (mg L^{-1}) the metal ion concentration after adsorption,

Co (mg L^{-1}) the initial metal ion concentration,

M the amount of adsorbent (g) and

V the volume of solution (L).

Percent removal was also evaluated using the formula:

Removal percentage (%) = Co-Ce/Co*100

The equilibrium amounts q_e (mg/g) adsorbed per unit mass of adsorbent were evaluated using Equation qe= (Co−Ce) V/W

whereq_e (mg/g) is the equilibrium amount of the metal ions V (L) is the volume of the W (g) is the mass of MPP used.

The kinetic tests were identical to those of equilibrium. The aqueous samples were taken at preset time intervals and the metal ions concentrations were measured. Theamount adsorbedat time t,*qt* (mg/g) was calculated using Equation

qt= (Co−Ct) V/W

where C_o and C_t (mg/L) are the liquid-phase concentration at the initial and any time t, respectively.

3.4 Kinetic Models

Inherent within this model, the following assumptions are valid specifically for the simplest case: the adsorption of a single adsorbate onto a series of equivalent sites on the surface of the solid.

The surface containing the adsorbing sites is a perfectly flat plane with no more corrugations (assume the surface is homogeneous). However, chemically heterogeneous surfaces can be considered to be homogeneousif the adsorbate is attracted to only one or more type of functional groups on the surface.

The kinetic data were fitted using the pseudo-first-order and pseudo-second-order models. The rate constant of adsorption is determined from the pseudo-first-order equation given as, log (qe−qt) =logqe−k12.303t

whereq_e and q_t are the amount of metal ions adsorbed (mg/g) at equilibrium and at time t (h), respectively while k_1 is the adsorption rate constant (h^{-1}).

The pseudo-second-order equation based on equilibrium adsorption is expressed as tqt=1k2qe2+1qet

where k_2 (g/mgh) is the rate constant of second-order adsorption.

As the pseudo-first-order and pseudo-second-order kinetic models could not identify the sorption mechanism, the kinetic results were further analyzed for the diffusion mechanism by applying the intraparticle diffusion model.

The intraparticle diffusion equation is expressed as, qt=kipt0.5+C

where k_{ip} is rate constant of the intra-particle diffusion equation and C gives information about the boundary layer thickness: larger value of C is associated with the boundary layer diffusion effect. If the adsorption process follows the intraparticle diffusion model, then q_t versus $t^{0.5}$ will be linear; if the plot passes through the origin, then intraparticle diffusion is the sole rate limiting step. Otherwise, some other mechanism along with intraparticle diffusion is also involved.

IV. RESULTS AND DISCUSSION

This current study compares the studies on the removal of nickel, manganese and zinc by adsorption on activated Eucalyptus and Camellia leaves. These adsorbents are low cost and non-conventional materials which could be used in water and waste water treatment by economical waste water treatment, plant for effluent discharged from many industries.

The experimental parameters which affect extent of adsorption of heavy metals are reported to be contact time, adsorbent dosage and pH of solution. The effect of these parameters on extent removal of Ni, Mn, Zn ions by adsorption on activated Camellia leaves has studied. The metal removal studies are shown in following tables which indicated that their removal was strongly affected by the different operating conditions.

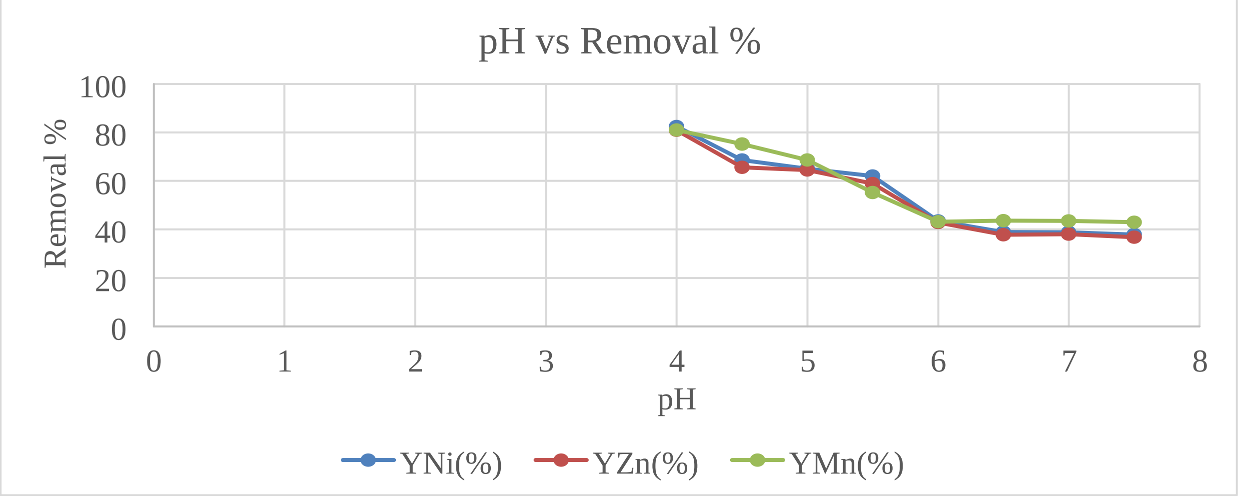
4.1 Removal of Ni, Mn, Zn by Activated Camellia Leaves

The percentage of removal of Ni, Mn, and Zn from aqueous solution by using activated Eucalyptus and Camellia leaves will be determined by plotting the standard graph. The concentration in raw and treated effluent was determined by SL-21 UV/VIS Spectrophotometer. For this purpose, potassium dichromate solutions of different concentration were prepared and their absorbance recorded by spectrophotometer.

Table No 4.1: Effect of pH

pH	Ni (%)	Zn (%)	Mn (%)
4	82.5	80.9	81
4.5	68.6	65.6	75.2
5	65	64.5	68.6
5.5	62	58.9	55.2
6	43.5	42.8	43.2
6.5	38.9	37.8	43.6
7	38.8	38	43.5
7.5	37.9	36.8	43

The effect of pH on the adsorption of $Ni^{2+}$and Cu^{2+} ions were carried out over the pH range of 2 to 10, while keeping all other parameters constant. Adsorption was found increased with the increasing of pH. This phenomenon could be explained by increasing total net negative charges of surface adsorbent which intensified electrostatic forces in the adsorption process. Moreover, with increasing pH, total number of negative groups available for the binding of metal ions increased and therefore competition between proton and metal ions became less pronounced.



4.1: Effect of pH

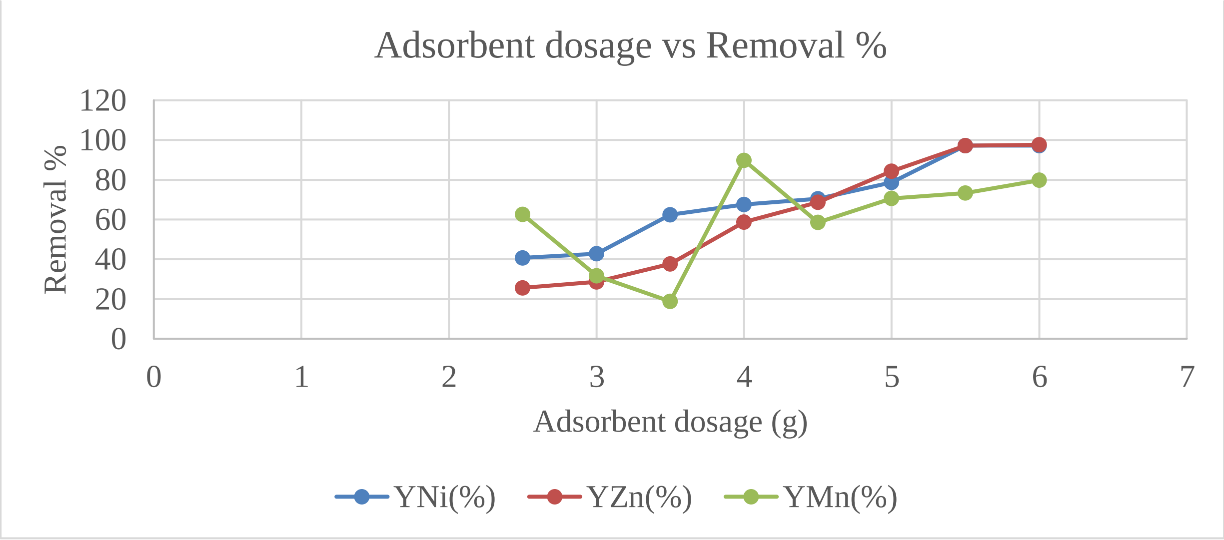
Result showed that the MBB possessed optimum sorption capacity for both Ni^{2+} and Cu^{2+} ions at pH 5. At lower pH than 8, the dominant forms of nickel were Ni^{2+}; while at pH more than 8, $Ni(OH)_2$ were present as precipitate. Whereas Cu $(OH)_2$ will be the dominant species at pH more than pH 6.

4.2 Effect of Adsorbent Dosage

Adsorbent dosage seemed to have great effect on adsorption process. The result of the effect of MBA dosage showed that removal efficiency increased as the adsorbent dosage increased. For 10 mg L^{-1}, adsorption percentage increased when the adsorbent dosage increased from 0.1 to 3.0 g at pH 5. The critical value of dosage of MBB was 1.0 g for both Ni^{2+} and Cu^{2+} ions. Increasing the amount of adsorbent added into a fixed concentration ions solution will increase the availability of active sites of the adsorbent. Therefore, adsorption percentage and efficiency will also increase.

Table 4.2: Tabulation for Adsorbent Dosage

Adsorbent dosage (g)	Ni (%)	Zn (%)	Mn (%)
2.5	40.7	25.6	62.5
3	42.7	28.6	31.6
3.5	62.4	37.6	18.8
4	67.5	58.7	89.8
4.5	70.5	68.6	58.6
5	78.6	84.2	70.6
5.5	97.2	97.2	73.4
6	97.2	97.6	79.8



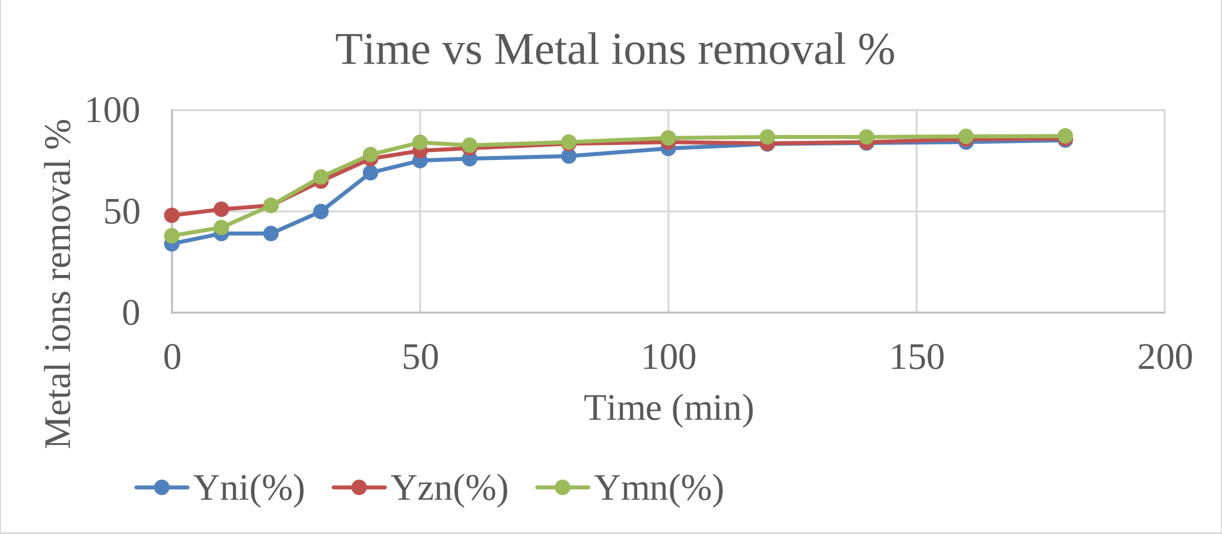
4.2 Graphs for Adsorbent Dosage

4.3 Effect of Reaction Time

Table 4.3: Tabulation for various time intervals

Time	Metal ion removal %		
	Ni	**Zn**	**Mn**
0	34	48	38
10	39	51	42
20	39	53	53
30	50	65	67
40	69	76	78
50	75	80	84
60	76	81.2	82.6
80	77.2	83.5	84.2
100	81	84.2	86.2
120	83.2	83.6	86.8
140	83.8	84.2	86.8
160	84.2	85.6	87
180	85.1	86	87.2

Adsorption Kinetics studies were carried out under the optimized conditions from 0 to 180 min. shows that kinetic of adsorption initially increased rapidly and reaches equilibrium within 60 minutes. There are three common step involved in adsorption process. The first step is mass transfer across the external boundary layer film of liquid surrounding the outside of the particle. Secondly is the adsorption process at individual site on the surface (internal or external) and the energy depends on the binding process (physical or chemical adsorption) this step is often assumed to be extremely rapid. Finally, diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid filled. Pores or by a solid surface diffusion mechanism. One or any combination of this adsorption process could be the rate-controlling mechanism.



4.3 Graph for various time intervals

The kinetic data obtained were fitted to linear form of pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic model known as the Lagergen equation is expressed as:

$$\text{Log}\ (qe\text{-}qt) = \log qe - k1t/2.303$$

Where, qt and qe are the amounts of ion adsorbed at time t and at equilibrium (mg g^{-1}), respectively, and k1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The slope and intercept of plots of log (qe −qt) versus t were used to determine the first-order rate constant k1 and equilibrium adsorption capacity qe. Pseudo-firstorder model is used to describe the reversibility of the equilibrium between liquid and solid phases. The pseudosecond-order kinetic model is given as:

$$t/qt = 1k_2qe^2 + 1/qe\ t$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g $mg^{-1}min^{-1}$). The plot of t/qt versus t gives a linear relationship, and k_2 and qe can be calculated from the slope and intercept of the line.

Table 3.4 Tabulation for Langmuir and Freundlich Isotherm

Isotherms		Ni	Zn	Mn
Langmuir	q_m	7.2098	5.8038	6.28
	K_L	0.1387	0.0271	0.086
	R^2	0.8759	0.9364	0.832
Freundlich	1/n	0.5666	0.7264	0.6526
	K_F	0.6162	0.2177	0.3565
	R^2	0.9993	0.9993	0.9993

V. SUMMARY AND CONCLUSION

The study on heavy metal removal by adsorption using Camellia leaf was carried out. Water is essential substance of all living organisms including plants, animals and human beings. Metal pollution of water has been receiving considerable attention due to increasing industrial pollution causing health hazards to living beings.

Result shows the kinetic rate constants, value of experimental qe and theoretical calculated qe for MBB. From the result, it can be concluded that pseudo-second-order equation provides the best correlation coefficient (R2) and agreement between the calculated qe and the experimental qevalues, suggesting that chemisorption is the ratedetermining based on isotherms.

The present study show that the activated carbon prepared from chemically treated Camellia leaves is an effective adsorbent for removal of nickel, manganese, zinc ions from aqueous solutions. The adsorption process is a function of the adsorbent and adsorbate concentrations, pH and time of agitation.

The adsorption capacity for activated Camellia leaves is 87.6% at their effective dose of adsorbents is 6g and in the 8pH. The effective pH for both adsorbents will be 8 respectively for removal Nickel, Manganese, Zinc. This result would be useful for the waste water treatment plants for removal of heavy metals.

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