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A Comparative Study of Chromium and Cadmium Removal from Their Common Aqueous Solution by Batch Operation Using Tea Factory Waste as Adsorbent

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ABSTRACT
The process of adsorption is a powerful tool for the treatment of industrial wastewater. In the recent years many studies have been conducted to evaluate the effectiveness of various locally available economical adsorbents for the removal of various heavy metals from the waste water. In the present study tea factory waste is used as adsorbent and its capacity to remove toxic heavy metals chromium and cadmium from their combined solution is investigated. Batch adsorption study is conducted to find the adsorption capacity of the adsorbent and the effect of the three important process parameters, i.e. agitation rate, adsorbent dose and initial metal ion concentration is evaluated. The maximum adsorption capacity of 24.88 mg/g and 23.92 mg/g is observed in case of cadmium and chromium respectively. It is also found that the removal efficiency of cadmium is higher than that of chromium in all cases. The experimental results are also found to be well fitted in the Langmuir and Freundlich Isotherm model.

Keywords: Adsorption, Tea Factory Waste, batch study, chromium, cadmium, isotherm, kinetic model.

I. Introduction

The presence of heavy metals in the natural water sources is a major concern of today, because such metals can cause serious health hazards to the human beings. The heavy metals are generally generated from the industries like metal processing, textile, battery manufacturing etc. and such heavy metals include lead, chromium, cadmium, zinc, arsenic, copper, mercury etc. In most of the cases the industrial wastewater disposed to the natural water bodies are the major sources of heavy metals in water. A number of methods are available for the treatment of industrial waste water containing such toxic metal contamination. Among them some important methods are reverse osmosis, ultra filtration, nano filtration, ion exchange, adsorption etc.

The phenomenon of higher concentration of any molecule species at the surface than in the bulk of a solid is known as adsorption. Adsorption is useful and economical mode of wastewater treatment. Many studies were conducted, which reported various low cost adsorbents for the effective removal of various toxic metals and dyes [1] from their aqueous solution phase. According to the recent studies the agricultural by products are found to very good adsorbent in many cases [2]. Agricultural by products like saw dust, soya cake, tea factory waste, coconut husk, sugar industry waste, rubber wood etc have been effectively utilized as low cost adsorbents. The efficiency of such adsorbents is modified by different physical and chemical techniques [3-6]. The use of agricultural waste as adsorbent for the removal of heavy metals also helps in solving the disposal problem and more over the resources utilized during their production are not wasted. The degree and rate of adsorption of metal ions into the adsorbent surface depends upon the physical and chemical properties of the adsorbent materials. The removal is generally caused by the complex formation between the metal ion and the functional groups present in the adsorbent.

A few numbers of literatures are available regarding the study of adsorption of heavy metals by tea factory waste as adsorbent. According to the study of Malkoc and Nuhoglu [7] tea factory waste can be utilized as an useful adsorbent for the removal of Chromium from wastewater. Datta et al [8] in their study showed the effect of various process parameters on the adsorption of Chromium by tea factory waste in the column operation. Removal of cadmium by various agricultural products as adsorbent is studied by Tushar Kanti Sen [9].

In most of the cases it is observed that a numbers of metals are disposed together in the natural water bodies and thus it is essential for any treatment technology to be sufficiently effective to remove such toxic materials from their combined solution. In the present study an effort is made to evaluate the effectiveness and the adsorption capacity of tea factory waste to remove Cr(VI) and Cd(II) from their mixed aqueous solution.

The tea factory waste has a good potential of acting as an effective adsorbent [10-12] because the physic chemical interaction of ion exchange and complex formation between metal ions and the functional groups present in the cell wall of tea factory waste is quite effective [13].

II. Materials & Experimental Method

2.1 Adsorbate

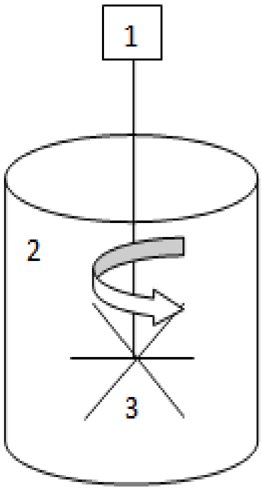
A stock solution of 1000 ppm is prepared using sufficient quantity of $K_2Cr_2O_7$ and $Cd(NO_3)_2$ salt of analytical grade in acidified distilled water. Then during the batch adsorption experiment the stock solution is diluted to the desired concentration required for the experiment.

2.2 Adsorbent

Tea factory waste generated during the process of its industrial preparation in the local factories is taken for the present study. Then the tea waste is washed first with distilled water and then with hot water (80°C) for 1 hour to remove surface impurities and hydrolysable tannins & other colored components respectively. The process was carried out until colourless solution of tea factory waste was spectrometrically visible at the experimental condition.

2.3 Experimental Setup &Procedure

For the experiment a known quantity of tea factory waste is taken and mixed with sufficient amount of synthetic solution prepared from the stock solution. The range of metal ion concentration taken for the present study varies from 5 mg/l to 15mg/l. The mixture is then agitated using mechanical stirrer and 5ml of sample is taken after a fixed interval of time. The sample is tested in the atomic absorption spectrophotometer in order to determine the final metal ion concentration after adsorption. The adsorbent dose, agitation rate and metal ion concentration is varied in a suitable range in the present study. The set up of the batch operation is shown in figure 1.



1. Electrical pump, 2. Container for batch study, 3. Agitator/ stirrer.

Fig1. Experimental set up of the batch operation.

III. Result & Discussion

3.1 Factors influencing adsorption of Chromium for batch study

In the present study the adsorption capacity of tea factory waste is determined in case of mixed aqueous solution of both Chromium and Cadmium.

3.1.1 Effect of Agitation Rate

Fig 2 & 3 shows the effect of agitation rate on the adsorption of Cd(II) and Cr(VI) adsorption. The graphical results in both the cases indicate that with the increasing agitation rate from 200 rpm to 800 rpm the metal ion adsorption also increases at constant pH of 5.0, adsorbent dose 2g/l, initial metal ion concentration of 20mg/l and at a temperature of about 25^0C. The adsorption capacity of Tea factory waste for Cr(VI) and Cd(II) in different agitation rate is presented by the fig 8 which show that the adsorption capacity of cadmium removal increases from 7.7 mg/g to 8.45 mg/g whereas in case of chromium it ranges between 6.9 mg/g to 8.1 mg/g.

3.1.2 Effect of Adsorbent Dose

Effect of TFW dose for removal of Cd(II) and Cr(VI) is shown in the figure 4 & 5 at constant pH of 5, initial concentration 20mg/l and temperature 25^0C. It is found that the adsorption capacity for cadmium removal increases from 24.88 mg/g to 12.7 mg/g with the increase of adsorbent dose from 0.25 g/l to 1 g/l. On the other hand the removal capacity for chromium for the same range of adsorbent dose changes from23.92 mg/g to 11.85 mg/g. The bar diagrams showing the adsorption capacity are given in fig 9.

3.1.3 Effect of Initial Concentration

The effect of initial metal ion concentration on the removal of heavy metal by tea factory waste as adsorbent is shown in the fig 6 & 7 for Cd(II) and

Cr(VI) respectively with constant pH 5, adsorbent dose 2g/l and temperature of about 25^{0}C. The removal efficiency decreases with increasing metal ion concentration for both the metals and it changes from 2.37 mg/g to 7.02 mg/g & 2.30 mg/g to 7.0 mg/g for cadmium and chromium respectively. Fig 10 shows the comparison of removal efficiency through bar diagrams.

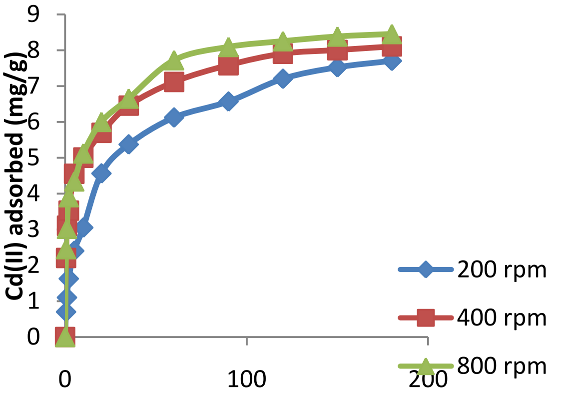


Fig 2. Plot of sorbed amount vs time for Cd(II)
Effect of Agitation Rate

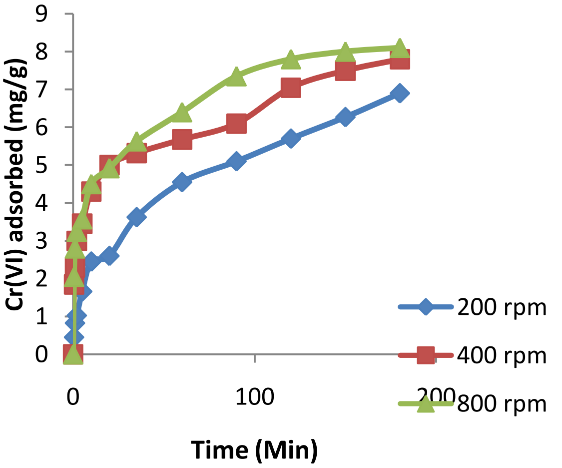


Fig 3. Plot of sorbed amount vs time for Cr(VI)
Effect of Agitation Rate

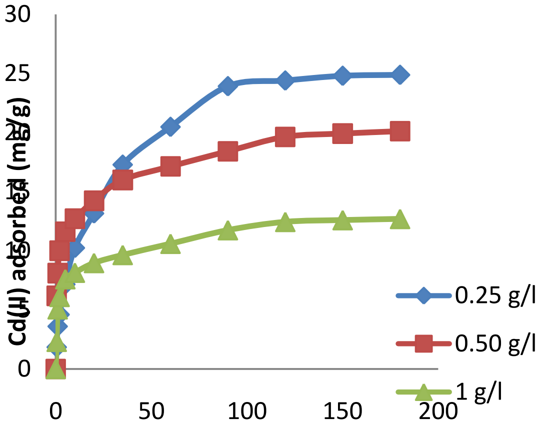


Fig 4. Plot of sorbed amount vs time for Cd(II)
Effect of Sorbent dose

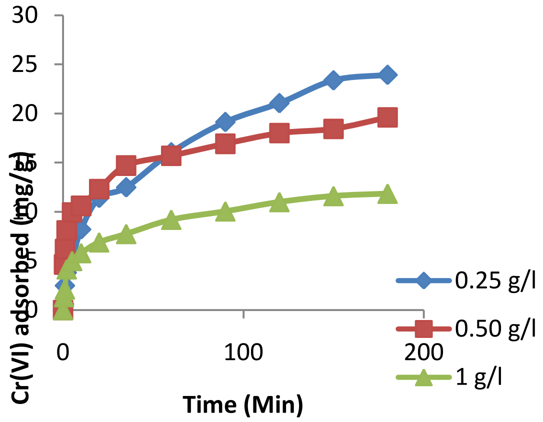


Fig 5. Plot of sorbed amount vs time for Cr(VI)
Effect of Sorbent dose

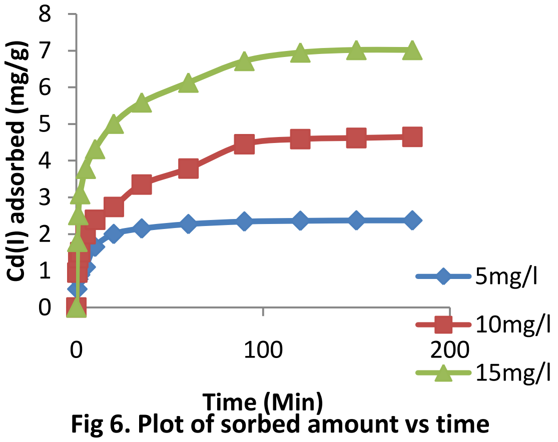


Fig 6. Plot of sorbed amount vs time for Cd(II)
Effect of Initial Concentration

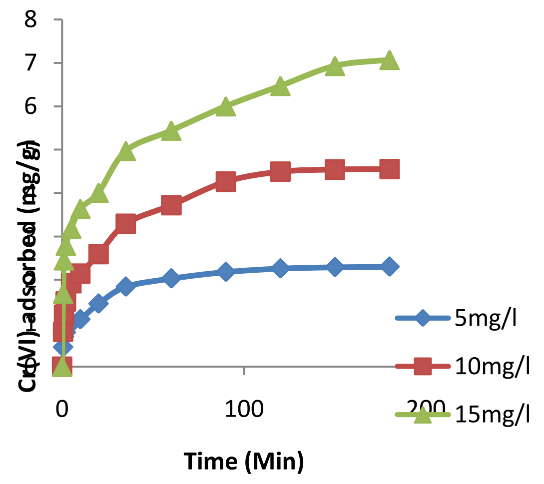


Fig 7. Plot of sorbed amount vs time for Cr(VI)
Effect of Initial Concentration

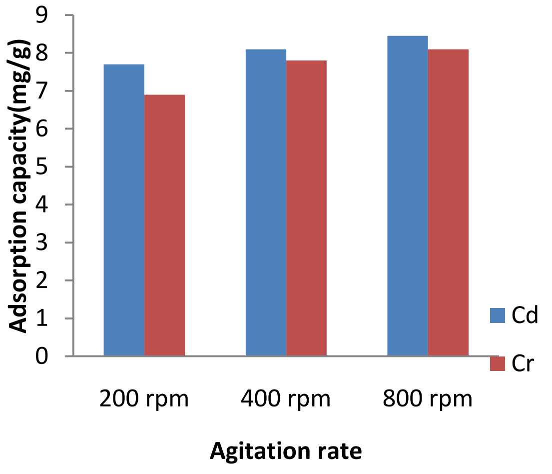


Fig 8. Comparison of adsorption capacities of Cr & Cd at different rate of agitation

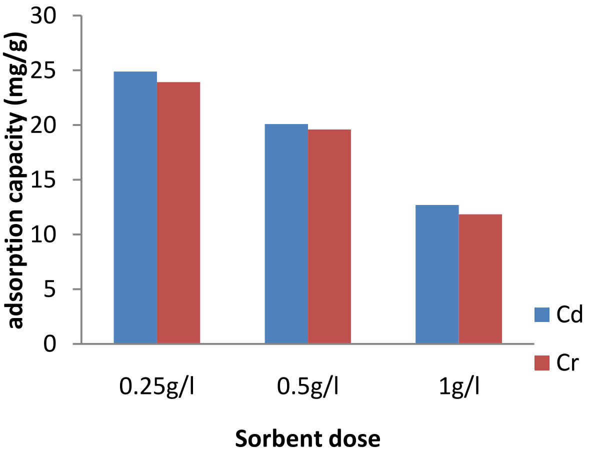


Fig 9. Comparison of adsorption capacities of Cr & Cd at different sorbent dose

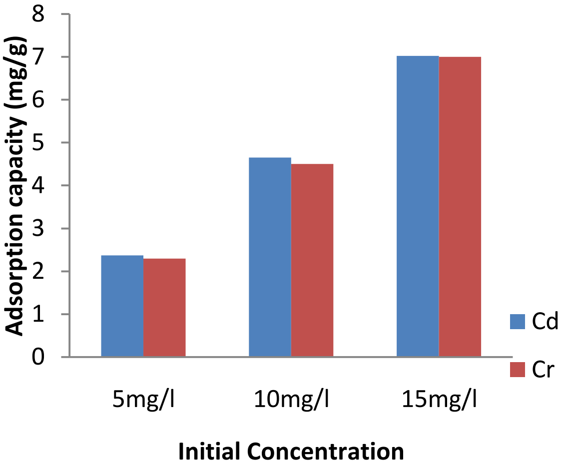


Fig 10. Comparison of adsorption capacities of Cr & Cd at different initial concentration

3.2 Adsorption Isotherms

A number of equilibrium models have been developed to describe the adsorption isotherm relationships [14]. In the present study two isotherm models namely Langmuir isotherm and Freundlich isotherm are considered to evaluate the equilibrium relationship.

3.3 1. Langmuir Isotherm

The Langmuir Isotherm was developed with the assumption that adsorption occurs on localized areas where no interaction between adsorbate molecule is there [15]. For solid liquid system the linearised form of the model is represemted by the following equation

$$1/q_e = 1/abC_e + 1/b$$

Where, C_e is the equilibrium adsorbate concentration in the solution (mg/l) and q_e is the solid phase concentration (mg/g) whereas 'a' represents the maximum adsorption capacity of the adsorbent (mg/g) and b represent the energy of adsorption [16].

A linear plot between C_e/q_e & C_e is drawn in order to determine the values of **a** & b by comparing the given equation with the general equation of straight line given in fig 11.

The values of Q_o & b obtained are given in the table 1 for both chromium and cadmium adsorption by tea factory waste.

3.4 2. Freundlich Isotherm Model

The linearised form of Freundlich isotherm equation is given by [17]

$$\ln qe = (1/n) \ln Ce + \ln K_f$$

Where, q_e is the amount absorbed at equilibrium (mg/g),Ce is the equilibrium concentration of the adsorbate (mg/l) and K_f and '1/n' are constants, which are considered to be relative indicators of adsorption capacity and adsorption intensity .The values of K_f and 1/n can be obtained from the intercept and slope respectively of the linear plot of experimental data of **ln qe** versus **ln Ce** graph shown in the figure 12.

The values of K_f and 1/n are given in table 1.

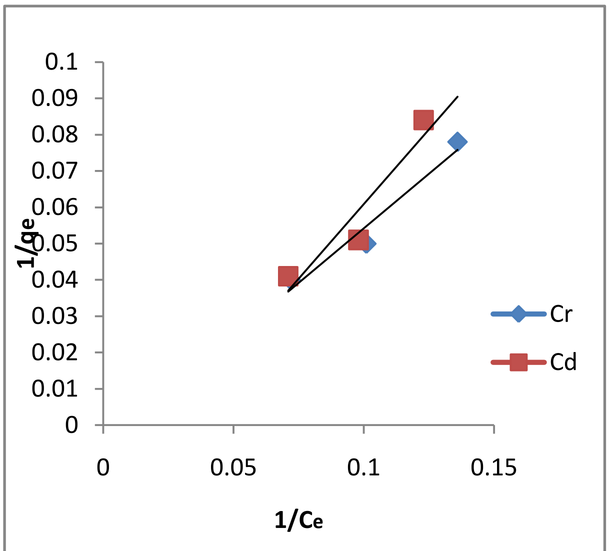


Fig 11. Lngmuir Isotherm for Cr & Cd

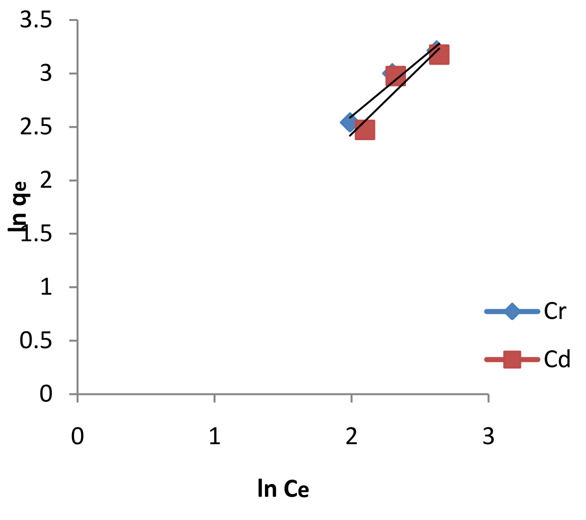


Fig 12. Freundlich Isotherm for Cr & Cd

Table 1. Langmuir and Freundlich Isotherm constants for Cr and Cd

Metal	Langmuir Isotherm			Freundlich Isotherm		
	Q_0	b	R^2	K_f	1/n	R^2
Cr	0.008	200	0.955	1.612	1.059	0.952
Cd	0.026	47.61	0.9	1.074	1.252	0.886

3.3. Kinetic Model

The kinetics of adsorption by tea factory waste have been analysed by three models namely Pseudo first order model, Pseudo second order model and Elovich modle. In the present paper the kinetic analysis by these three kinetic models have been carried out for the most effective adsorption efficiency condition that is at the pH of 5, initial concentration 20mg/l and temperature 25^0C with adsorbent dose of 0.25 g/l. The rate constants and correlation coefficients have been calculated from the related graphical representation.

3.3.1. Pseudo First Order Model

The pseudo order equation is generally expressed as follows [18]

$$dq_t/dt = K(q_e - q_t)$$

where, q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively(mg/g) and K is the rate constant. In the integrated form the equation becomes

$$\log(q_e - q_t) = \log(q_e) - (k/2.303)t$$

The related plot of **$\log(q_e-q_t)$** vs **Time(t)** is given in the figure 13 and the calculated parameters along with the correlation coefficient is provided in the table 2.

3.3.2. Pseudo Second Order Model

The Second order rate equation is represented as [19]

$$1/C - 1/C_0 = K_2\, t$$

Where **t** is time in min, **C** is adsorbent dose mg/l, C_0 initial adsorbent dose in mg/l. second order rate constant 'k_2' values were determined from slope of the linearised plot between '1/C' and 't' as given in the figure 14 for both cadmium and chromium and are given in table 2.

3.3.3. Elovich Model

The Elovich equation is represented as [20]

$$q = (1/b_e) \ln (ab_e) + (1/b_e) \ln(t)$$

Where, q is the adsorption capacity at time t. a represents the rate of adsorption at zero coverage & b_e represents extend of surface coverage and activation energy for adsorption. The constants a and b along with correlation coefficient determined from the linearised plot of **ln t** vs **q** is given in table 2 and the graphical plot is given in the figure 15.

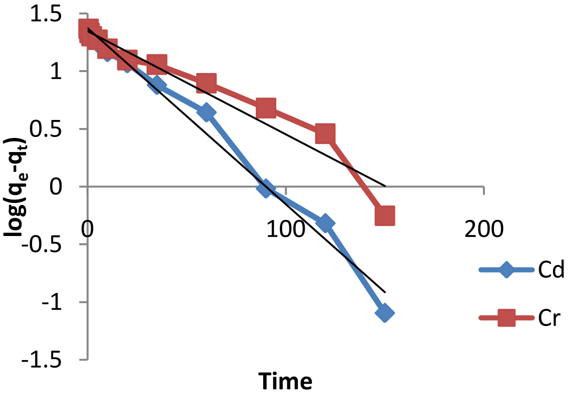


Fig 13. Pseudo First order model for Cr & Cd

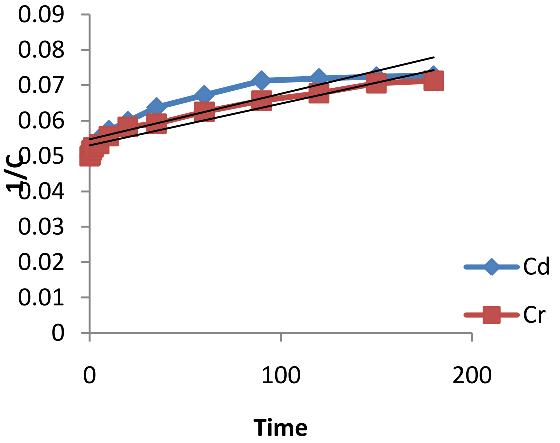


Fig 14. Pseudo First order model for Cr & Cd

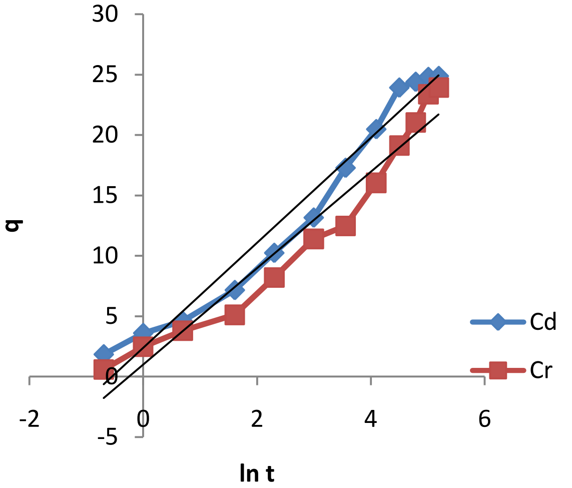


Fig 15. Pseudo First order model for Cr & Cd

Table 1. Langmuir and Freundlich Isotherm constants for Cr and Cd

Kinetic Model	Pseudo First Order		Pseudo Second Order		Elovich		
	k	R^2	k	R^2	a	$1/b_e$	R^2
Cadmium	0.015	0.985	0.0005	0.836	7.496	4.344	0.967
Chromium	0.009	0.942	0.001	0.924	7.224	3.987	0.948

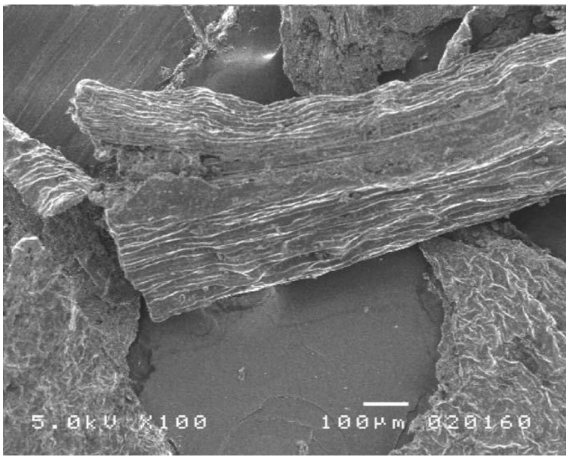


Fig16. Typical SEM micrograph for the particles of waste tea before adsorption [21].

Fig17. Typical SEM micrograph of the particles of waste tea after adsorption

IV. Conclusion

The experimental results obtained and the results found from the isotherm models indicates that the tea factory waste is a very useful and effective low cost adsorbent which can be employed for the removal of heavy metals. The value of correlation coefficient in case of both Langmuir and Freundlich Isotherm is much nearer to unity which indicates a good fixation of the experimental results in the described isotherms. The results also show that the removal efficiency is higher for cadmium than chromium. The microscopic structure of adsorbent obtained by researchers using SEM before and after the adsorption is shown in fig 16 and fig 17 respectively. A further study may be conducted to identify the causes behind this phenomenon using the knowledge of microstructure of the adsorbent obtained from the SEM analysis.

The highest adsorption capacity of 24.88 mg/g and 23.92 mg/g is observed in case of cadmium and chromium respectively is found at the pH of 5, initial concentration 20mg/l and temperature 25^{0}C with adsorbent dose of 0.25 g/l. The adsorption rate is also indicates to be increased with the agitation rate.

The experimental result for the highest adsorption capacity is fitted in three kinetic models to evaluate the kinetics of adsorption. It is indicated by the correlation coefficient that both the experimental results for chromium and cadmium is well fitted in the Pseudo First order kinetic models with correlation coefficient 0.942 and 0.985 respectively.

The result indicates that Tea factory waste can be well used in removal of mentioned heavy metal, and such information can be widely used for the treatment of industrial waste water containing such metals as well as leachate [22] generated from municipal solid waste.

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