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Study of Various Pretreatment Methods for Tea Waste for the Removal of Nickel Ni (II) Ions from Synthetic Waste Water by Adsorption

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ABSTRACT

The adsorption study was carried out to evaluate the effects of various pretreatments on tea waste (TW) for the removal of Ni (II) metal ions from synthetic waste water. The tea water was chemically treated with 0.1M different NaOH, Na_2S, HCHO, KOH, Na_2CO_3, $H_2C_2O_4$, HCL, H_2S0_4, H_3PO_4, HNO_3 solutions. It was observed that certain chemicals NaOH, Na_2S, HCHO, KOH, Na_2CO_3 increased (92.1%-74.8%) the removal efficiency substantially whereas other chemicals $H_2C_2O_4$, HCL, H_2S0_4, H_3PO_4, HNO_3(24.9%-0.6%) reduced it drastically as compared with untreated tea waste 65.1%. The removal efficiency with NaOH and Na_2S pretreatments was 92.1% and 92%. These two pretreatments were further compared by changing different reaction parameters. These were compared by changing the pH value, contact time, adsorbent dose and initial Ni(II) ion concentration along with the study of their equilibrium conditions. The Langmuir model described the adsorption isotherm best. The Langmuir adsorption capacity was found to be 30.31 mg/g for ATTW and 27.03 mg/g for STTW at pH 6. The pretreatment with 0.1 M NaOH was found to be the best treatment method for the removal of Ni (II) metal ions from synthetic waste water

Keywords: Adsorption, tea waste, Nickel, pretreatment

INTRODUCTION

The fast change in the life style of modern age has given rise to rapid industrialization. These industries discharge their effluents which contains the various heavy metals like nickel, lead, cadmium, copper, mercury and chromium in it. The contamination and accumulation of these heavy metals are of serious nature and pose a threat to the environment and public health.

Various methods have been used for the removal of heavy metals from waste water such as adsorption, chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, membrane technologies etc [1-6]. The adsorption method is relatively cheaper and effective with good removal efficiency. Recently the tea waste was reported to be one of the low cost and easily available adsorbent for heavy metals removal [7-8]. However, it was reported in [9] that the efficiency of the adsorption by tea waste could further be improved by subjecting it to various pretreatments by certain bases and other chemicals. These chemicals may change the chemistry of cell wall of tea waste and change the metal binding sites for it. Nickel ions Ni (II) are found in the effluents of various industries like metallurgy, paint and pigments, electroplating, petroleum refining, battery manufacture [10-13]. Nickel is non-biodegradable and tends to accumulate in living organisms. The higher amount of Nickel than the permissible level causes various diseases like skin dermatitis, renal infection, diarrhoea, lung cancer [14]. The permissible concentration of Ni (II) is 0.1 ppm [15-16].

The present work is carried out to study the effects of various pretreatments on tea waste by different chemicals, acids and bases for the adsorption of Ni (II) ion in synthetic waste water.

MATERIALS AND METHODS

Instruments Used

For the specific surface area (SSA) and pore volume determination of tea wastes Surface Area Analyser (BET) Thermo Finnigan Italy, was used. Atomic Absorption Spectrophotometer (AAS 4141) ECIL, India, using air acety-

lene flame was used for the determination of Ni ions in the samples. pH meter model PHEP Hanna Instrument, Italy was used for pH measurements. Zeta potential measurements were taken by SurPASS Electro Kinetic Analyser (Anton Paar).

Chemicals and Reagents

Standard stock solution of 1000 ppm was prepared by dissolving $Ni(NO_3)_2.6H_2O$ (Thomas Baker) in double distilled water. Suitable dilutions of Ni(II) solutions were prepared from it. The pH of the solution was adjusted using HNO_3 and NaOH solutions.

Tea Waste and Pretreated Tea Waste

Tea waste (TW) of brand name Tata Tea was collected in bulk from GGSIP University, New Delhi, India, hostel mess and was used for adsorption experiments. To remove residual tea colour (tannins) the raw tea waste was first subjected to steam treatment under 70 kPa pressure for 25 min using a pressure cooker. This process was repeated several times until the supernatant became fully colourless. This steam treated tea waste was then dried in an oven for 24 hours at (80 ± 5^0C) temperature, and then it was grinded by a grinder. The grinded tea wastes particles were sieved to obtain particle size finer than 0.149 mm and stored in an air tight container for further use. A weighed amount of uniform sized this TW was transferred into a beaker and was thoroughly mixed for maximum 3 h with0.1M concentration of 10 different chemical solutions of NaOH, Na_2S, HCHO, KOH, Na_2CO_3, $H_2C_2O_4$, HCl, H_2SO_4, H_3PO_4, HNO_3 taken one at a time. This mixture was filtered with vacuum filter and washed several times with distilled water. It was dried in an oven at (85 ± 5◦C) and stored in a desiccator as pretreated tea waste sample for further use.

Batch Adsorption Experiment with Tea Waste and Pretreated Tea Waste

The 11 samples of 100 ml Ni ion solution of 100 ppm concentration were prepared from the stock solution. Pretreated tea waste of 0.6 g was added to ten samples. In one sample 0.6 g of untreated tea waste was added. The pH value of the sample solution was fixed at 6 by adding 0.1 M HCl or 0.1 M NaOH solutions. The samples were kept at 303 K temperature, at a constant stirring speed of 150 rpm in a temperature controlled orbital shaker for a contact time of 2 h for equilibrium. The samples were filtered thereafter and the residual concentration was determined using atomic absorption spectrophotometer(AAS). Each batch experiment was conducted two times and the average values were taken in the data analysis. The percentage adsorption of Ni(II) ions and the adsorption capacity was calculated according to the following general equations: -

$$\%\ \text{of Removal (R)} = \frac{(\text{Co} - \text{Ce})}{\text{Co}} \text{X}\ 100 \quad (1)$$

$$\text{qe} = \frac{(C_0 - C_e)V}{M} \quad (2)$$

Where C_o-initial concentrations of Ni (II) ion solution, (ppm), Ce-concentrations of Ni (II) ion solution at equilibrium, (ppm), M-amount of adsorbent (g),q_e-amount of adsorbate Ni (II) ions adsorbed per unit weight of the sorbent atequilibrium, (mg /g),V-volume of Ni (II) solution (ml).

RESULTS AND DISCUSSIONS

The values of % removal of Ni (II) ions are shown in Table.1. For ease of understanding these values are also plotted on a bar graph in Fig.1.It was observed from Fig.1 that the maximum adsorption 92.1% was found with (ATTW) 0.1 M NaOH alkali treated tea waste as compared to 65.1% with untreated tea waste. At the same time, it was also observed that almost similar 92.0% adsorption was obtained with (STTW) 0.1 M Na_2S sodium sulphide treated tea waste. To find out the best pre-treatment out of these two further investigations were made.

Characterization of the Adsorbent

ZETA Potential

The Zeta potential is a parameter which describes the surface charging behaviour of the substance at different pH values of the solution. The variation of Zeta potential with pH value of ATTW and STTWat room temperature, 303 K, is shown in Fig.2. The pH_{zpc} (zero-point charge of pH for ATTW) lies near pH 2.7. It means that the surface of ATTW is positively charged below pH 2.7 and negatively charged above pH 2.7. The pH_{zpc} (zero-point charge of pH for STTW) lies near pH 2.9. It means that the surface of STTW is positively charged below pH 2.9 and negatively charged above pH 2.9. Therefore, the surface of adsorbents favours the adsorption of positively charged Ni (II) ions above pH 2.7 for ATTW and pH 2.9 for STTW due to opposite polarity.

BET Surface Area and Pore Volume

The specific surface area and pore volume of ATTW and STTW was determined from the surface are a analyser using nitrogen gas by the Brunauer, Emmett and Teller (BET) method. The various properties of both the adsorbents are shown in Table -2.

Table-1 Removal % of Ni (II) ions by TW and Pretreated TW

S.No.	Chemical	Ni (II) ion % removal
1.	NaOH (0.1 M)	92.10
2.	Na_2S (0.1 M)	92.00
3.	HCHO (0.1 M)	90.03
4.	KOH (0.1 M)	88.80
5.	Na_2CO_3 (0.1 M)	74.80
6.	$H_2C_2O_4$ (0.1 M)	24.90
7.	HCl (0.1 M)	6.90
8.	H_2SO_4 (0.1 M)	4.50
9.	H_3PO_4 (0.1 M)	2.90
10.	HNO_3 (0.1 M)	0.60
11.	Untreated TW	65.10

Table-2 Measured Physico-Chemical Properties of Adsorbents ATTW and STTW

S.No.	Items	ATTW	STTW
1.	pH $_{Zpc}$ (Zero point charge)	2.7	2.9
2.	Specific Surface area BET (m^2 / g)	225.3	182.5
3.	Average particle size (mm)	0.149	0.149
4.	Pore Volume (cm^3 / g)	0.175	0.152

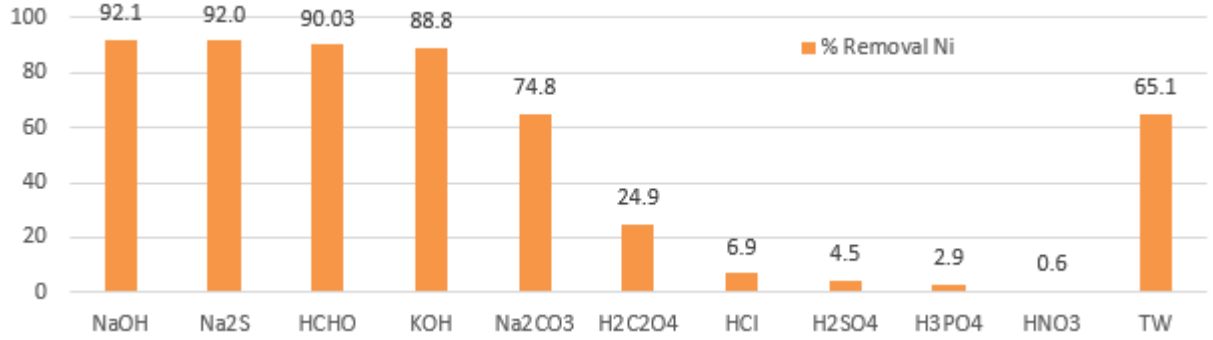

Fig.1 Removal % of Ni(II) ions with tea waste and pretreated tea waste

Effect of Parameters

Effect of Initial Ni (ll) Ion Concentration

The effect of initial Ni (II) ion concentration on the percent removal of Ni(II) is shown in Fig.3.The initial concentration was varied from 20 ppm to 200 ppm in 10 samples of Ni(II) ion solution. The adsorbent dose was 0.6 g/100 ml Ni ion solution at 150 rpm shaking with pH 6 at 303 K temperature for contact time 2 h. It was observed that there is a gradual decrease in the metal uptake by both the adsorbent ATTW and STTW. Initially it goes up to maximum value of 98.5 % and 98.2% of ATTW and STTW at 20 ppm concentration respectively. Then it decreases upto 78.0 % and 76.5% at 200 ppm concentration for ATTW and STTW respectively. This might be due to the fact that initially more fresh adsorption sites are available on both the adsorbents and gradually they are occupied and becomes partly saturated.

Effect of Adsorbent Dose

The effect of dose of ATTW and of STTW on the adsorption of Ni (II) ions is shown in Fig.4.The initial concentration of Ni ion solution was 100 ppm with other conditions same as in previous one. The dose was varied from 0.2 to 2 g in 10 samples each. As the dose increases from 0.2 to 2 g, the number of sites for sorption also increases and 96.5 % and 95.4% uptake was achieved at around 2 g dose of ATTW and STTW respectively. Initially, the sites are occupied almost fully by the available metal ions. But the rate of increase was slower at higher adsorbent dose after 0.6 g.

Effect of Contact Time

The effect of contact time on the extent of adsorption of Ni (II) is shown in Fig.5. The reaction conditions were same with adsorbent dose of 0.6 g. The removal % of Ni was increased from 48.1 % to 92.9 % for ATTW and 45.1% to 89.5% for STTW in contact time variation from 0.25 h to 7 h. The equilibrium was achieved within 90 min for ATTW and 110 min for STTW.

Effect of pH value

The effect of pH on the Ni adsorption is shown in Fig.6.The pH value of the sample was varied from 1-10 in 10 samples. At the lower pH values the removal % was very low because at pH less than 2.7 (pH_{zpc} at zero-point charge

for ATTW) for ATTW and 2.9 (pH_{zpc} at zero-point charge for STTW) for STTW the surface charge of the becomes positive, which restricts the approach of positively charged Ni(II) metalcations. Whereas at higher pH above 2.7 & 2.9 for ATTW and STTW respectively it attracts positively charged metal ions and binding occurs. The maximum equilibrium uptake for Ni (II) ions was in between pH 5 to 6 value. After pH 8 higher removal was observed which might be due to the hydroxide precipitation reaction.

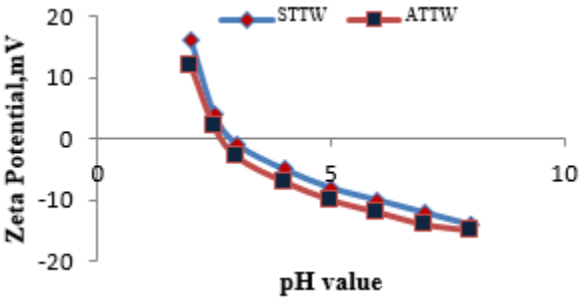

Fig. 2 Zeta potential of ATTW and STTW as a function of solution pH

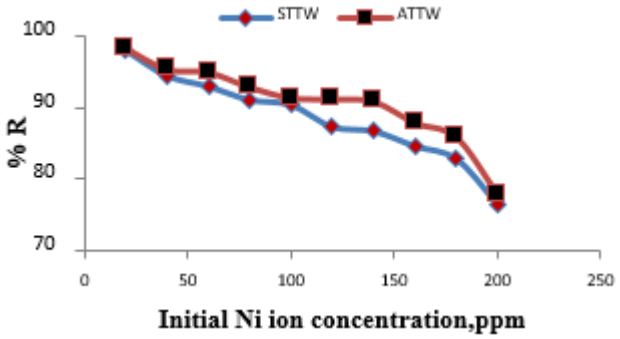

Fig. 3 Change in (%) removal of Ni with initial Ni (ll) ion concentration 20-200 ppm

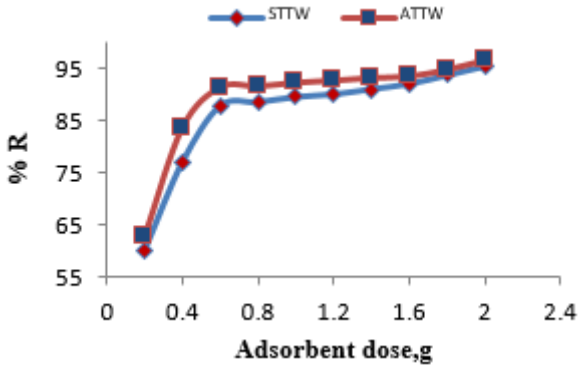

Fig. 4 Change in (%) removal of Ni with dose of adsorbent

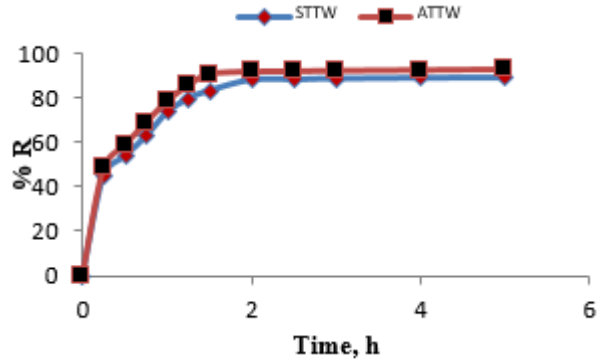

Fig. 5 Change in (%) removal of Ni with Contact time

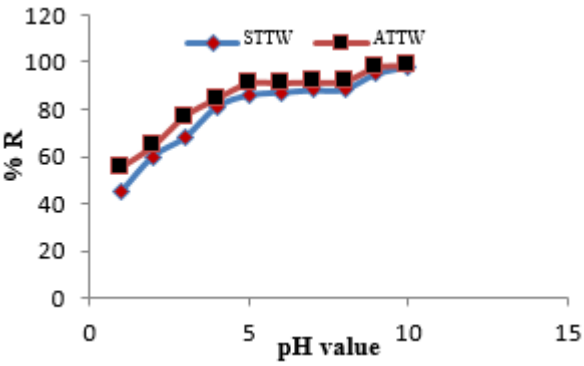

Fig. 6 Change in (%) removal of Ni with pH value

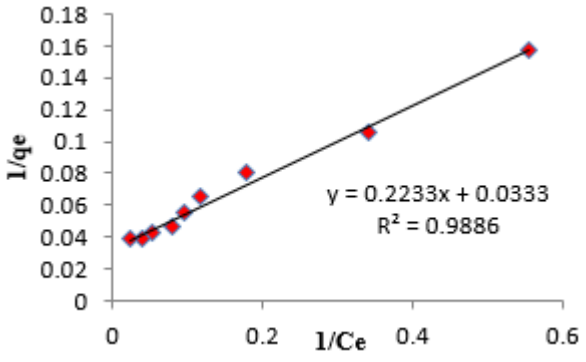

Fig. 7 Linear plot of Langmuir isotherm for the adsorption of Ni(II) on ATTW

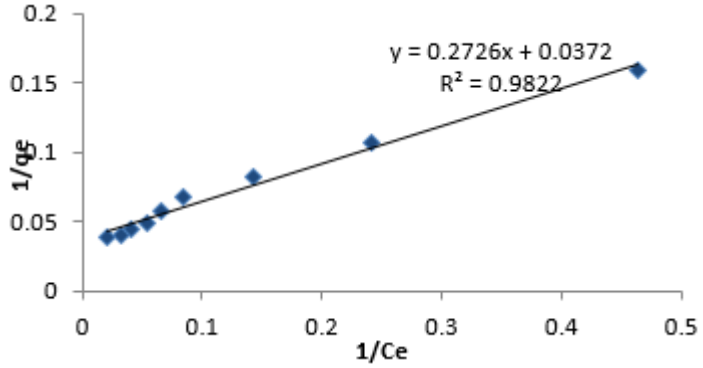

Fig. 8 Linear plot of Langmuir isotherm for the adsorption of Ni(II) on STTW

Table-3 Langmuir Isotherm Constants for the Adsorption of Ni (II) on ATTW and STTW

Isotherm constants	q_m, (mg/g)	K_L, (L/mg)	R_L (L/mg)	R^2
ATTW	30.31	0.147	$0.03 < R_L < 0.2$	0.988
STTW	27.03	0.136	$0.03 < R_L < 0.2$	0.982

Adsorption Isotherm

The Langmuir Adsorption Isotherm

Langmuir isotherm model assumes the monolayer adsorption, homogeneous surface and negligible interaction forces between adsorbed molecules [10]. The linear form of Equation (3) is -

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (3)$$

Where, K_L-Langmuir constant related to the free energy of adsorption (L/mg), q_m-maximum adsorption capacity (mg/g), R_L-Langmuir separation factor, q_m and K_L can be found from the linear plot of 1/ q_e vs 1/ C_e from the Fig.7. for ATTW and Fig.8. for STTW. The maximum Langmuir adsorption capacity was found to be 30.31 mg/g for ATTW and 27.03 mg/g for STTW.

CONCLUSION

It can be concluded from the comparative study of ATTW and STTW that pretreatment with 0.1M NaOH has better removal efficiency and adsorption capacity 30.31 mg/g than STTW under various conditions. Therefore, alkali pretreatment method was found to be the best pretreatment for the adsorption of Ni (II) metal ions from synthetic waste water on tea waste.

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