

Iron doped spent tea waste charcoal as potential adsorbent for treatment of electroplating industry wastewater

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ABSTRACT

Potentiality of spent tea waste charcoal has been determined as low cost adsorbent for the removal of heavy metals (Nickel and Chromium) from the waste water with a twofold objectives of solid waste management alongwith effective treatment of effluent. The iron nanoparticle doped tea waste charcoal (Fe-TWC) was synthesized and characterized using powder XRD, SEM and EDX. Synthesized Fe-TWC was found quite effective in removing high concentrations of Nickel and Chromium from the simulated samples as well as actual industrial samples. Adsorption data follows Langmuir adsorption and pseudo-second order kinetic model. Thermodynamic parameters have also been assessed. This study indicated that Fe-TWC can be used as an effective, low cost and environment friendly adsorbent for the treatment of electroplating waste effluent.

Keywords: tea waste, nickel, chromium, kinetics, thermodynamics

1 INTRODUCTION

Release of chromium and nickel from electroplating and many other industries is one of the serious issues that is threatening the environment with its negative effects [1-3]. The concentration of Cr(VI) in wastewaters range from 0.5-270 mg L⁻¹ while the allowable limit for safe discharge according to EPA and NEQS is 0.1 mg L⁻¹ [4] and 1.0 mg L⁻¹, respectively and for Ni(II) it is 1.0 mg L⁻¹ according to NEQS [5]. Hence, many methods [6-10] have been researched out but adsorption either by using agriculture waste or biosorbents remains the best option due to its low cost and ease of process [4, 11-16]. Recently, the trend shifted to use of nanomaterials owing to their high adsorption capacities attributed to high surface to volume ratio [17-19]. Considering the viability of charcoal and nanomaterials in effective treatment of heavy metal containing industrial wastewaters, the present research wash was designed with the twofold incentive; a) to manage solid waste i.e. spent tea and b) to treat the

electroplating industry wastewater cost effectively, had led to the high adsorption capacities.

2 EXPERIMENTAL

All the chemicals used in study are of analytical grade and distilled water was used throughout the study.

2.1 Synthesis of Adsorbent

Synthesis of spent tea charcoal: Dried thoroughly washed spent tea (150 g), taken in a crucible, was burned under nitrogen atmosphere for 2 hrs followed by fine grinding when it attained room temperature.

Synthesis of Fe-doped charcoal: To the flask containing suspension of charcoal (40.0 g) and FeCl₂·4H₂O (10.0 g) in 500 mL of distilled water, aqueous solution of NaBH₄ (9.0 g/ 250 mL) was added drop wise with vigorously shaking. After that the suspension was filtered and the residue containing charcoal doped with iron was dried in oven for 3 hrs at 70 °C and was kept in air tight jar until further used.

2.2 Adsorption studies

Optimization studies on simulated samples: Metal adsorption experiments were carried out in batch mode by using simulated samples of Cr(VI) (200 mg L⁻¹) and Ni(II) (1000 mg L⁻¹) in distilled water prepared from K₂Cr₂O₇ and NiCl₂·6H₂O, respectively. Distilled water was used through out the study. Metal adsorption % was optimized by varying five parameters i.e. contact time, temperature, initial pH, initial metals ion concentration and catalyst dose.

Industrial wastewater treatment: Industrial wastewater sample (IS) were collected, based on seasonal variations (January and May), from the main drain pipe of electroplating industries before treatment by following the composite sampling technique. The samples were collected in pre-washed dried tightly capped plastic bottles and kept in refrigerator prior to analysis.

50 mL sample of each of the IS is taken and treated under optimized set of conditions, with 1.0 g of adsorbent, filtered and analyzed using atomic absorption spectrophotometer.

2.3 Characterization

Fe-TWC was analyzed using powder X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Electron Dispersive X-ray diffraction (EDX). SEM/EDX images and data were recorded using S3700N, Hitachi, Japan. PANalytical spectrometer was used for XRD measurements by scanning in the range of 5.0125–119.9875° with step size of 0.0250 and scan step time of 0.1000 s.

Metal ion solutions were analyzed using Perkin Elmer Atomic Absorption Spectrometer.

2.4 Models applied

Kinetic models: Pseudo-first order (Eq. 1) and pseudo-second order (Eq. 2) models are as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

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

where, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of adsorbent at equilibrium and at time t (min), respectively. k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants for pseudo-first order and pseudo-second order, respectively.

Adsorption models: Langmuir adsorption model is expressed as follows (Eq. 3):

$$\frac{1}{qt} = \left(\frac{1}{q_{\max} K_L}\right) \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (3)$$

where C_e = equilibrium concentration in solution in mg L^{-1} , q_t = amount of metal adsorbed / g of the adsorbate at equilibrium (mg g^{-1}), q_{\max} = maximum adsorption capacity (mg g^{-1}), K_L = Langmuir constant related to rate of adsorption and R_L = separation factor for equilibrium which is equal to $1/(1 + K_L C_0)$.

Eq. 4 explains the Freundlich model where K_F = adsorption capacity and $1/n$ = heterogeneity factor.

$$\log qt = \log K_F + \frac{1}{n} \log Ct \quad (4)$$

Thermodynamic parameters: Standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°), are calculated as:

$$\Delta G = -RT \ln K_C \quad (5)$$

$$\text{where, } K_C = \frac{C_s}{C_e} \quad (6)$$

$$\ln K_C = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right) \quad (7)$$

where, K_C is equilibrium constant, C_s (mg L^{-1}) is equilibrium concentration of adsorbent, C_e (mg L^{-1}) equilibrium concentration in solution, R ($\text{J mol}^{-1} \text{K}^{-1}$) is ideal gas constant and T (K) is temperature.

3 RESULTS AND DISCUSSION

3.1 Characterization of Fe-TWC

Fig. 1 presents the diffractogram of Fe-TWC along with standard spectra matching which shows the formation of Fe(0) with peak at 2θ values of 44.26° belonging to hkl 110,

respectively. Broadening of peaks also points towards smaller particle size of iron which when calculated using Debye Scherer equation comes out to be 14.28 nm.

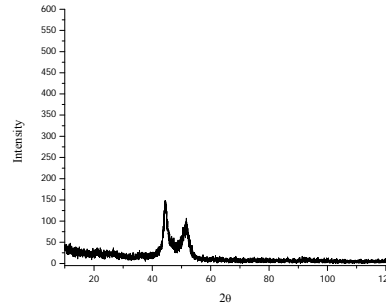


Figure 1: Powder XRD pattern of Fe-TWC showing matching with standard spectra.

SEM/EDX images recorded for Fe-TWC (Fig. 2) also confirmed the doping of white particles of iron on big lumps of black charcoal there by giving more surface area to the charcoal for greater adsorption. EDX analysis (Fig. 2b) shows the composition of Fe-TWC on weight % basis as C (57.49), O (31.51) and Fe (9.41) as major components along with Ca (0.51), P (0.28), Si (0.25), Al (0.23), S (0.16) and Mg (0.15) as minor components.

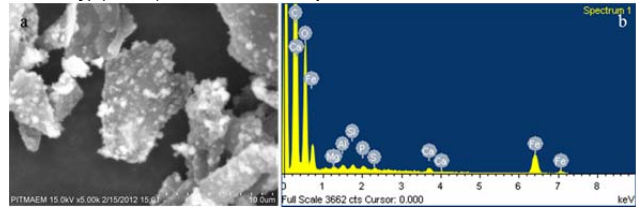


Figure 2: a) SEM and b) EDX images of Fe-TWC.

3.2 Adsorption studies

Effect of contact time: To study the effect of contact time metal ion solutions were allowed to stir at room temperature with 0.10 g of Fe-TWC for different time periods (10-150 min). Significant increase in adsorption capacity for both the metals with increase in contact time (Fig. 3) was observed until equilibrium is achieved which is 130 min for Cr(VI) and 110 min for Ni(II).

Applicability of the contact time studies to pseudo-first and pseudo-second order models (Fig. 3 inset) conforms to the latter one as judged by correlation coefficient values (R^2) and agreement between $q_{e,cal}$ and $q_{e,exp}$ (Table 1) [4].

Effect of temperature: For both metals, increase in adsorption capacity was noticed until equilibrium reaches at 70°C (Fig. 4), affirming the adsorption process is endothermic. Positive Values of ΔH° and ΔS° , as calculated from slope and intercept of $\ln K_C$ vs T^{-1} plot (Fig. 4 inset), respectively are tabulated in Table 2, show that the reaction in both cases is endothermic with disorder around the adsorbent's surface. But the adsorption of Cr(VI) on to Fe-TWC is spontaneous ($-\Delta G^\circ$) and for Ni(II) it is non-spontaneous ($+\Delta G^\circ$).

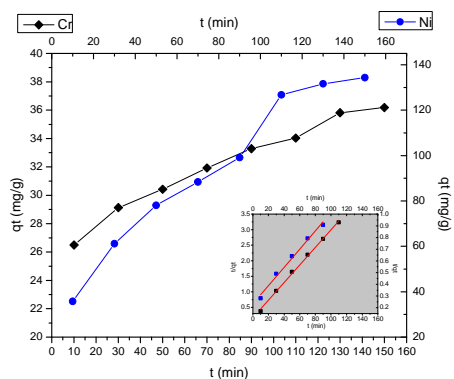


Figure 3: Effect of contact time on adsorption of Cr(VI) and Ni(II) on to Fe-TWC along with inset showing fitting to pseudo-second order.

M ion	$q_{e, exp}$ (mg g ⁻¹)	Pseudo-first order			Pseudo-second order		
		k_1 (10 ⁻²)	$q_{e, cal}$ (mg g ⁻¹)	R ²	k_2 (10 ⁻⁴)	$q_{e, cal}$ (mg g ⁻¹)	R ²
Cr	35.81	1.57	11.10	0.988	0.63	34.36	0.998
Ni	126.75	3.62	229.00	0.677	2.61	128.21	0.989

Table 1: Pseudo-first order and pseudo-second order parameters for Cr(VI) and Ni(II) adsorption on Fe-TWC.

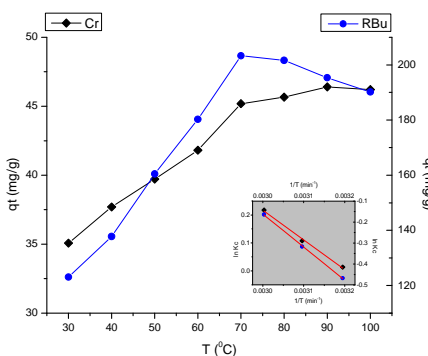


Figure 4: Effect of temperature on adsorption of Cr(VI) and Ni(II) on to Fe-TWC along with inset showing Plot of $\ln K_C$ vs T^{-1} .

M ion	T (K)	K_C	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹)	R ²
Cr	313	1.013	-0.034	8.82	28.28	0.996
	323	1.114	-0.289			
	333	1.242	-0.832			
Ni	313	0.626	1.217	13.16	0.04	0.999
	323	0.728	0.851			
	333	0.849	0.454			

Table 2: Thermodynamic parameters' values for adsorption of Cr(VI) and Ni(II) on Fe-TWC.

Effect of pH: Adsorption of both Cr(VI) and Ni(II) is pH dependent as depicted in Fig. 5. For Cr(VI) increase in pH was accompanied by decrease in adsorption capacity and maximum was observed at pH 2. The existence of

chromium in its (VI) and (III) oxidation states depends a lot on pH and with increase in pH, the prevalence of main specie i.e. $HCrO_4^-$ shifts towards other forms [4].

In case of Ni(II) the maximum adsorption was observed at pH 5. Significant decrease in adsorption of Ni(II) occurs with decrease in pH as at lower pH H^+ ions starts competing with the metal ions [20]. At higher pH (>7) the studies were not carried out due to hydroxide formation.

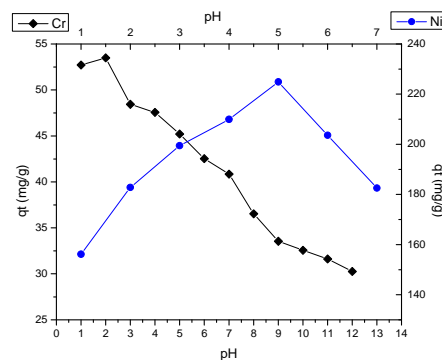


Figure 5: Effect of pH on adsorption of Cr(VI) and Ni(II) on to Fe-TWC.

Effect of initial metal ion concentration: The increase in adsorption capacity of the adsorbent was noticed for both the metals with increase in metal concentration (Fig. 6) but overall the percentage adsorption decreases with increase in metal ion concentration. The maximum adsorption for Cr(VI) was observed to be at 200 mg L⁻¹ and for Ni(II) at 600 mg L⁻¹, hence the Fe-TWC has better adsorption potential for Ni(II) as compared to Cr(VI).

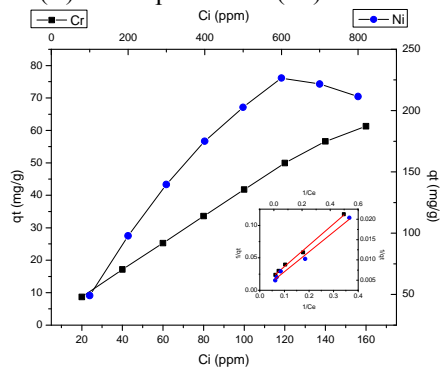


Figure 6: Effect of initial metal ions concentration on Cr(VI) and Ni(II) adsorption on Fe-TWC along with inset showing applicability to Langmuir model.

Langmuir and Freundlich models were also applied to see the best fit model based on the R² value (Table 3) and as it was observed that in both the cases i.e. Cr(VI) and Ni(II), Langmuir model holds good (Fig. 6 inset).

M ion	Langmuir constants			Freundlich constants		
	q_{max} ($mg\ g^{-1}$)	K_L ($L\ mg^{-1}$)	R^2	K_F	n	R^2
Cr	238.09	0.01	0.996	3.27	1.09	0.995
Ni	200.08	0.18	0.988	47.95	3.00	0.932

Table 2: Adsorption isotherm parameters' values for Cr(IV) and Ni(II) adsorption on Fe-TWC

Effect of adsorbent dose: Fig. 7 presents the effect of variation in adsorbent dose on metal adsorption capacity of the Fe-TWC. It can be seen that as the weight of adsorbent increases there is decrease in adsorption capacity until the equilibrium is reached at adsorbent weight of 1.0 g after which there is no appreciable increase in percentage adsorption.

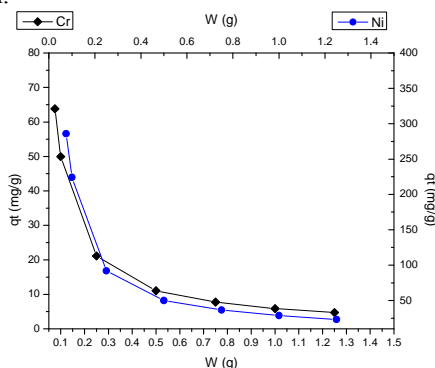


Figure 7: Effect of adsorbent dose, W (g) on adsorption of Cr(VI) and Ni(II) on to Fe-TWC.

3.3 Treatment of industrial samples

Effectiveness of Fe-TWC was also checked on actual industrial samples (IS) and the results hence obtained are presented in Fig. 8. IS-1 and IS-2 were collected in January while IS-3 and IS-4 were in the month of May. The overall percentage decrease in chromium concentration after treatment with 0.1 g adsorbent was from 24.9 – 59.3 %, while in case of nickel the decrease is from 24.32 – 35.05 %.

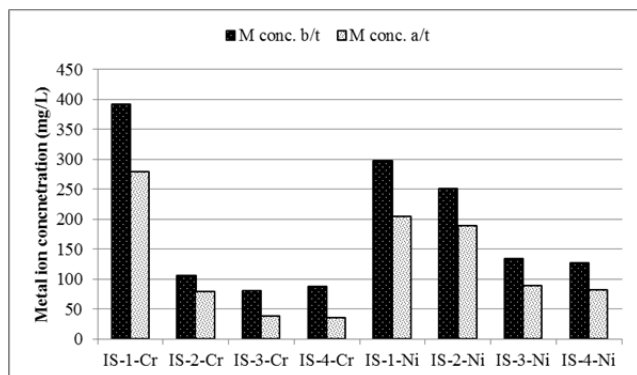


Figure 8: Concentration ($mg\ L^{-1}$) of metals in industrial samples before and after treatment with Fe-TWC.

Hence, the prepared adsorbent is able to remove metal in larger concentrations as compared to the only tea waste ($15.26\ mg\ g^{-1}$) [20].

4 CONCLUSION

Iron doped spent tea waste charcoal was used in for the effective treatment of electroplating industry wastewater that contains large concentrations of the heavy metals like Cr(VI) and Ni(II). The adsorbent was characterized by high adsorption capacities that for both metals fall in the range of $200\text{-}240\ mg\ g^{-1}$ of adsorbent. The method offers easy, cost effective and environmental friendly way of tackling the pollution issues.

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