



Treatment of electroplating industry wastewater using iron nanoparticle doped spent tea waste charcoal

Ramma S. Butt¹, Rabia Nazir^{2*}, Muhammad Naeem Khan², Almas Hamid¹, Farah Deeba³

¹*Kinnaird College for Women, 93 Jail Road, Lahore, Pakistan*

²*Applied Chemistry Research Centre, PCSIR Laboratories Complex, Ferozpur Road, Lahore, Pakistan*

³*Centre for Environmental Protection Studies, PCSIR Laboratories Complex, Ferozpur Road, Lahore, Pakistan*

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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 the three fold objective of solid waste management for effective and green treatment of heavy metals' highly contaminated effluent. Iron nanoparticles 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 Ni (II) and Cr (VI) from the simulated samples as well as actual industrial samples. Adsorption data follows Langmuir adsorption and pseudo-second order kinetic model for both the metals. 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.

*Corresponding Author: Rabia Nazir ✉ rabiapcsir@yahoo.com

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 impacts (Royle H, 1975; Costa M, 2003; Cempel M and Nikel G, 2006). The concentration of Cr(VI) in wastewaters range from 0.5-270 mg L⁻¹ while the allowable limit for safe discharge according to Environmental Protection Agency (EPA) and National Environmental Quality Standards (NEQS) is 0.1 mg L⁻¹ (Demirbas E *et al.*, 2004) and 1.0 mg L⁻¹, respectively and for Ni(II) it is 1.0 mg L⁻¹ according to NEQS (Government of Pakistan, 1997). Hence, many methods (McAnally S *et al.*, 1984; Gzara L and Dhahbi M, 2001; Rengaraj S *et al.*, 2003; Gao P *et al.*, 2005; Owlad M *et al.*, 2009) 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 (Veglio F and Beolchini F, 1997; Boddu VM *et al.*, 2003; Demirbas E *et al.*, 2004; Malkoc E, 2006; Argun ME *et al.*, 2007; Pehlivan E and Altun T, 2008; Rafatullah M *et al.*, 2009). Among these tea waste also gained some attention as potential adsorbent for adsorption of either dyes (Uddin MT *et al.*, 2009) or heavy metals like arsenic, copper, lead, cadmium, chromium (Cay S *et al.*, 2004; Amarasinghe BMWPK and Williams RA, 2007; Malkoc E and Nuhoglu Y, 2007; Shaikh MS *et al.*, 2011) with adsorption capacities in the range of 2.59 to 73 mg of metal per gram of adsorbent for different metals (Cay S *et al.*, 2004; Ahluwalia SS and Goyal D, 2005; Amarasinghe BMWPK and Williams RA, 2007). The maximum adsorption capacity reported in case of Cr (VI) for adsorption on tea waste was 54.65 mg g⁻¹ (Malkoc E and Nuhoglu Y, 2007). In an attempt to increase adsorption capacities, charcoals derived from these wastes were employed either with or without modification (Monser L and Adhoum N, 2002; Park S-J and Jang Y-S, 2002; Demirbas A, 2009). Amount of iron impregnated into the activated charcoals by different modification procedures was found to be directly related to the arsenic removal percentage (Chen W *et al.*, 2007) and recently enhanced adsorption

capacities for Pb (II) were also observed for bamboo charcoal that was loaded with nickel (Wang Y *et al.*, 2013).

To further get higher adsorption rates and adsorption efficiencies the trend recently shifted to the use of nanomaterials which are known for their high surface to volume ratios (Hu J *et al.*, 2005; Hoch LB *et al.*, 2008; Brar SK *et al.*, 2010; Asgari G *et al.*, 2012). Among these materials, zero-valent iron remains a popular choice (Rangsivek R and Jekel M, 2005; Boparai HK *et al.*, 2011) due to its wide range of environmental cleanup applications (Lackovic JA *et al.*, 2000; Cundy AB *et al.*, 2008).

Hence, considering the viability of both charcoal and nanomaterials in effective treatment of heavy metals containing industrial wastewaters - the present research was designed with the three-fold incentive i.e. a) to manage solid waste i.e. spent tea, b) to treat the electroplating industry wastewater cost effectively and c) environmental friendly approach that had led to the high adsorption capacities.

Materials and methods

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

Synthesis of Adsorbent

The adsorbent was prepared by following a two-step approach first the charcoal was prepared from spent tea followed by its doping with iron.

Synthesis of spent tea charcoal

Spent black tea was collected from local hotels and restaurants, washed with water and dried in open air. 150 g of this dried spent tea was taken in a crucible and heated in a furnace under nitrogen atmosphere at 600 °C for 2 h 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 vigorous shaking. The course of reaction was monitored by filtering a small portion of reaction mixture and noting the change in colour of filtrate from yellowish brown to colourless indicating the reduction of Fe²⁺ to Fe⁰. After that the suspension was filtered and the residue containing charcoal doped with iron was washed with distilled water followed by oven drying for 3 hrs at 70 °C. The dried material was then kept in air tight jar until further used.

Adsorption studies

Metal Ion solution preparation: Simulated samples of metal ion solutions (1000 mg L⁻¹) were prepared in distilled water by employing NiCl₂·2H₂O and K₂Cr₂O₇. Working solutions were prepared from stock solutions by dilution as per requirement.

Optimization studies on simulated samples: Metal adsorption experiments were carried out in batch mode by using simulated samples of Ni (II) and Cr (VI) in distilled water. Metal adsorption % was studied as a function of five parameters i.e. contact time, temperature, initial pH, initial metal ion concentration and catalyst dose and adsorption capacity of adsorbent, $q_{e, exp}$ (mg/g) was calculated by Equation (1):

$$q_{e, exp} = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and C_e (mg L⁻¹) are the metal ion concentrations before and after treatment, V (L) is volume of metal ion solution taken and W (g) is the weight of adsorbents used.

For determining the metal adsorption capacity of the Fe-TWC adsorbent 50 mL of the metal ion solution (1000 mg L⁻¹ for Ni (II) and 200 mg L⁻¹ for Cr (VI)) was agitated with 0.1 g of adsorbent for different time intervals while maintaining the known temperature and pH. After that the contents were Cannula filtered followed by thorough washing of the residue. The filtrate and washings were transferred to 50 mL

measuring flask and the volume was made up to the mark with distilled water prior to analysis.

Industrial wastewater collection and treatment: Industrial samples (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 seasonal variations were taken into account just for the process changes (in case if there are any) and different amounts of metals drained into the effluent. 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 industrial wastewater (IS) is taken and treated under optimized set of conditions, with 1.0 g of adsorbent, filtered and analyzed using atomic absorption spectrophotometer.

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 (FAAS). FAAS was equipped with an air-acetylene burner and controlled by an Intel personal computer.

Models applied

Kinetic models: The rate constants for adsorption of Ni (II) and Cr (VI) on to Fe-TWC were determined by employing pseudo-first order (Eq. 2) and pseudo-second order (Eq. 3) models which are as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of metal adsorbed 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.

Intra-particle diffusion model was also employed to get insight into the adsorption phenomenon. Weber and Moris plot i.e. q_t vs $t^{0.5}$ was used to investigate the model according to the following equation 4:

$$q_t = k_{id}t^{0.5} + C_i \quad (4)$$

where k_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the rate parameter of stage i and C_i is the thickness of boundary layer.

Adsorption models: Four models i.e. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) are applied to the adsorption data to study the relationship between mass of adsorbate per unit weight of adsorbent and metal ion concentration and other related parameters.

Langmuir adsorption model which addresses the homogeneity of the adsorbent along with constant adsorption potential and uniform energies, is expressed as follows (Eq. 5):

$$\frac{1}{q_e} = \left(\frac{1}{q_m K_L}\right) \frac{1}{C_e} + \frac{1}{q_m} \quad (5)$$

Where, C_e = equilibrium concentration in solution in mg L^{-1} , q_e = amount of metal adsorbed per gram of the adsorbate at equilibrium (mg g^{-1}) where q_m (mg g^{-1}) is the maximum capacity of adsorbent and K_L (L mg^{-1}) is the Langmuir constants which is related to the energy of adsorption. A dimensionless constant, R_L , defined as the separation factor for equilibrium is helpful in defining the essential characteristics of the model. The equation that holds for its calculation is $1/(1 + K_L C_0)$.

Eq. 6 explains the Freundlich model where K_F = adsorption capacity and $1/n$ = heterogeneity factor.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

C_t (mg L^{-1}) is the concentration of metal ions after treatment with Fe-TWC, q_t (mg g^{-1}) is the amount of metal adsorbed per gram of adsorbent, K_F and n are constants which are calculated from the intercept and slope of $\log q_t$ vs $\log C_e$. This model assumes that adsorption takes place on heterogeneous surface.

Third model that is applied is Temkin which is defined as Eq. 8 and takes into account the adsorbate and adsorbent interactions without giving appreciable focus on adsorbate concentration. This model also holds good for heterogeneous surfaces.

$$q_e = B \ln A + B \ln C_e \quad (7)$$

Where, A (L g^{-1}) is the Temkin isotherm equilibrium binding constant and B (J mol^{-1}) is the constant related to heat of sorption which is calculated as follows:

$$B = \frac{RT}{b_T} \quad (8)$$

R ($\text{J mol}^{-1} \text{K}^{-1}$) is the universal gas constant, T (K) is the temperature and b_T is the Temkin constant.

To get insight into the adsorption process Dubinin-Radushkevich (D-R) isotherm is also applied that assumes adsorbent surface to be heterogeneous and is defined by the expression 9:

$$\ln q_e = \ln q_d - K \epsilon^2 \quad (9)$$

Where q_e (mg g^{-1}) is the amount of metal ions adsorbed per gram of adsorbent, q_d (mg g^{-1}) is the adsorption capacity of adsorbent, ϵ is the Polanyi potential calculated from $RT \ln(1 + 1/C_e)$. C_e (mg L^{-1}) is the equilibrium concentration of metal ions in solution, K ($\text{mol}^2 \text{J}^{-2}$) is the constant for adsorption energy and R ($\text{J K}^{-1} \text{mol}^{-1}$) is the gas constant and T (K) is the temperature.

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

$$\Delta G = -RT \ln K_C \quad (10)$$

where, $K_C = \frac{C_s}{C_e}$ (11)

$$\ln K_C = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{RT} \right) \quad (12)$$

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.

Results and discussion

The potentiality of spent tea waste charcoal as adsorbent for treatment of Ni (II) and Cr (VI) contaminated wastewater was studied after doping it with iron nanoparticles. The adsorbent, Fe-TWC, prepared was characterized prior to its use by employing various techniques like FT-IR, SEM, EDX and powder XRD.

Characterization of Fe-TWC

Powder XRD and particle size: Fig. 1 presents the diffractogram of Fe-TWC along with standard spectra matching which shows the formation of Fe(O) with peak at 2θ values of 44.260° 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.

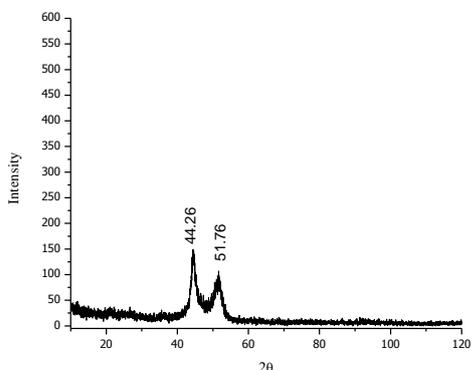


Fig. 1. Powder XRD pattern of Fe-TWC showing matching with standard spectra.

Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX): 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) showed 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.

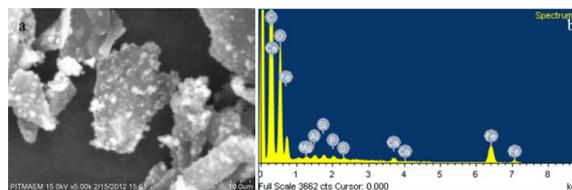


Fig. 2. Fe-TWC images for a) SEM showing presence of white particles of iron on surface of black charcoal and b) EDX confirming doping of iron in charcoal.

Adsorption studies

Effect of contact time and kinetic studies: 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).

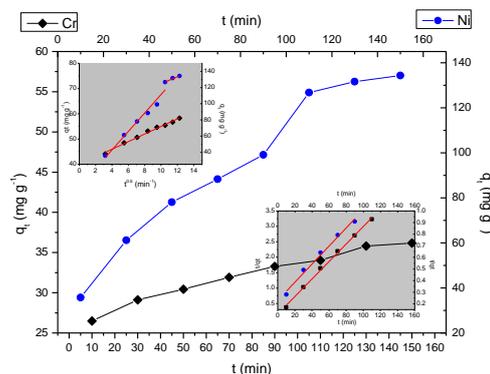


Fig. 3. Effect of contact time on adsorption of Cr (VI) and Ni (II) on to Fe-TWC along with lower inset showing fitting to pseudo-second order and upper inset showing applicability to intra-particle diffusion model.

Applicability of the contact time studies to pseudo-first order and pseudo-second order (Fig. 3 inset) models 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) (Demirbas A, 2009).

Intra-particle diffusion model was also applied to both Cr(VI) and Ni(II) and results are presented in Fig. 3 and the parameters obtained as result of data fitting are given in Table 1. The fitting of Cr (VI) data

to single line with high intercept value (line not passing through origin) and Ni (II) data to two lines indicated that adsorption on to Fe-TWC intra-particle diffusion is not the sole contributor, other phenomenons might also be taking part resulting in high adsorption capacity of the adsorbent (Argun ME *et al.*, 2007). Enhanced binding capacity in both the cases was indicated by the higher k_d values as supported by earlier reserches (Demirbas E *et al.*, 2004) (Demirbas E *et al.*, 2004).

Table 1. Pseudo-first order, pseudo-second order and intra-particle diffusion parameters for Cr (IV) and Ni (II) adsorption on Fe-TWC.

M ion	$q_{e,exp}$ (mg g ⁻¹)	Pseudo-first order			Pseudo-second order			Intra-particle diffusion					
		k_1 (10 ⁻²)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_2 (10 ⁻⁴)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_{id1} (mg g ⁻¹ min ^{-0.5})	C_{i1} (mg g ⁻¹)	R_1^2	k_{id2} (mg g ⁻¹ min ^{-0.5})	C_{i2} (mg g ⁻¹)	R_2^2
Cr	35.81	1.57	11.10	0.9912	0.63	34.36	0.9975	1.51	39.96	0.9914	-	-	-
Ni	126.75	3.62	229.00	0.6773	2.61	128.21	0.9889	11.41	2.25	0.9669	4.33	81.69	0.9795

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, depicted 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 ($+\Delta G^\circ$).

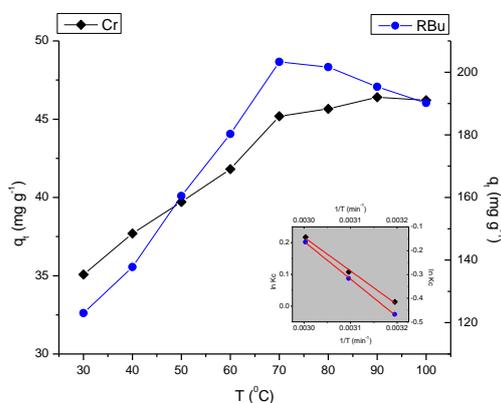


Fig. 4. Effect of temperature on adsorption of Cr (VI) and Ni (II) on to Fe-TWC along with inset showing Plot of $\ln K_c$ vs T^{-1} .

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

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	0.9965
	323	1.114	-0.289			
	333	1.242	-0.832			
Ni	313	0.626	1.217	13.16	0.04	0.9995
	323	0.728	0.851			
	333	0.849	0.454			

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 on pH and with increase in pH, the prevalence of main specie i.e. $HCrO_4^-$ shifts towards other forms (Demirbas E *et al.*, 2004). Earlier studies also supported the fact that chromium is mostly adsorbed in $HCrO_4^-$ form which exists at lower pH (Argun ME *et al.*, 2007).

In case of Ni (II) the maximum adsorption was observed at pH 5 which is in accordance with earlier studies carried out for Ni (II) adsorption onto tea waste (Aikpokpodion P *et al.*, 2010) (Aikpokpodion P *et al.*, 2010). Significant decrease in adsorption of Ni

(II) occurs with decrease in pH as at lower pH H⁺ ions starts competing with the metal ions (Malkoc E and Nuhoglu Y, 2005). At higher pH (>7) the studies were not carried out due to hydroxide formation.

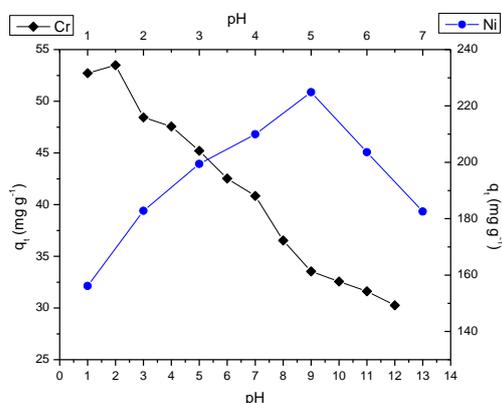


Fig. 5. Effect of pH on adsorption of Cr (VI) and Ni (II) on Fe-TWC.

Langmuir, Freundlich, Temkin and D-R models were applied to the Ni (II) and Cr (VI) adsorptions on the Fe-TWC, the parameters hence obtained are given in Table 2. The best fit model was determined based on the R² value (Table 2) and as it was observed that in both the cases i.e. Cr (VI) and Ni (II), Langmuir model holds good (Fig. 6 inset).

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) as also affirmed by thermodynamic studies (ΔG values).

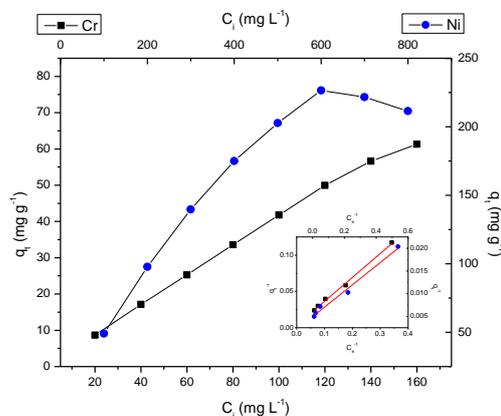


Fig. 6 Effect of initial metal ions concentration on Cr (VI) and Ni (II) adsorption on Fe-TWC along with inset showing applicability to Langmuir model.

Earlier studies for Cu and Ni on to charcoal also conforms to the similar findings (Argun ME *et al.*, 2007) but with very low adsorption capacities i.e. 3.22 and 3.29 mg g⁻¹ as calculated from Langmuir isotherm. The adsorption capacity obtained in current studies is also much higher than the one earlier reported for Ni (II) adsorption (38.3 mg g⁻¹) on to iron oxide nanoparticle doped tea waste (Panneerselvam P *et al.*, 2011). The value of energy as obtained from the D-R models is less than 8 kJ mol⁻¹ implies that adsorption of both Ni (II) and Cr (VI) on to Fe-TWC are physical in nature.

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

M ion	Langmuir constants			Freundlich constants			Temkin Constants			D-R isotherm		
	q_{max} (mg g ⁻¹)	K_L (L mg ⁻¹)	R ²	K_F	N	R ²	A (L g ⁻¹)	b_T (kJ mol ⁻¹)	R ²	q_d (mg g ⁻¹)	E (kJ mol ⁻¹)	R ²
Cr	238.09	0.01	0.9970	3.27	1.09	0.9951	1.85	0.13	0.9448	19.19	0.408	0.8952
Ni	200.08	0.18	0.9881	47.95	3.00	0.9319	2.04	0.07	0.9889	69.52	0.707	0.8967

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 dose of adsorbent increases there is decrease in adsorption capacity of both the metals (Cr (VI) and Ni

(II)) until the equilibrium is reached at adsorbent dose of 1.0 g after which there is no appreciable increase in the percentage adsorption. The rate of adsorption is directly related to the number of active sites available for adsorption which increases with

increase in adsorbant dose. This direct relationship is observed until the equilibrium is achieved (Argun ME *et al.*, 2007).

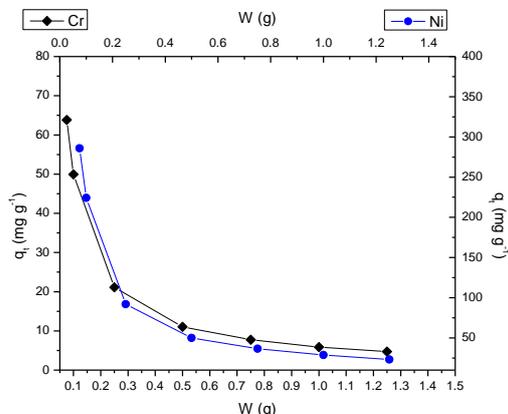


Fig. 7. Effect of adsorbent dose, *W*, on adsorption of Cr (VI) and Ni (II) on to Fe-TWC.

The list of optimized parameters that were finalized after performing the set of five parameters is given in Table 3 along with adsorption capacity, q_e (mg g^{-1}), and percentage adsorption (%).

Table 3. List of optimized parameters for the adsorption of Cr (VI) and Ni (II) onto Fe-TWC.

Parameters	Cr (VI)	Ni (II)
Contact time (min)	130	110
Temperature ($^{\circ}\text{C}$)	70	70
Initial pH	2	5
Metal ion concentration (mg L^{-1})	200	600
Adsorbent dose (g)	1.0	1.0
Metal adsorbed (%)	98.02	95.92
q_e (mg g^{-1})	238.09	200.08

Treatment of industrial samples

Effectiveness of Fe-TWC was also checked on actual industrial samples (IS) collected from chromium and nickel electroplating industries 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 month of May. The overall percentage decrease in chromium concentration after treatment with 1.0 g adsorbent was from 24.9 – 59.3 %, while in case of nickel the decrease is from 24.32 – 35.05%.

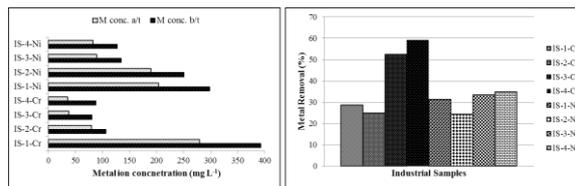


Fig. 8. Concentration of metals in industrial samples before (b/t) and after treatment (a/t) with Fe-TWC (left) and % removal (right).

Hence, the prepared adsorbent is able to remove heavy metals in larger concentrations from simulated as well as actual industrial effluents as compared to the only tea waste (15.26 mg g^{-1}) (Malkoc E and Nuhoglu Y, 2005).

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 $200\text{-}240 \text{ mg g}^{-1}$ of adsorbent. The method offers easy, cost effective and environmental friendly way of tackling the pollution issues.

References

Ahluwalia SS, Goyal D. 2005. Removal of Heavy Metals by Waste Tea Leaves from Aqueous Solution. *Engineering in Life Sciences*, **5**, 158-162.

Aikpokpodion P, Ipinmoroti R, Omotoso S. 2010. Biosorption of nickel (II) from aqueous solution using waste tea (*Camella cinencis*) materials. *American-Eurasian Journal of Toxicological Sciences*, **2**, 72-82.

Amarasinghe BMWPK, Williams RA. 2007. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, **132**, 299-309.

Argun ME, Dursun S, Ozdemir C, Karatas M. 2007. Heavy metal adsorption by modified oak

sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials*, **141**, 77-85.

Asgari G, Rahmani AR, Faradmal J, Mohammadi S, Motaleb A. 2012. Kinetic and isotherm of hexavalent chromium adsorption onto nano hydroxyapatite. *Journal of Research in Health Sciences*, **12**, 45-53.

Boddu VM, Abburi K, Talbott JL, Smith ED. 2003. Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. *Environmental Science and Technology*, **37**, 4449-4456.

Boparai HK, Joseph M, O'Carroll DM. 2011. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *Journal of Hazardous Materials*, **186**, 458-465.

Brar SK, Verma M, Tyagi R, Surampalli R. 2010. Engineered nanoparticles in wastewater and wastewater sludge—Evidence and impacts. *Waste Management*, **30**, 504-520.

Cay S, Uyanık A, Özaşık A. 2004. Single and binary component adsorption of copper (II) and cadmium (II) from aqueous solutions using tea-industry waste. *Separation and Purification Technology*, **38**, 273-280.

Cempel M, Nikel G. 2006. Nickel: A review of its sources and environmental toxicology. *Polish Journal of Environmental Studies*, **15**, 375-382.

Chen W, Parette R, Zou J, Cannon FS, Dempsey BA. 2007. Arsenic removal by iron-modified activated carbon. *Water Research*, **41**, 1851-1858.

Costa M. 2003. Potential hazards of hexavalent chromate in our drinking water. *Toxicology and Applied Pharmacology*, **188**, 1-5.

Cundy AB, Hopkinson L, Whitby RL. 2008. Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Science of the total environment*, **400**, 42-51.

Demirbas A. 2009. Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. *Journal of Hazardous Materials*, **167**, 1-9.

Demirbas E, Kobya M, Senturk E, Ozkan T. 2004. Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water SA*, **30**, 533-540.

Demirbas E, Kobya M, Senturk E, Ozkan T. 2004. Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water S. A.*, **30**, 533-540.

Gao P, Chen X, Shen F, Chen G. 2005. Removal of chromium (VI) from wastewater by combined electrocoagulation–electroflotation without a filter. *Separation and Purification Technology*, **43**, 117-123.

Government of Pakistan. 1997. National Environmental Quality Standards - Pakistan Environmental Legislation.

Gzara L, Dhahbi M. 2001. Removal of chromate anions by micellar-enhanced ultrafiltration using cationic surfactants. *Desalination*, **137**, 241-250.

Hoch LB, Mack EJ, Hydutsky BW, Hershman JM, Skluzacek JM, Mallouk TE. 2008. Carbothermal synthesis of carbon-supported nanoscale zero-valent iron particles for the remediation of hexavalent chromium. *Environmental Science & Technology*, **42**, 2600-2605.

- Hu J, Chen G, Lo IMC.** 2005. Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. *Water Research*, **39**, 4528-4536.
- Lackovic JA, Nikolaidis NP, Dobbs GM.** 2000. Inorganic arsenic removal by zero-valent iron. *Environmental Engineering Science*, **17**, 29-39.
- Malkoc E.** 2006. Ni (II) removal from aqueous solutions using cone biomass of *Thuja orientalis*. *Journal of Hazardous Materials*, **137**, 899-908.
- Malkoc E, Nuhoglu Y.** 2005. Investigations of nickel (II) removal from aqueous solutions using tea factory waste. *Journal of Hazardous Materials*, **127**, 120-128.
- Malkoc E, Nuhoglu Y.** 2007. Potential of tea factory waste for chromium (VI) removal from aqueous solutions: thermodynamic and kinetic studies. *Separation and Purification Technology*, **54**, 291-298.
- McAnally S, Benefield L, Reed RB.** 1984. Nickel removal from a synthetic nickel-plating wastewater using sulfide and carbonate for precipitation and coprecipitation. *Separation Science and Technology*, **19**, 191-217.
- Monser L, Adhoum N.** 2002. Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. *Separation and Purification Technology*, **26**, 137-146.
- Owlad M, Aroua MK, Daud WAW, Baroutian S.** 2009. Removal of hexavalent chromium-contaminated water and wastewater: A review. *Water, Air and Soil Pollution*, **200**, 59-77.
- Panneerselvam P, Morad N, Tan KA.** 2011. Magnetic nanoparticle (Fe₃O₄) impregnated onto tea waste for the removal of nickel (II) from aqueous solution. *Journal of Hazardous Materials*, **186**, 160-168.
- Park SJ, Jang YS.** 2002. Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr (VI). *Journal of colloid and interface science*, **249**, 458-463.
- Pehlivan E, Altun T.** 2008. Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell. *Journal of Hazardous Materials*, **155**, 378-384.
- Rafatullah M, Sulaiman O, Hashim R, Ahmad A.** 2009. Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. *Journal of Hazardous Materials*, **170**, 969-977.
- Rangsivek R, Jekel M.** 2005. Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibria, processes and implications for stormwater runoff treatment. *Water Research*, **39**, 4153-4163.
- Rengaraj S, Joo CK, Kim Y, Yi J.** 2003. Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H. *Journal of Hazardous Materials*, **102**, 257-275.
- Royle H.** 1975. Toxicity of chromic acid in the chromium plating industry. *Journal of Hazardous Materials*, **10**, 39-53.
- Shaikh MS, Qureshi K, Bhatti I.** 2011. Utilization of tea waste for the removal of arsenic (III) from aqueous solution. *Sindh Univ. Res. Jour. (Sci. Ser.)*, **43**, 97-104.
- Uddin MT, Islam MA, Mahmud S, Rukanuzzaman M.** 2009. Adsorptive removal of methylene blue by tea waste. *Journal of Hazardous Materials*, **164**, 53-60.
- Veglio F, Beolchini F.** 1997. Removal of metals by biosorption: A review. *Hydrometallurgy*, **44**, 301-316.

Wang Y, Wang X, Wang X, Liu M, Wu Z, Yang L, Xia S, Zhao J. 2013. Adsorption of Pb (II) from aqueous solution to Ni-doped bamboo charcoal.

Journal of Industrial and Engineering Chemistry, **19**, 353-359.