Removal of Chromium and Nickel from Electroplating Wastewater using Magnetite Particulate Adsorbent: (1) Effect of pH, Contact Time and Dosage, (2) Adsorption Isotherms and Kinetics

Donatus Dube[1], Champaklal T. Parekh[1] & Bothwell Nyoni[1]

[1] Department of Applied Chemistry, National University of Science & Technology, Bulawayo, Zimbabwe

Correspondence: Donatus Dube, Department of Applied Chemistry, National University of Science & Technology, Bulawayo, P.O. Box AC 939, Ascot, Zimbabwe. Tel: 263-928-2842. E-mail: donatus.dube@nust.ac.zw

Abstract

Wastewater discharged into municipal sewer systems from electroplating process plants contains a heavy load of metal ions and often requires pre-discharge treatment. Treatment of wastewater to reduce the concentration of metal ions employing an adsorption process has been studied using a wide range of adsorbents. In this work, the concentrations of chromium and nickel ions in wastewater samples from a local electroplating shop were found to be above the limits set out by the Bulawayo City Council, and the Environmental Management Agency, a statutory agency under the Ministry of Environment and Tourism, Government of Zimbabwe. Furthermore, the removal of chromium and nickel ions from the wastewater using magnetite as an adsorbent is studied. Magnetite particulate adsorbent used in this experiment has demonstrated to be an effective adsorbent material. At the optimum process operating pH of 4 – 7 the absorbent was able to achieve removal rates of up to 99% for chromium and 98% for nickel. The adsorption processes for chromium and nickel have been proven to be physical in nature using the Dubinin-Radushkevich isotherm model. Also, the adsorption kinetics data fit well with pseudo second-order kinetic model.

Keywords: adsorption, chromium, electroplating, magnetite, nickel, wastewater

1. Introduction

Nickel, chrome, copper and bronze plating are some of the methods employed to enhance the durability and attractiveness of metallic products. There are many electroplating plants operating in different municipalities. Such electroplating plants however have the potential of generating wastewater that contains substantial amounts of heavy metals like copper, nickel, zinc, chromium , cadmium, etc. High levels of some of these heavy metals may result in poisoned municipal waters that may be a hazard to both the humans and the environment. For example high concentrations of chromium (in excess of 0.5 ppm) particularly in its hexavalent form may result in human carcinogenic and mutagenic effects (Sarkar & Saha, 1992; Goel, 1997). Copper administered in small quantities is important to the human body because it helps build strong bones, healthy skin and hair. However, high concentration of copper (above 3.0 ppm) in drinking water may lead to liver, kidney and brain damage. Copper has a lesser negative effect on humans as compared to other metals such as lead and chromium (Khan, 2011). The intake of nickel in considerable concentrations may cause formation of free radicals in body tissue which leads to various DNA complications (Forgacs et al., 2012).

Treatment of industrial wastewater is an important part of efforts aimed at reducing effluent toxicity to levels that are tolerable before discharging into the water systems and water bodies. A number of measures and experimentations have been undertaken to reduce the level of toxic heavy metals in industrial wastewater. Many authors have reported on the effectiveness of powdered activated carbon (PAC) in the adsorption of copper and chromium from aqueous solutions. Tewari et al. (1989) report that adsorption of chromium and copper by PAC is dependent upon the pH. Adsorption is at its peak at pH 5.5 and 8.0. Patil et al. (2006) compared the use of PAC with Indian powdered babhul bark (PBB) in the removal of nickel and reported that although PAC achieved higher

removal rates (> 80%) of Ni than PBB the later was more economical to use as there is no requirement for regeneration as it can easily be disposed of. The use of magnetite nanoparticles has also been studied extensively (Carlos et al., 2013). Yean et al. (2005) found that adsorption of heavy metals especially arsenic and lead onto nano-sized magnetite increased with decreasing particle diameter. Copper can be removed using bentonite reacted with ammonium chloride (Abdelhamid et al., 2012) while fly ash was found to remove copper by 62% - 98% (Luo et al., 2011). Karega et al. (2015) studied batch and column adsorption of chromium from electroplating wastewater by ion exchange method. The study concluded that ion exchange method has the capacity to remove chromium by 80% at column bed height of 14 cm and a flowrate of 1 ml/min.

In the present study an electroplating unit employing copper and nickel plating was selected for wastewater process evaluation and removal of chromium and nickel to acceptable levels. The chemical treatment currently employed was found inadequate to reduce the levels of the heavy metals to acceptable limits of the Bulawayo City Council (BCC) in which the plant operates. The metal ion discharge is also above the Environmental Management Agency (EMA) levels. For example characterization of effluent discharge sampled on 30/09/2013 revealed a concentration of chromium to be 12.47 ppm against a BCC standard of < 10 mg/L and EMA < 2.0 ppm and Ni to be 29.8 ppm against BCC target of < 10 ppm and EMA < 0.9 ppm. Such high levels of chromium and nickel in the sampled effluent is an indicator of the inadequacy of the current treatment method. The current study was motivated by the desire to augment the current treatment method so that the discharged wastewater has no potential of poisoning BCC water bodies and boreholes.

2. Method

The study was performed with wastewater obtained from rinsing tanks of an electroplating plant in Bulawayo City Council (BCC) industrial area, Zimbabwe.

2.1 Plant Description

The electroplating units employed at the plant are of two types, Cyanide - Copper plating and Nickel plating. Prior to electroplating, the materials being processed first go through degreasers and acid pickling with 50% HCl by volume. These are then rinsed with water, neutralized with NaOH and $NaNO_3$, etched and then thoroughly rinsed with hot water.

a)   Cyanide - Copper plating
A combination of cyanide and copper is employed in this unit. Materials thus electroplated are thoroughly rinsed with hot water. This is then followed by oxidation using potassium polysulfide. The materials are then subjected to another rinse with hot water before lacquering, employing a ratio of one part passivator water and two parts montalak coating. Effluent water from the rinsing is channeled to the effluent treatment section of the electroplating plant.

b)   Nickel plating
This electroplating unit employs nickel and chrome. The electroplated materials are neutralized with sodium meta-bisulphite prior to a thorough rinse with water. The wastewater (containing nickel and chromium) emanating from this unit is pumped to the effluent treatment section of the electroplating plant.

2.2 Existing treatment process

Figure 1 shows the treatment process. The first stage of effluent treatment involves destroying the complexing agent e.g. cyanide salts before metal precipitation as hydroxides by oxidation with sodium hypochlorite in alkaline conditions for waste water with concentrations up to 1000 ppm cyanides salts.

$$CN^-_{(aq)} + OCl^-_{(aq)} \rightarrow OCN^-_{(aq)} + Cl^-_{(aq)} \tag{1}$$
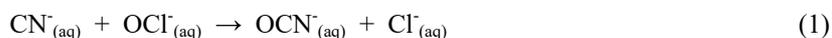
Step 1

Conversion of cyanide to cyanate ion in a two reaction sequence at pH above 10. Reaction time is from 30 minutes to 2 hours.

Step 2

This involves oxidation of cyanide with hypochlorite at pH 8.5 to increase the kinetics, with a reaction time of from 10 minutes to 1 hour. At this stage the pH of the effluent is checked and adjusted to the optimum pH at which metals will precipitate. The metal composition of the effluent is determined and the effluent is treated accordingly. The hexavalent chromium (Cr^{+6}) is reduced to the trivalent state (Cr^{+3}) using sodium bisulfide. The trivalent chromium is then precipitated using calcium hydroxide at pH 7.5. Copper is precipitated as a hydroxide at a pH range of 9-10. Copper cyanide is removed by activated carbon since presence of cyanide as ammonia

may interfere with the precipitation of copper. Nickel is precipitated at a pH range of 10-11.

After treatment for the respective metals, a flocculating agent is introduced to increase the speed of settling. Settlement of sludge by gravity is allowed to take place for about 2 hours depending on the settling velocity of precipitates produced. The wastewater (effluent) is then released to the final precipitation tank, after which the water is channeled into the municipal sewage system at a discharge rate of 9 m^3 for a period of 2 days.
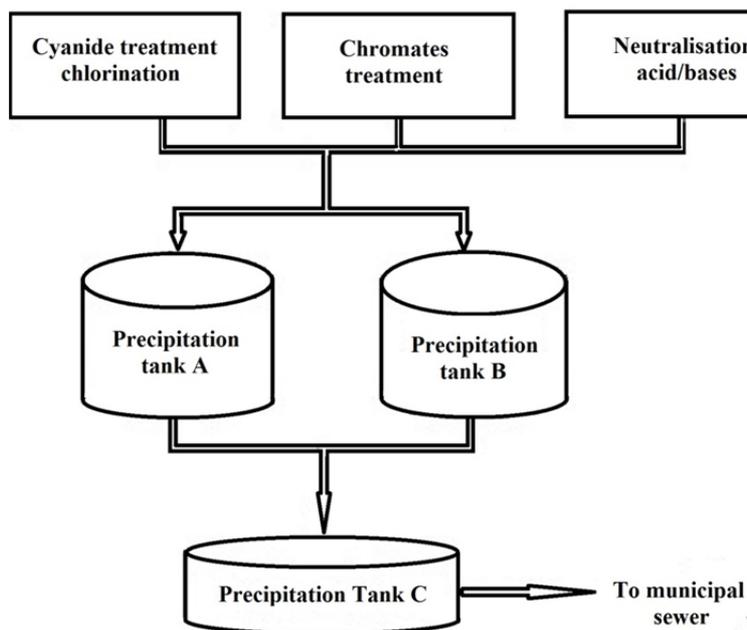
Figure 1. Current effluent treatment flowchart

2.3 Method of Analysis

Magnetite powder (Cermag10.1) with grain size < 50μm prepared under patent at the Department of Applied Chemistry Laboratory, National University of Science and Technology, Bulawayo, Zimbabwe, was used as the adsorbent material. Distilled water was used for the preparation of reagents and analyses. Wastewater generated from the two electroplating precipitation (holding) tanks A and C (Figure 1) was sampled into PET (Polyethylenetrephthalate) containers and labeled sample S1 and sample S2 for characterization respectively. The containers were sealed and preserved prior to analysis and treatment.

All parameters were measured in accordance with standard procedures suggested in the Standard Methods for the Examination of Water and Wastewater, (American Public Health Association [APHA], 1999). Chromium (as total Cr) was determined by colorimetric method using UV-Vis Lambda 2 model. Nickel was analysed using the Spec 20 Atomic Absorption Spectrometer (AAS). pH and conductivity values were directly read from a Multi meter (PCS Testr 35).

2.4 Effect of pH on Adsorption

A known mass of the adsorbent was added to six 250 ml volumetric flasks containing a sample of known metal ion concentration. The pH of the solutions was adjusted to 3, 4, 5, 6, 7 and 8 using 0.1M HCl or NaOH and monitored using a pH meter (Corning pH meter 220, USA). The mixtures were agitated at 150 rpm at room temperature and normal pressure (25 °C) for 60 minutes. At the end of the experiment, the solution was filtered to remove the adsorbent and the metal ion concentration analysed using AAS. An average of three AAS measurements was taken as the residual metal ion concentration value.

2.5 Effect of pH on Adsorption

A known mass of the adsorbent was added to six 250 ml volumetric flasks containing a sample of known metal ion concentration. The pH of the solutions was adjusted to 3, 4, 5, 6, 7 and 8 using 0.1M HCl or NaOH and monitored using a pH meter. The mixtures were agitated at 150 rpm at room temperature and normal pressure (25 °C) for 60 minutes. At the end of the experiment, the solution was filtered to remove the adsorbent and the

metal ion concentration analysed using AAS. An average of three AAS measurements was taken as the residual metal ion concentration value.

2.6 Effect of Adsorbent Dosage

Varying masses of the adsorbent were added to 1000 ml of a 12.2 and 29.8 ppm chromium and nickel ion solution, respectively. The mixture was agitated at 150 rpm for a certain time period, after the agitation was stopped the mixture was left for an extended time period up to 48 hours. The mixture was filtered and the residual metal ion concentrations of the filtrate were determined using AAS. An average of three AAS readings was taken as the residual metal ion value.

2.7 Batch Adsorption Study

A known mass of adsorbent was added to 500 ml of metal ion containing solution. The mixtures were agitated at 150 rpm for more than 60 minutes at an optimum pH determined by initial experiments. The experiment was repeated for different initial metal concentrations. The equilibrium concentrations of the metal ion in each sample were determined using AAS after filtration. The amount of metal adsorbed by the adsorbent at equilibrium (q_e) and the percentage removal were calculated using Equations (2) and (3) respectively.

$$q_e = \frac{(C_i - C_e)V}{M} \tag{2}$$

$$removal \ (\%) = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \tag{3}$$

where C_i and C_e are the initial and equilibrium concentrations in ppm of the metal ions respectively, V is the volume in litres of the solution and M is the mass in grams of the adsorbent.

3. Results and Discussion

3.1 Wastewater Characterization

Characterization results for the effluent samples taken on 30/09/2013 are shown on Table 1. The results for electroplating shop waste water (Table 1) indicate that the concentration values of chromium, nickel and conductivity for the two samples collected, were way above the maximum allowable limits as set out by BCC and EMA. Such high values of toxic chromium and nickel is a cause for concern as it has a potential of poisoning water that BCC processes for domestic use. Moreover, the high values are an indicator of the ineffectiveness of the effluent treatment methods currently employed at the plant. The high levels of heavy metals in the effluent from the electroplating plant prompted the researchers to investigate effectiveness of an adsorption method for further treating the effluent to bring it to the levels required by the authorities.

Table 1. Characterization results for waste water samples from electroplating shop.

Sample ID	Cr (ppm)	Ni (ppm)	pH	Conductivity (μS/cm)
S1	12.17	29.8	8.35	1963
S2	10.53	263.0	8.05	1448
BCC Standard	< 10	< 10	6 – 12	≤ 300
EMA Standard	< 2	< 0.9	6 – 10	< 2 000

3.2 Effect of pH on Metal Adsorption

The results displayed in Figure 2 reveal that the optimum operating pH for the wastewater adsorption process is in the range pH 6 to 7. The results are in agreement with previous research (Marwani et al., 2013; Ibrahim & Jimoh, 2011) where the optimum pH for the adsorption of metal ions falls in the range 5 to 7. At low pH values, the solution is highly protonated (H^+ ions) which results in a high positive charge density on the surface of the adsorbent which repels the positively charged metal ions. At higher pH values the solution is less protonated because of dominant negatively charged hydroxide ions. The surface of the adsorbent attains a high negative charge density which attracts more metals ions.
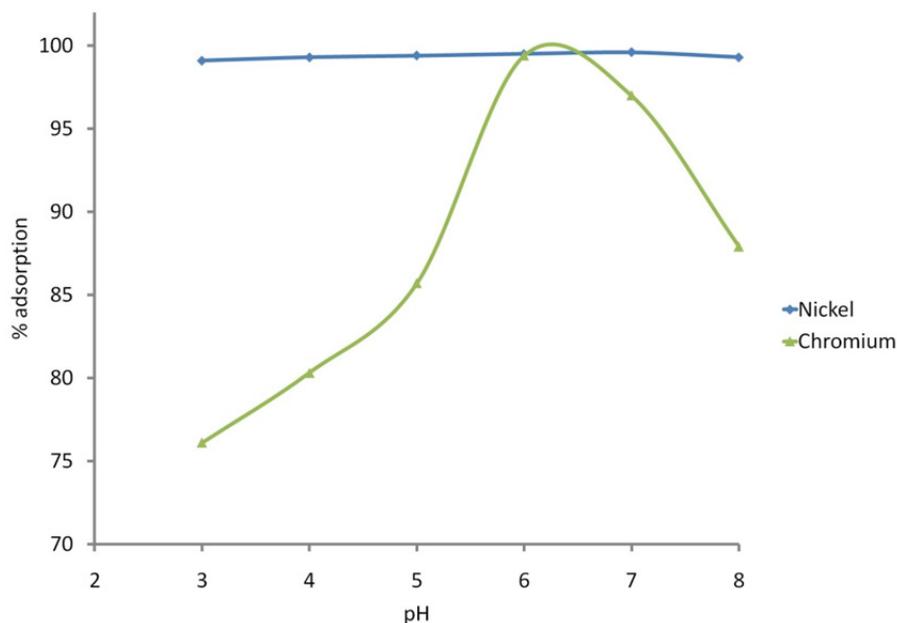
Figure 2. Effect of pH on adsorption of Cr ions

3.3 Effect of Adsorbent Dosage on Metal Adsorption

Table 2. Adsorption results for chromium in electroplating wastewater (Sample S1)

Dosage (g/L)	10 minutes stirring			30 minutes stirring			60 minutes stirring		
	12 h contact	24 h contact	48 h contact	12 h contact	24 h contact	48 h contact	12 h contact	24 h contact	48 h contact
0	12.20	12.2	12.17	12.19	12.17	12.17	12.20	12.15	12.16
10	9.82	7.02	5.33	9.76	7.02	5.32	10.01	7.00	5.31
20	9.53	6.45	5.04	9.42	6.43	4.99	9.21	6.43	4.98
30	9.02	6.04	4.09	8.97	6.04	4.01	8.88	5.94	4.00
40	8.48	4.87	3.72	8.23	4.88	3.58	7.92	4.80	3.58
50	8.13	4.15	2.07	7.77	4.19	2.07	5.04	4.17	2.07
60	7.91	3.00	1.93	7.59	3.09	1.92	4.31	3.01	**1.90**

Table 3. Adsorption results for nickel in electroplating wastewater (Sample S1)

Dosage (g/L)	10 minutes stirring			30 minutes stirring			60 minutes stirring		
	12 h contact	24 h contact	48 h contact	12 h contact	24 h contact	48 h contact	12 h contact	24 h contact	48 h contact
0	30.2	29.8	29.8	30.0	29.4	29.8	30.0	29.6	29.8
10	28.6	20.0	16.0	28.2	20.4	16.0	27.2	20.6	15.2
20	27.0	18.2	14.4	25.2	18.2	14.2	26.2	17.4	14.2
30	24.2	14.8	13.2	21.8	14.6	12.8	24.0	14.6	12.6
40	20.2	10.4	8.8	18.6	10.4	8.8	22.2	10.2	8.0
50	16.2	7.8	5.8	11.2	8.0	5.2	19.8	8.6	4.8
60	10.8	4.0	2.6	8.4	3.8	1.6	17.8	3.0	1.6

The amount of adsorbent in a solution is related to the number of active sites available for an adsorption process; therefore the metal uptake is expected to increase with increase in amount of adsorbent (Sartape et al., 2013). This trend is clear in Table 2 and 3, the residual metal ion concentration decreases down the table columns as the dosage is increased. As the contact time is increased from 12 to 48 hours, a decrease in the final concentration of the metal ion is noted. The information in Tables 2 and 3 does not show any evidence of desorption even after prolonging the adsorption without any agitation.

3.4 Effect of Contact Time on Metal Ion Adsorption

Contact time is an important parameter for adsorption processes. A short contact time means less chances of attaining equilibrium and a longer contact time means the higher the chances of attaining equilibrium. More time after reaching equilibrium may result in the metal-adsorbent complexes formed breaking down into individual species. The graphs on Figure 3 show the adsorption of chromium and nickel ions, as a function of contact time for varying concentrations. The equilibrium for chromium adsorption is attained after 50 minutes. The relationship between initial concentration and the percentage metal removal is also shown in Figure 3. The magnitude of the difference between the initial and equilibrium concentration, referred to as the concentration gradient directly affects the amount of metal adsorbed. The results presented in Figure 3 indicate that as the concentration of the solution is increased the amount of metal ion adsorbed per unit adsorbent mass increases. The equilibrium amount of chromium increased from 0.017 to 0.083 mg/g with an increase of 2 to 10 ppm chromium ion concentration. Also for the same increase of nickel ion concentration, the equilibrium amount of nickel increased from 0.02 to 0.12 mg/g.
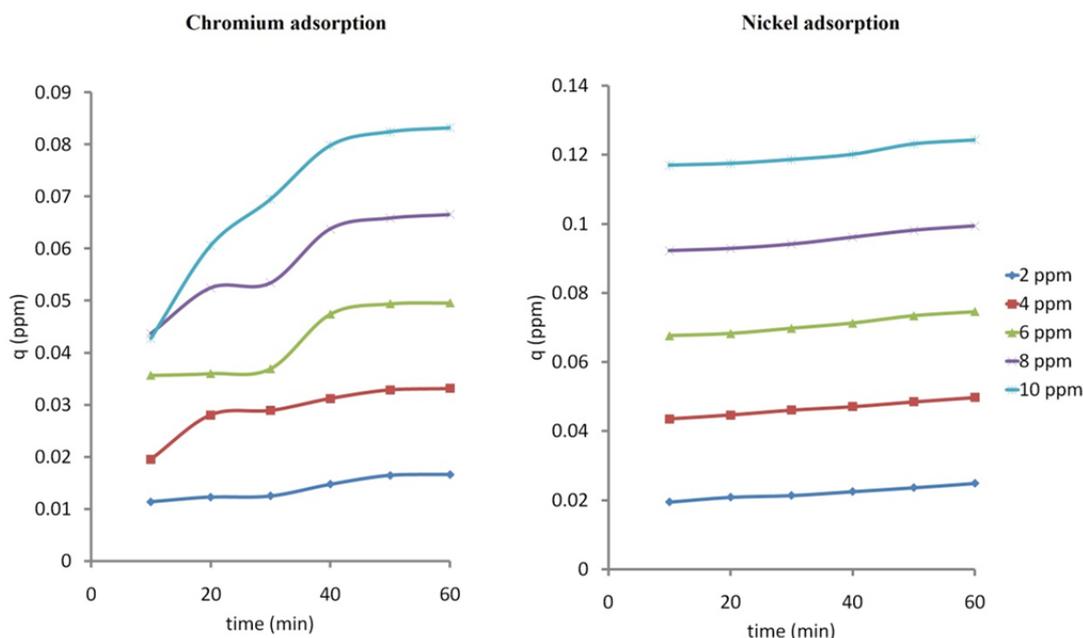
Figure 3. Effect of contact time on adsorption of chromium and nickel metal ion

3.5 Adsorption Isotherms

The experimental data was fitted into four adsorption models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models, these models have been widely used to describe metal ion adsorption processes. The Langmuir isotherm was developed based on the assumption that each site can accommodate only one molecule of the adsorbate with no molecule migration and the energy of adsorption is constant all over the surface (Richardson et al., 2002). The maximum adsorption occurs when the monolayer of adsorbate molecules becomes saturated on the adsorbent surface and having a constant energy of adsorption. The linear form of the model is:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}bC_e}$$

(4)

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), q_{max} is the maximum adsorption capacity on monolayer adsorbent saturation (mg/g), C_e is the equilibrium metal ion concentration in solution (ppm), b is the Langmuir affinity constant (L/mg). A plot of $1/q_e$ against $1/C_e$ for each metal ion gave a straight line with a slope of $1/q_{max}b$ and y-intercept of $1/q_{max}$ (figures not shown). Furthermore the dimensionless quantity, the separation factor, R_L (Equation 4) can be used to confirm the favourableness of the adsorption process for the conditions used in the experiment.

$$R_L = \frac{1}{1 + bC_0}$$

(5)

where C_0 is the highest initial metal ion concentration.

The Freundlich isotherm was developed so as to model the multilayer adsorption on heterogeneous surfaces (Freundlich, 1906). The linear form of the model is:

$$Inq_e = Ink_f + \left(\frac{1}{n}\right) InC_e$$

(6)

where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), C_e is the concentration of the adsorbate at equilibrium (ppm), k_f is the Freundlich constant related to adsorption capacity and n is a dimensionless heterogeneity coefficient. A plot of lnq_e against InC_e for each metal ion gave a straight line with a slope of $1/n$ and y-intercept of Ink_f (figure not shown)

The effects of adsorbate interactions on adsorption were investigated and it was noted that in these interactions the energy of adsorption of all the molecules in a layer is a function of temperature and it will decrease linearly as the adsorbent surface is loaded with adsorbate. The Temkin isotherm has been used in gas and protein adsorption studies (Johnson & Arnold, 1995). The linear form of the model is given as (Ho et al., 2002)

$$q_e = \frac{RT}{b} InA + \frac{RT}{b} InC_e$$

(7)

where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), C_e is the concentration of the adsorbate at equilibrium (ppm), b is the Temkin constant related to heat of adsorption (J/mol), A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol.K) and T is the absolute temperature (K). A plot of q_e against InC_e for each metal ion should give a straight line with gradient RT/b (figure not shown).

The Dubinin-Radushkevich model is used for adsorption of metal ions onto microporous carbonaceous materials. The model can be used for characterizing the adsorbent material and estimating the average free energy value for the adsorption process (Areco et al., 2014). The linear form of the equation is given as:

$$Inq_e = InK_{DR} - \beta\varepsilon^2 , \quad \text{where}$$

(8)

$$\varepsilon = RTIn\left(1 + \frac{1}{C_e}\right)$$

(9)

where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), C_e is the concentration of the adsorbate at equilibrium (ppm), K_{DR} is the adsorption capacity of the adsorbent per unit weight (mol/kg) and ε is a constant related to the energy of adsorption. A plot of lnq_e against ε^2 will give a straight line with a slope of $-\beta$ and y-intercept of InK_{DR} (figure not shown). Furthermore the mean energy of adsorption can be evaluated from the equation:

$$E = \frac{1}{\sqrt{2\beta}}$$

(10)

The results shown in Table 2 show that the adsorption of chromium is best described by the Langmuir isotherm with q_{max} = 14.08 mg/g and the separation factor (R_L value) of 0.485 which shows that the process is favorable ($R_L < 1$). Nickel adsorption follows the Temkin isotherm model. The constants A and b are reported as 9.94 L/g and 8880 J/mol respectively, for nickel. The value of the Temkin constant, b, (= 8880 J/mol for nickel) is a direct measure of the maximum binding energy for the metal ion's adsorption. It can be deduced that the interactions between the metal ions and the magnetite adsorbent are more pronounced for chromium than for nickel because of the huge difference between the values of the Temkin constant, b, (= 8880 and 61939 J/mol for nickel and chromium, respectively). It has been reported that if the mean energy of adsorption is less than 8000 J/mol, the adsorption process is physical in nature (Ceyhan & Baybas, 2001). The R^2 values for the Dubinin-Radushkevich plots for the two metals are high ($R^2 > 0.9$). Therefore, calculated values for the mean energy of adsorption extracted from the Dubinin-Radushkevich model can be used to conclude that the adsorption process is physical in nature.

Table 4. Adsorption isotherm models parameters

		Chromium	Nickel
(1) Langmuir			
	q_{max}(mg/g)	14.08	0.157
	b (L/mg)	0.106	92.25
	R_L	0.485	0.001
	R^2	0.986	0.840
(2) Freundlich			
	n	0.945	0.218
	k_f(mg/g)	0.803	708.4
	R^2	0.976	0.928
(3) Temkin			
	T (K)	298	298
	A (L/g)	57.4	9.94
	b (J/mol)	61939	8880
	R^2	0.868	0.948
(4) Dubinin-Radushkevich			
	β	3×10^{-8}	2×10^{-7}
	K_{DR}	0.189	17.37
	E (J/mol)	4082	1581
	R^2	0.952	0.938

3.6 Adsorption Kinetics

The experimental data was tested for two kinetic models, i.e. the pseudo first-order and pseudo second-order kinetic models which have been used extensively to describe the kinetics of metal ion adsorption processes (Ho & McKay, 1998; Ho & McKay, 2000; Al-Qunaibit et al., 2005)

The adsorption process was tested for pseudo first-order kinetics by using a model which is usually written as follows (Ho & McKay, 1998

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{11}$$

where q_t is the amount of metal ion adsorbed (mg/g) at time t, k_1 is the pseudo first-order rate constant (min^{-1}). If the process follows pseudo first-order kinetics, a plot of log (q_e - q_t) against t (Figures not shown) should give a straight line enabling the calculation of k_1 and q_e from the gradient and y-intercept respectively. The model parameters are shown in Table 5. It is clear that the adsorption of chromium and nickel does not follow pseudo first-order kinetics model because the R^2 values are not satisfactory and the calculated q_e values do not match with the experimental values. The coefficients of determination for copper model fitting are satisfactory, however the calculated q_e values do not match with the experimental values and therefore it is concluded that the adsorption process does not follow pseudo first-order kinetics.

The pseudo second-order kinetic model is written as (Ho & McKay, 2000)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{12}$$

where k_2 is the pseudo second-order rate constant (g/mg min). A plot of t/q_t against t (Figure 4) gives a straight line that enables the determination of q_e from the slope and k_2 from the y-intercept. The experimental data for the adsorption of the three metals fits the pseudo-second order kinetic model with high R^2 values. It is clear from Table 5 that the experimental and calculated values of q_e for the three are in good agreement.

Table 5. Pseudo first-order and pseudo second-order kinetic model parameters (*Conditions:* 150 rpm agitation, temperature = 298K)

		Pseudo first-order kinetics			**Pseudo second-order kinetics**		
C_i	$q_{e,\,exp}$	k_1	$q_{e,\,cal}$	R^2	k_2	$q_{e,\,cal}$	R^2

(ppm)	(mg/g)	(min^{-1})	(mg/g)		(g/mg.min)	(mg/g)	
Chromium							
2	0.016	0.074	0.019	0.738	4.82	0.019	0.970
4	0.033	0.085	0.036	0.905	2.99	0.038	0.997
6	0.049	0.104	0.092	0.772	1.65	0.057	0.961
8	0.066	0.085	0.079	0.886	1.41	0.077	0.988
10	0.083	0.097	0.152	0.944	0.66	0.105	0.996
Nickel							
2	0.025	0.032	0.008	0.933	7.44	0.026	0.993
4	0.050	0.037	0.011	0.941	7.18	0.051	0.998
6	0.075	0.039	0.014	0.762	5.97	0.076	0.998
8	0.099	0.041	0.014	0.854	5.99	0.101	0.999
10	0.040	0.040	0.014	0.762	5.70	0.126	0.999
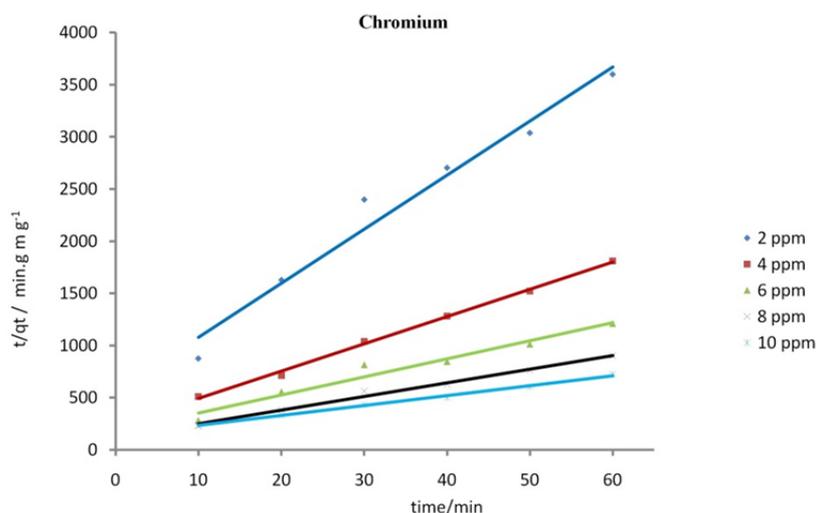
Figure 4. Pseudo second-order plot for the adsorption of nickel onto magnetite (*Conditions:* 150 rpm agitation, temperature = 298K)
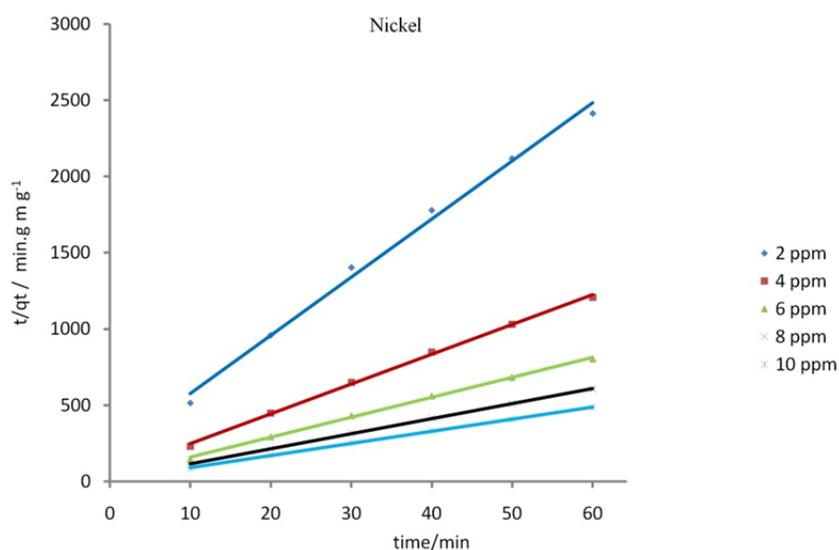
Figure 5. Pseudo second-order plot for the adsorption of chromium onto magnetite (*Conditions:* 150 rpm agitation, temperature = 298K)

4. Conclusion

Analysis of wastewater samples from the electroplating plants revealed that the chromium metal ion concentrations are way above the recommended maximum limits as per BCC and EMA standards. The use of magnetite as an adsorbent for the removal of chromium in the treatment of wastewater from electroplating plants has been demonstrated to be feasible. Batch adsorption studies revealed that the adsorption fitted well with Langmuir isotherm for chromium and Temkin isotherm for nickel. The kinetics for both nickel and chromium adsorption follow a pseudo second-order model.

Acknowledgments

References

Abdelhamid, B., Ourari, A., & Ouali, M. S. (2012). Copper (II) ions removal from aqueous solution using bentonite treated with ammonium chloride. *American Journal of Physical Chemistry, 1*(1), 1-10. http://dx.doi.org/10.11648/j.ajpc.20120101.11

Al-Qunaibit, M. H., Mekhemer, W. K., & Zaghloul, A. A. (2004). The adsorbtion of Cu(II) ions on bentonite – a kinetic study. *Journal of Colloid Interface Science, 283*, 316-321. http://dx.doi.org/10.1016/j.jcis.2004.09.022

American Public Health Association. (1999). *Standard Methods for the Examination of Water and Wastewater*.

Areco, M. M., Rodriguez, M. C., & Afonso, M. S. (2014). Asterococcus superbus as a biosorbent of copper, zinc, cadmium and lead: adsorption isotherm and kinetic modelling. *International Journal of Environment and Health, 7*(1), 83-99. http://dx.doi.org/10.1504/ijenvh.2014.060126

Carlos, L., Einschlag, F. S. G., González, M. C., & Mártire, D. O. (2013). Applications of Magnetite Nanoparticles for Heavy Metal Removal from Wastewater. In F. S. G. Einschlag (Ed.), *Waste Water - Treatment Technologies and Recent Analytical Developments,* (pp. 63-78). Rijeka: Croatia, Intech. http://dx.doi.org/10.5772/54608

Ceyhan, O., & Baybas, D. (2001). Adsorption of Some Textile Dyes by Hexadecyltrimethylammomiun Bentonite. *Turkish Journal of Chemistry, 25*(2001), 193-200. http://dx.doi.org/10.1155/2013/681769

Cotten, G. B., Navratil, J. D., & Eldredge, H. B. (1999, Mar). *Magnetic adsorption method for the treatment of metal contaminated aqueous waste.* Paper presented at the Waste Management Conference, Tucson, Arizona. Retrieved from http://www.wmsym.org/archives/1999/index.html

Forgacs, Z., Massanyi, P., Lukac, N., & Somosy, Z. (2012). Reproductive toxicology of nickel – review. *Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances and Environmental Engineering, 47*(9), 1249-1260. http://dx.doi.org/10.1080/10934529.2012.672114

Freundlich, H. M. F. (1906). Uber die adsorption in losungen. *Z. Physico Chemica, 57*(1906), 384-470.

Goel, P. K. (1997). *Water pollution, causes, effects and control*. (2nd ed.). New Delhi, New Age International.

Ho, Y. S., & McKay, G. (1998). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environment Protection, 76*(4), 332-340. http://dx.doi.org/10.1205/095758298529696

Ho, Y. S., & McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Research*, *34*(3), 735-742. http://dx.doi.org/10.1016/S0043-1354(99)00232-8

Ho, Y. S., Porter, J. F., & McKay, G. (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water, Air, Soil Pollution, 14*(1/4), 1-33. http://dx.doi.org/10.1023/A:1021304828010

Hur, J., Shin, J., Yoo, J., & Seo, Y. S. (2015). Competitive Adsorption of Metals onto Magnetic Graphene Oxide: Comparison with Other Carbonaceous Adsorbents. *The Scientific World Journal, 2015*, 1-11. http://dx.doi.org/10.1155/2015/836287

Ibrahim, M. B., & Jimoh, W. L. O. (2011). Bioremediation of Ni(II) and Cd(II) from aqueous solution. *Indian Journal of Science & Technology, 4*(5), 333-340. http://dx.doi.org/10.17485/ijst/2011/v4i5/30047

Johnson, R. D., & Arnold, F. H. (1995). The Temkin isotherm describes heterogeneous protein adsorption. *Biochim. Biophys. Acta., 1247*(2), 293-297. http://dx.doi.org/10.1016/0167-4838(95)00006-G

Karega, S., Bhargavi, M., & Divekar, S. V. (2015). Treatment of wastewater from chrome plating industry by ion exchange method. *International Journal of Research in Engineering and Technology, 4*(7), 393-401. http://dx.doi.org/10.15623/ijret.2015.0407063

Khan, T. A. (2011). Trace elements in the drinking water and their possible health effects in Aligarh City, India. *Journal of Water Research and Protection, 3*, 552-530. http://dx.doi.org/10.4236/jwarp.2011.37062

Luo, J., Shen, H., Markstrom, H., Wang, Z., & Niu, Q. (2011). Removal of Cu^{2+} from aqueous solution using fly ash. *Journal of Minerals & Materials Characterisation & Engineering, 10*(6), 561-571. http://dx.doi.org/10.4236/jmmce.2011.106043

Marwani, H. M., Albishri, H. M., Jalal, T. A., & Soliman, E. M. (2013). Study of isortherm and kinetic models of lanthanum adsorption on activated carbon loaded with recently synthesized Schiff's base. *Arabian Journal of Chemistry, 1*(1), 1-9. http://dx.doi.org/10.1016/j.arabjc.2013.01.008

Patil, S. J., Bhole, A. G., & Natarajan, G. S. (2006). Scavenging of Ni(II) metal ions by adsorption on PAC and Babhul Bark. *Journal of Environmental Science & Engineering, 48*(3), 203-208. http://dx.doi.org/10.5897/AJPAC2014.0591

Richardson, J. F., Harker, J. H., & Backhurst, J. R. (2002). *Coulson and Richardson's Chemical Engineering, Particle Technology and Separation Processes.* (5th edn.). Oxford, Butterworth-Heinemann.

Sarkar, R., & Saha, N. (1992). *General & Inorganic Chemistry, Part I.* (2nd ed.). New Delhi, New Central Book Agency.

Sartape, A. S., Mandhare, A. M., Jadhav, V. V., Raut, P. D., Anuse, M. A., & Kolekar, S. S. (2013). Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arabian Journal of Chemistry, 1*(1), 1-10. http://dx.doi.org/10.1016/j.arabjc.2013.12.019

Yean, S., Cong, L., Yavuz, C. T., Mayo, J. T., & Colvin, V. L. (2005). Effect of magnetic particle size on adsorption and desorption of arsenite and arsenate. *Journal of Materials Research, 20*(12), 3255-3264. http://dx.doi.org/10.1557/jmr.2005.0403

Copyrights