

ADSORPTION FEASIBILITY IN THE Cr(TOTAL) IONS REMOVAL FROM WASTE PRINTING DEVELOPER

J. KIURSKI *
S. ADAMOVIĆ
I. OROS
J. KRSTIĆ
I. KOVAČEVIĆ

University of Novi Sad, Faculty of Technical Sciences
Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia

Received: 24/06/11
Accepted: 03/10/11

*to whom all correspondence should be addressed:
e-mail: kiurski@uns.ac.rs

ABSTRACT

In this article, the technical feasibility of various commercial adsorbents (activated carbon, clinoptilolite, and their mixture) for removal of Cr(total) ions from waste printing developer has been represent. Experimental tests were performed in laboratory batch mode. The adsorption data were analyzed using the Freundlich, Langmuir and Dubinin-Kaganer-Radushkevich (DKR) isotherm models. It was found that the Freundlich isotherm gave better results than the Langmiur and DKR models, with the corresponding correlation coefficients (R^2): 0.981, 0.996 and 0.997 for mixture (NZ+AC), AC and NZ, respectively. The adsorption capacities of Cr(total) ions followed the order: (NZ+AC)>AC>NZ. The adsorption efficiencies of Cr(total) ions removal were 38.5 to 39.9%. Due to easy availability and good efficiency, the mixture of clinoptilolite and activated carbon is an ideal adsorbents for removal of Cr(total) ions from waste printing developer.

KEYWORDS: Heavy metals, natural adsorbents, adsorption isotherms, batch mode, printing waste.

INTRODUCTION

Electroplating, metalworking and printing industries discharge large amounts of heavy metals, including chromium (Cr) ions, in their effluents. Several processing techniques are available to reduce the concentrations of heavy metals in wastewater, including precipitation, flotation, ionexchange, solvent extraction, adsorption, cementation onto iron, membrane processing, and electrolytic methods.

Adsorption onto activated carbon is a well-known method for removing toxic metal ions, but the high cost of activated carbon restricts its use in developing countries, with small factories in particular often being unable to support expensive wastewater treatment methods. Cheap and effective alternatives for the removal of heavy metals should reduce operating costs, reduce the prices of products, improve competitiveness, and benefit the environment. The adsorption abilities of a number of low-cost adsorbents (e.g., cheap zeolites, clay, coal fly ash, sewage sludge, agriculture waste and biomass) have been determined for the removal of heavy metals from wastewater (Thing-Chu Hsu, 2009; Babel and Kurniawan, 2003; Jiuhui, 2008; Kiurski *et al.*, 2008; 2009; 2010a; Oke *et al.*, 2008; Thompson *et al.*, 2001; Rožić *et al.*, 2004).

Processing of plates consumes three primary resources: chemistry to develop or process the plates, energy to run the processing unit, and water to rinse the plate, dilute the chemistry, or clean the unit. Similarly, processing generates waste which must be disposed of, in the form of spent chemistry, waste water, and containers. Each plate type and process consumes different amounts of these resources, depending on the imaging laser, emulsions used, and chemical and physical reactions required to develop or wash-up the plate. All waste matters are specialists in providing a one - stop waste chemical and hazardous waste disposal and recycling service of up to 99% of all printing waste, removing the need for multiple waste management suppliers (Thompson *et al.*, 2001). From

small independent printers to the larger multi national print and mailing suppliers, all waste matters can provide a tailored waste management service to ensure hazardous waste recycling problems are a thing of the past.

The role of printing developer in the plate or film development process is to convert the latent images to visible ones. The most present components of fresh printing developer are potassium silicate, sodium silicate, sodium carbonate, potassium hydroxide, D-sorbitol, sodium sulfite, potassium bromide, metol [4-(methylamino)phenol sulfate] and hydroquinone. After the development process, waste printing developer is enriched by plate surface compounds: novolac, organic polymeric binders, photosensitive compounds, dyes and some others. Heavy metal, chromium, found in waste printing developer comes from the dye residue.

Waste printing developer needs a proper treatment and disposal if its pH value is strongly alkaline (≥ 12.5). Thus it may be a potential hazard if discharged into water recipients. Also, cumulative organics considerably increase the chemical oxygen demand and the toxicity of waste. The requirements for an adequate treatment of waste developer are to be met, to prevent increased concentrations of some metals and organic pollutants from the printing industry (Rožić *et al.*, 2004; Vengris *et al.*, 2004).

The present study was undertaken to evaluate the efficiency of an activated carbon, clinoptilolite, and their mixture as adsorbents for removal of chromium ions in waste printing developer. In this paper, we have reported the applicability of the adsorption of chromium (total) ions onto desired natural adsorbents.

MATERIAL AND METHODS

Samples of fresh and waste printing developer were taken from the pre-press unit of a Novi Sad (Serbia) offset printing plant.

The adsorption of Cr(total) ions from waste printing developer was investigated using natural zeolite (NZ, clinoptilolite, High Tech zeolite producer, Turkey), activated carbon (AC, Norit Row 0.8 Supra, USA) and the mixture of NZ and AC (NZ+AC), as adsorbents (Kiurski *et al.*, 2010b).

All the chemicals were of analytical reagent grade (Merck, Germany). Equilibrium time were determined with working solution prepared by diluting the stock metal solution (1000 mg L^{-1}) with deionized water in order to obtain the real concentration of 4.674 mg L^{-1} Cr(total) ions in waste printing developer (measured by ICP-MS). The known amount of the each adsorbent (0.2 g) was shaken (shaking speed 26 rpm) with 25 mL of working solution, while the time varied from 60 to 110 min. At the end of the predetermined time interval, the solutions were centrifuged for 10 minutes at 3000 rpm (Centrifuge, Tehnica Železniki, Slovenia) and then filtered through a quantitative cellulose filter paper (Advantec, grade 5C). Concentration of Cr(total) ions were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using a PerkinElmer Elan 5000 mass spectrometer. The adsorption study was carried out by shaking different amounts of NZ, AC or NZ+AC (0.04-0.24 g with an increment of 0.04 g) in 100 mL stopper bottles, with 25 mL of waste printing developer at pH 10.9, temperature 23.4°C and shaking speed 26 rpm. At the end of the equilibrium adsorption process, the residual Cr(total) concentrations were determined in the same way as in the equilibrium time experiment.

RESULTS

The adsorption experimental data of Cr(total) ions in relation of contact time are shown in Figure 1. The adsorption of Cr(total) ions increased first and then remained constant until the equilibrium was attained, which occurred after 90 minutes for all the adsorbents. Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the chromium ions on the carbon and clinoptilolite surfaces (Arivoli *et al.*, 2007).

Based on the trend of the curves in Figure 1, it can be predicted that the optimal contact time for adsorption on (NZ+AC) would be also 90 minutes.

The experimental data analyzed according to the linear form of the Langmuir (Rao *et al.*, 2006, Kocaoba *et al.*, 2007), Freundlich (Sprynskyy *et al.*, 2006; Kocaoba *et al.*, 2007) and Dubinin - Kaganer - Radushkevich (DKR) (Erdem *et al.*, 2004) isotherms.

The Langmuir isotherm represented by the following equation (1):

$$\frac{1}{Q_e} = \frac{1}{Q_m b} \frac{1}{C_e} + \frac{1}{Q_m} \quad (1)$$

where C_e is the equilibrium concentration of Cr(total) ions (mg L^{-1}), Q_e is the amount adsorbed at equilibrium (mg kg^{-1}) and Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of $1/Q_e$ versus $1/C_e$ suggest the applicability of the Langmuir isotherms (Figure 2). Values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 1. The experimental data of Langmuir adsorption parameters have negative slopes and intercepts, which suggesting that the adsorption behavior of the tested systems does not follow the assumption of the Langmuir approach.

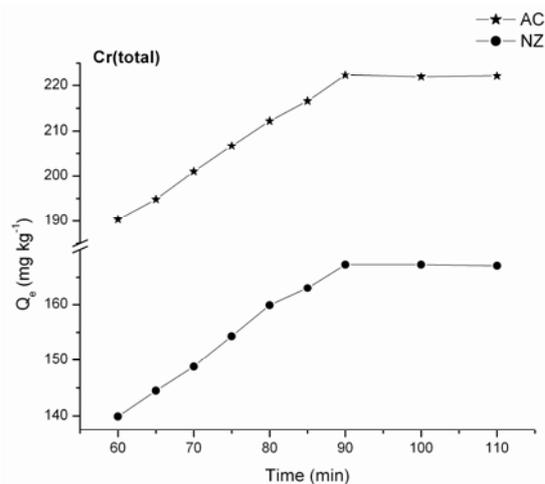


Figure 1. Effect of contact time on adsorption of Cr(total) ions by NZ and AC, $[\text{Cr}(\text{total})] = 4.674 \text{ mg L}^{-1}$; pH = 5.7; Dose = $0.2 \text{ g } 25 \text{ mL}^{-1}$

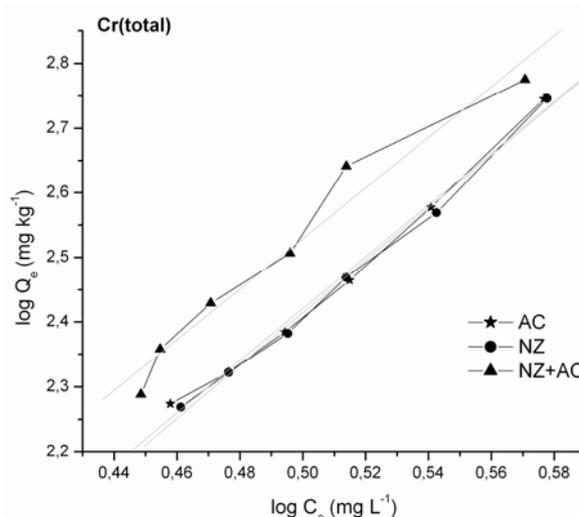


Figure 2. Langmuir isotherm for the adsorption of Cr(total) ions by various adsorbents

Table 1. Langmuir adsorption parameters for various adsorbents

Langmuir adsorption isotherm constants for Cr(total) ions			
Adsorbent	Q_m (mg kg^{-1})	b	R^2
NZ	-100.50	-0.23	0.995
AC	-102.35	-0.22	0.996
(NZ+AC)	-112.11	-0.23	0.912

The Freundlich equation was also employed for the adsorption of Cr(total) ions on the adsorbents. The Freundlich isotherm have represented as in equation (2):

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where Q_e is the amount of Cr(total) ions adsorbed (mg g^{-1}), C_e is the equilibrium concentration of Cr(total) ions in solution (mg L^{-1}) and K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of Cr(total) ions follows the Freundlich isotherm (Figure 3).

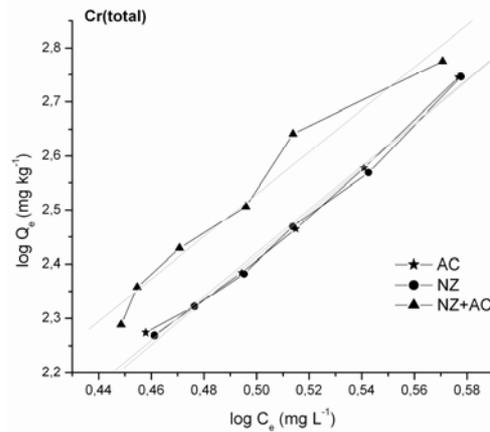


Figure 3. Freundlich isotherm for the adsorption of Cr(total) ions by various adsorbents

The calculated values of K_f and n , Table 2, show the increase of electrostatic force like Van der Waal's between the adsorbents surface and Cr(total) ions due to the increasing of negative charges on the adsorbent surface. However, the values clearly show the dominance in adsorption capacity. The intensity of adsorption is an indicative of the bond energies between chromium ions and adsorbent and the possibility of slight chemisorptions rather than physisorption of chromium ions (Arivoli *et al.*, 2007). However, the multilayer adsorption of chromium ions through the percolation process may be possible. The values of n were lower than one indicating the adsorption is less favorable.

Table 2. Freundlich adsorption parameters for various adsorbents

Freundlich adsorption isotherm constants for Cr(total) ions			
Adsorbent	K_f (mg kg ⁻¹)	n	R^2
NZ	2.42	0.25	0.997
AC	2.59	0.25	0.996
(NZ+AC)	3.73	0.26	0.981

From Table 2 it can be concluded that adsorbent (NZ+AC) is the most effective for the Cr (total) ions removal from printing developer because its adsorption capacity is highest (3.73 mg kg⁻¹). The DKR isotherm for describing the adsorption of metal ions on all adsorbents was used in the following form equation (3):

$$\ln Q_e = \ln X_m - \beta \varepsilon^2 \tag{3}$$

Where Q_e is the amount of Cr(total) ions adsorbed per unit weight of adsorbent (mg kg⁻¹), X_m is the maximum adsorption capacity (mg kg⁻¹), β is the coefficient of activity related to the mean sorption energy (mol² J⁻²), and ε is the Polanyi potential, which is equal to (4):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{4}$$

Where R is the gas constant (J mol⁻¹ K⁻¹) and T is the temperature (K). The values for β and X_m are obtained from the slope and intercept of the plot of $\ln Q_e$ versus ε^2 .

The adsorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same adsorption potential. The adsorption potential is independent of the temperature, but depends on the nature of the sorbent and sorbate. The adsorption energy can be calculated using the following equation (5) (Erdem *et al.*, 2004):

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The DKR plots of $\ln Q_e$ in function of ε^2 for the adsorption of investigated Cr(total) ions on the tested adsorbents are shown in Figure 4. The DKR parameter (β) gives negative values for all the adsorbents, because it was calculated from a negative slope, while the parameter X_m was calculated

from the intercept. The values of the DKR parameters and the corresponding correlation coefficients are summarized in Table 3.

Table 3. DKR adsorption parameters for various adsorbents

DKR adsorption isotherm constants for Cr(total) ions				
Adsorbent	X_m (mg kg ⁻¹)	β (mol ² J ⁻²)	E (J mol ⁻¹)	R^2
NZ	3453.90	-0.5534	0.95	0.988
AC	3355.68	-0.5427	0.96	0.969
(NZ+AC)	2903.38	-0.4525	1.05	0.974

The positive values of adsorption energy correspond to the endothermic process for all investigated adsorbents.

The efficiency of adsorbent (NZ+AC) is 39.9%, Figure 5. The efficiency of adsorbent was calculated from the equation (6):

$$E = \frac{100(C_0 - C_e)}{C_0} \quad (6)$$

Where E is the adsorption efficiency (%), C_0 is the initial concentration of Cr(total) ions (mg L⁻¹), C_e is the equilibrium concentration of Cr(total) ions (mg L⁻¹) (Sprynskyy *et al.*, 2006; Kocaoba *et al.*, 2007).

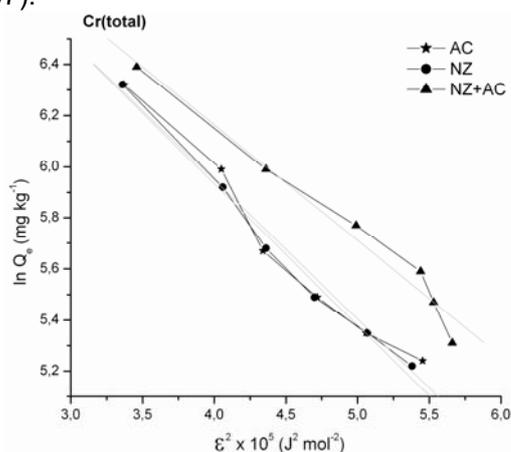


Figure 4. DKR isotherm for the adsorption of Cr(total) ions by various adsorbents

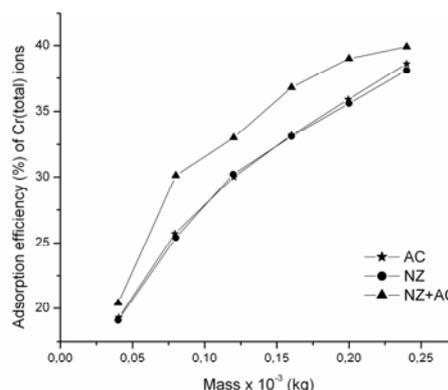


Figure 5. Efficiency of adsorbents in Cr(total) ions removal

The adsorption efficiencies of the adsorbents used in the removal of Cr(total) ions are illustrated in Table 4. The concentration of Cr(total) ions of waste printing developer is almost 3 times higher in relation to the fresh developer. It is evident that after the adsorption process, concentration of Cr(total) ions decreased approximately 1.5 times, or almost 33%.

Table 4. Concentrations of Cr(total) ions in the printing developers

Concentration (mg L ⁻¹) ± RD				
Before adsorption		After adsorption		
Fresh developer	Waste developer	NZ*	AC*	NZ+AC*
1.528 ± 0.076	4.674 ± 0.234	3.258 ± 0.163	3.251 ± 0.163	3.122 ± 0.156

*Waste developer after adsorption on NZ, AC or (NZ+AC)

CONCLUSIONS

The removal of Cr(total) ions from waste printing developer using three adsorbents (NZ, AC and their mixture) was most effective within the first 90 minutes of contact.

The adsorption processes were interpreted in terms of the Freundlich, Langmuir and DKR isotherm models. The experimental data correlated reasonably well by the Freundlich and DKR adsorption isotherms and the isotherm parameters were calculated. It was found that the Freundlich isotherm gave the best agreement over the whole adsorption range; the corresponding correlation coefficients (R^2) being 0.997. These investigations pointed out that the use of inexpensive adsorbents may be an effective way for remove Cr(total) ions from waste printing developer. The adsorption capacities of adsorbents show the following decreasing order: (NZ+AC)>NZ>AC.

ACKNOWLEDGMENT

The authors acknowledge the financial support of the Ministry of Science and Technological Development of the Republic of Serbia (Project No. 34014).

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