

REMOVAL OF Ni (II) AND Cr (VI) IONS FROM AQUEOUS SOLUTION USING BY-PRODUCT FROM THE PRODUCTION OF ALUMINIUM

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In this paper comparative adsorption equilibrium studies of Ni (II) and Cr (VI) ions on commercial activated carbon (CAC) and carbon anode dust (CAD) are presented. The equilibrium studies confirmed that Freundlich model best describes the adsorption systems CAC + Cr (VI), CAD + Ni (II) and CAD + Cr (VI). The Dubinin-Radushevich isotherm can be used to describe system CAC + Ni (II). The results indicate that the intra-particle diffusion model is applicable for adsorption system CAC + Cr (VI) and pseudo-second kinetic model is applicable for adsorption systems CAC + Ni (II), CAD + Cr (VI) and CAD + Ni (II). Obtained results indicate that adsorption of Ni (II) and Cr (VI) ions on CAC and CAD depends on the temperature.

Key words: aluminium product, Ni (II) and Cr (VI) ions, toxic metals, carbon adsorbents, adsorption

INTRODUCTION

The accumulation of toxic metals in food, water and air is a very big problem [1-3]. Because of the accumulation, the concentration of toxic metals in foods may be higher than those in water and air. This can lead to poisoning of people and animals. Some heavy metals are essential for plant growth. However, after a certain concentration they become poison for plants and microorganisms [4]. Different methods are used to remove toxic metals. The best and most commonly used method is adsorption on activated carbons (AC) [5, 6]. A new trend is the use of inexpensive adsorbents, such as various industrial wastes for the removal of heavy metals from wastewaters [7, 8]. This study presents a comparison of adsorption properties of activated carbon and industrial waste - anode dust which is solid residue from aluminum production.

MATERIALS AND METHODS

Commercial activated carbon (CAC) (Merck) and carbon anode dust (CAD) were used as adsorbents. The adsorption experiments were carried out in a batch process at 293, 313 and 333 K. The known weight (0,375 g) of adsorbent material was added to 25 mL of the metal ion solutions with initial concentrations of 50 mg/L to 500 mg/L. The solution was filtered at preset time intervals and the residual metal ion concentration

was measured by atomic absorption spectrometer (Analytik Jena, ZEE nit 650).

RESULTS AND DISCUSSION

The chemical composition of carbon anode dust was determined by standard elemental analysis and results in wt. % are: C = 94,49; Si = 1,73 ; Al = 1,69 ; S = 1,50; Fe = 0,34; Na = 0,089; V = 0,072; Ca = 0,044 and Ni = 0,043. The BET surface area of CAD was found to be 6,48 m²/g, with total pore volume of 2,37·10⁻² cm³/g. This indicated that the CAC had greater surface properties (BET surface area 777,22 m²/g and total pore volume 31,20·10⁻² cm³/g), which means that commercial activated carbon might have more adsorption sites. Textural properties of the CAC and CAD are different because of the nature of the basic material and methods and the extent of activation.

Adsorption kinetics

Figure 1 shows the adsorption kinetics of Ni (II) and Cr (VI) ions from aqueous solutions on the CAC and CAD at 293 K.

Figure 1 shows that the kinetics of adsorption of Ni (II) ions on the CAC and CAD were high in the beginning of the experiment. The reason for this is the large number of sites available for adsorption at the beginning of the process [9].

The obtained results show that the adsorption of Ni ions on the CAC and CAD reached equilibrium after 30 min, i.e. after 60 min for the adsorption of Cr (VI) on the CAC and CAD. It is obvious that the adsorption of Ni (II) ions on the CAC and CAD is better than adsorp-

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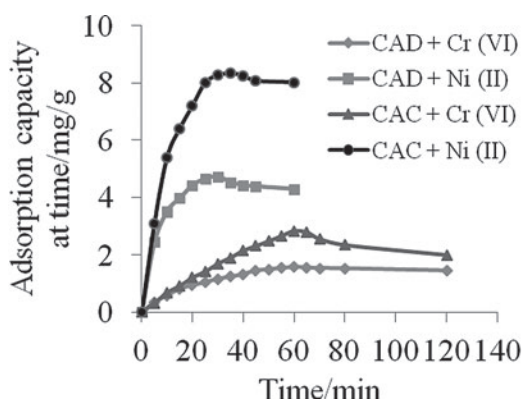


Figure 1 Comparison of kinetics of Ni (II) and Cr (VI) ions on the CAC and CAD at 293 K for initial concentration of 200 mg/L

tion of Cr ions. The reason for this is the small ionic radius of Ni (II) ions. Therefore they easily diffuse into the adsorbent [10].

The pseudo Webber-Morris's first-order equation is generally expressed as follows [5]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (L/min).

The Hoo's pseudo second-order adsorption kinetic rate equation is expressed as [5]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where k_2 is the rate constant of pseudo second-order adsorption (g/mg min).

The Webber-Morris's intra-particle diffusion equation is generally expressed as follows [5]:

$$q_t = k_i t^{0.5} + C \quad (3)$$

where k_i and C are intra-particle diffusion rate constants (mg/g min^{0.5}).

The obtained parameters for all of kinetic models are given in Table 1.

Table 1 shows that the first-order kinetic model did not adequately fitted the experimental values (for all

Table 1 The obtained parameters for all kinetic models

Kinetic parameters	CAC + Ni (II)	CAC + Cr (VI)	CAD + Ni (II)	CAD + Cr (VI)
k_1 /L/min	0,1394	0,0481	0,1616	0,0675
q_e /mg/g	12,125	12,125	6,197	2,364
r^2	0,9373	0,9343	0,9587	0,9084
k_2 /g/mgmin	132,51	5,74	29,41	0,448
q_e /mg/g	12,196	9,116	5,845	2,383
r^2	0,9933	0,9670	0,9989	0,9956
k_i /mg/gmin ^{0.5}	0,0981	0,0926	0,0081	0,0749
C	2,2964	2,8563	1,8423	2,9643
r^2	0,9717	0,9762	0,9527	0,9560

values $r^2 < 0,95$). On the other hand, the pseudo-second order rate equation and intra-particle diffusion kinetic models for adsorption Ni (II) and Cr (VI) ions on CAC and CAD models correlated very well with the data ($r^2 = 0,9527$ to $0,9989$). Intra-particle diffusion model and pseudo-second kinetic model have a higher r^2 values than the pseudo first-order kinetic model. This means that the intra-particle diffusion model and pseudo-second kinetic model are applicable for the analyzed adsorption systems. Because the applicability of both models, analyzed adsorption systems are complex and involve several mechanisms. It is well known that the adsorption in the system with the pseudo-second-order kinetic takes place by chemisorption. The intra-particle diffusion model may include the simultaneous adsorption in surface layers, macroporous and microporous diffusion [11].

Adsorption isotherms

Interaction of solutes with the adsorbent can be described using adsorption isotherms. Figure 2 shows the equilibrium adsorption isotherms of Ni (II) and Cr (VI) ions on CAC and CAD.

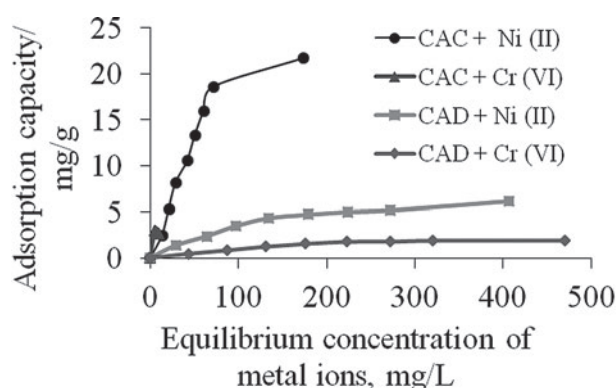


Figure 2 Comparison of adsorption isotherms of Ni (II) and Cr (VI) ions on CAC and CAD at 293 K

The CAC had a relatively large adsorption capacity if compared to some data obtained from the literature [12].

The CAC used in this work had a 3,6 times higher adsorption capacity for Ni (II) ions and 1,4 times higher adsorption capacity for Cr (VI) ions in contrast to CAD. The high adsorption capacity of the commercial activated carbon used in this study was the results of its relatively large surface area and its mesoporous structure.

Adsorption isotherms study was carried out using three isotherms models: Langmuir, Freundlich and Dubinin-Radushevich. The linear Langmuir isotherm (Equation 4), Freundlich isotherm (Equation 5) and Dubinin-Radushevich model (Equation 6) can be expressed as [5]:

$$q_e = q_m \frac{q_e}{K_L \cdot c_e} \quad (4)$$

$$\ln q_e = \ln K_F + 1/n \ln c_e \quad (5)$$

$$\ln q_e = \ln q_m - k\varepsilon^2 \quad (6)$$

where c_e is the equilibrium concentration of metal ions (mg/L), q_m is maximum adsorption capacity (mg/g) and q_e is equilibrium adsorption capacity (mg/g) of metal ions. K_F (mg/g) and n are Freundlich constants. K_F is the adsorption capacity of adsorbent and n is the intensity of adsorption. K_L is Langmuir constant related to energy of the adsorption, ε is $RT \ln(1 + (1/c_e))$, k is Dubinin-Radushevich constant.

The applicability of the adsorption isotherm for the description of adsorption process was determined using the correlation coefficient (r^2 value). Table 2 summarizes all the constants and correlation coefficients (r^2) of the used isotherms models. Based on the obtained correlation coefficients (Table 2), Freundlich model best describes the adsorption systems CAC + Cr (VI), CAD + Ni (II) and CAD + Cr (VI). This indicates that the used adsorbents CAC and CAD have a heterogeneous surface. The obtained results also indicate the formation of multilayer coverage of Ni (II) and Cr (VI) ions at the outer surface of CAC and CAD. Similar results were obtained by adsorption of Cr (VI), Ni (II), Cu (II) and other heavy metals on carbon adsorbents [13-15]. Langmuir model is not suitable for the description of the analyzed systems CAC + Cr (VI), CAD + Ni (II) and CAD + Cr (VI) (the correlation coefficient is higher in the case of application of Freundlich model). In addition, the Langmuir model is not suitable for the description of the analyzed system CAC + Ni (II) ions. Equilibrium could probably be achieved at higher initial concentrations than 500 mg/L. The correlation coefficient for the

Dubinin-Radushevich isotherm is 0,9079 (system CAC + Ni (II)). This isotherm can be used to describe system CAC + Ni (II).

Thermodynamic study

For the determination of process changes in standard enthalpy, entropy and free energy, because of transfer of unit mole of solute from solution onto the solid-liquid interface, it is necessary to consider the thermodynamic parameters. Changes in the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined from the values of the thermodynamic equilibrium constant K_L (Langmuir constant). The thermodynamic parameters were determined by the following equations:

$$K_L = \frac{c_{Ac}}{c_e} \quad (7)$$

$$\Delta G^\circ = -RT \ln K_L \quad (8)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where c_e is the equilibrium concentration of Ni (II) and Cr (VI) ions (mg/L), c_{Ac} is the solid phase concentration at equilibrium (mg/L).

The calculated values of ΔH° , ΔS° and ΔG° are given in Table 3.

The adsorption process is endothermic if the adsorbate must displace more than one water molecule that it might be adsorbed. Because of this, ΔH° will have a positive value. If the total adsorbed energy for breaking the bond is less than the total energy released for the

Table 2 The adsorption constants and correlation coefficients of isotherms model

Adsorption system	Langmuir			Freundlich			Dubinin-Radushevich		
	K_L / L/mg	q_m / mg/g	r^2	K_F / mg/g	n	r^2	q_m / mg/g	k / g ² /kJ ²	r^2
CAC + Ni (II)	0,0354	18,631	0,0516	0,3818	1,1580	0,8779	19,6746	7·10 ⁻⁵	0,9079
CAC + Cr (VI)	-1,1939	2,5066	0,9443	3,8613	-6,4475	0,9809	2,6653	-6·10 ⁻⁷	0,8860
CAD + Ni (II)	0,0070	8,3317	0,9354	0,2299	1,755	0,9532	4,7441	0,0002	0,8260
CAD + Cr (VI)	0,0036	1,966	0,7199	0,0504	1,5711	0,9152	1,7491	0,0005	0,8020

Table 3 The calculated values of ΔH° , ΔS° and ΔG°

Adsorbent + Adsorbate	T/K	$-\Delta G^\circ$ / kJ/mol	ΔH° / kJ/mol	ΔS° / J/mol
CAD + Ni (II) $r^2=0,9998$	293	9 521,69	17,942	-10,991
	313	8 919,36		
	333	8 373,02		
CAD + Cr (VI) $r^2=0,9451$	293	15 063,69	11,936	28,769
	313	15 589,92		
	333	15 476,10		
CAC + Ni (II) $r^2=0,9364$	293	4 985,039	-28,635	-113,918
	313	6 468,596		
	333	9 612,354		
CAC + Cr (VI) $r^2=1,0000$	293	4 878,899	-28,222	-112,996
	313	7 157,501		
	333	9 396,978		

formation of bond between the adsorbent and adsorbate, the process is exothermic [16]. In this case, the additional energy is released as heat. Because of this, ΔH° will have a negative value. Data in Table 3 indicate that the adsorption of Ni (II) and Cr (VI) ions on CAC was exothermic process and adsorption of Ni (II) and Cr (VI) ions on CAD was endothermic process. A positive value of ΔS° indicates an increase in the degree of freedom of the adsorbed particles. The adsorption processes of Ni (II) ions on CAD, Cr (VI) ions on CAC and Ni (II) ions on CAC are enthalpy driven, because of negative value of ΔS° . In the adsorption process of Cr (VI) ions on CAD there is an increased randomness at the solid/solution interface [17].

CONCLUSION

The study of adsorption properties of commercial adsorbents (CAC) and waste materials (CAD) was determined that Freundlich model is better to describe the adsorption of Cr (VI) in both CAC and CAD and adsorption of Ni (II) in CAD. Dubinin-Radushevich adsorption model was best in describing the adsorption of Ni (II) to the CAC. Results show that the particles within the diffusion model is applicable for the system CAC adsorption of Cr (VI) and the pseudo-second kinetic model is related to the adsorption system CAC Ni (II), CAD Cr (VI) and CAD Ni (II). Adsorption of Ni (II) and Cr (VI) ions in the CAC is an exothermic process, and the adsorption of Ni (II) and Cr (VI) ions to the CAD is an endothermic process. It is possible to use both adsorbents for the adsorption of Cr (VI) and Ni (II) ions from aqueous solutions. It is recommended to use CAD because it is economically feasible than CAC.

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