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THE USE OF METALLURGICAL WASTE MATERIAL FROM ALUMINIUM PRODUCTION FOR THE REMOVAL OF CHROMIUM (VI) IONS FROM AQUEOUS SOLUTION

WYKORZYSTANIE METALURGICZNEGO ODPADU MATERIAŁU Z PRODUKCJI ALUMINIUM DO USUWANIA JONÓW CHROMU (VI) Z ROZTWORU WODNEGO

Carbon anode dust originates from the baking and transport process of anodes for aluminium production and is not recycled. This is non-toxic waste material and can be used as valuable secondary raw material in many processes. In this paper, removal of chromium (VI) ions from aqueous solution by adsorption on carbon anode dust was investigated. The diffusion of chromium ions were tested for film diffusion model, intraparticle diffusion model and heterogeneous diffusion model. It was found that the adsorption process is controlled by intraparticle diffusion. The obtained adsorption capacity for Cr (VI) ions is a good indicator of carbon anode dust potential for use in aqueous sorption system.

Keywords: adsorption, carbon anode dust, chromium (VI) ions, diffusion

Pył z and węglowych pochodzi z procesu wypalania i transportu anod do produkcji aluminium i nie jest poddawany procesowi recyklingu. Jest to nietoksyczny odpad materiału i może być wykorzystywany jako cenny surowy materiał wtórny w wielu procesach. W niniejszej pracy badano proces usuwania jonów chromu (VI) z roztworu wodnego przez adsorbpcję na pyłe z anod węglowych. Przeprowadzono dyfuzję jonów chromu przy użyciu warstwowego, wewnątrz-cząsteczkowego i heterogenicznego modelu procesu dyfuzji. Stwierdzono, że proces adsorbpcji (pochłaniania powierzchniowego) jonów chromu jest kontrolowany przez dyfuzję wewnątrz-cząsteczkową. Uzyskana wydajność (pojemność) adsorbpcji dla jonów chromu (VI) jest dobrym wskaźnikiem potencjalnego wykorzystania pyłu and węglowych w systemie wodnej sorpcji.

1. Introduction

In the Hall-Heroult process aluminium is produced by the electrolytic reduction of alumina dissolved in an electrolyte containing cryolite. For the reduction process, carbon anode has been used. The remaining parts of spent anodes from the aluminium production are called anode butts. There are two anode butts, the raw anode butts and the pre-baked anode butts. The cleaned anode butts are crushed and reused in the production of new anodes (about 20% of the anode is recycled). The carbon anode dust originates from the baking and transport process of anodes and is not recycled [1, 2]. This is non-toxic waste material that has to be disposed on the specially arranged depots. This process is rarely applied; it is expensive and requires a lot of space. Therefore, it is necessary to find its use as a secondary raw material. Many toxic heavy metals have been discharged to the environment as industrial wastes, causing serious soil and water pollution. Heavy metals are not biodegradable

and tend to accumulate as metalloorganic complexes in living organisms, which increase their concentrations in biological cycles. One of the most dangerous types of contamination is the continuous, primarily of Cr, Pb, Ni, Zn, Cu and Cd ions. Many of these metals are essential for life in trace concentrations, but higher concentrations have various toxic effects [3]. Chromium is a toxic metal and widely used in the industry. Of its two oxidation states, Cr (III) and Cr (VI), the hexavalent form is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties [4]. Extensive use of chromium, e.g., in electroplating, tanning, textile dyeing and as biocide in cooling water of power plants invariably results in discharge of chromium containing effluents. The convectional physical-chemical methods for removal of dissolved chromium ions from effluents include reverse osmosis, ion exchange, reduction precipitation and lime coagulation [5-7], which are very expensive. Among the treatment processes which were

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available, adsorption on low cost solid waste materials has been widely used [8, 9].

The adsorption phenomenon has still been found economically appealing for the removal of toxic metals from waste water.

The aim of this paper is to evaluate the kinetic model that can be used to describe the chromium ions uptake within heterogeneous and porous particles of carbon anode dust.

2. Materials and methods

2.1. Characterization of sample

Carbon anode dust (CAD), which is solid residue from aluminium production, was used as adsorbent.

The chemical composition of carbon anode dust was determined by standard chemical 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 X-ray diffraction pattern (XRD) of the sample was obtained using a power X-ray diffractometer ($\text{CuK}\alpha$ radiation, $2\theta = 2\text{-}60^\circ$). Fig. 1 shows the result of the diffraction analysis.

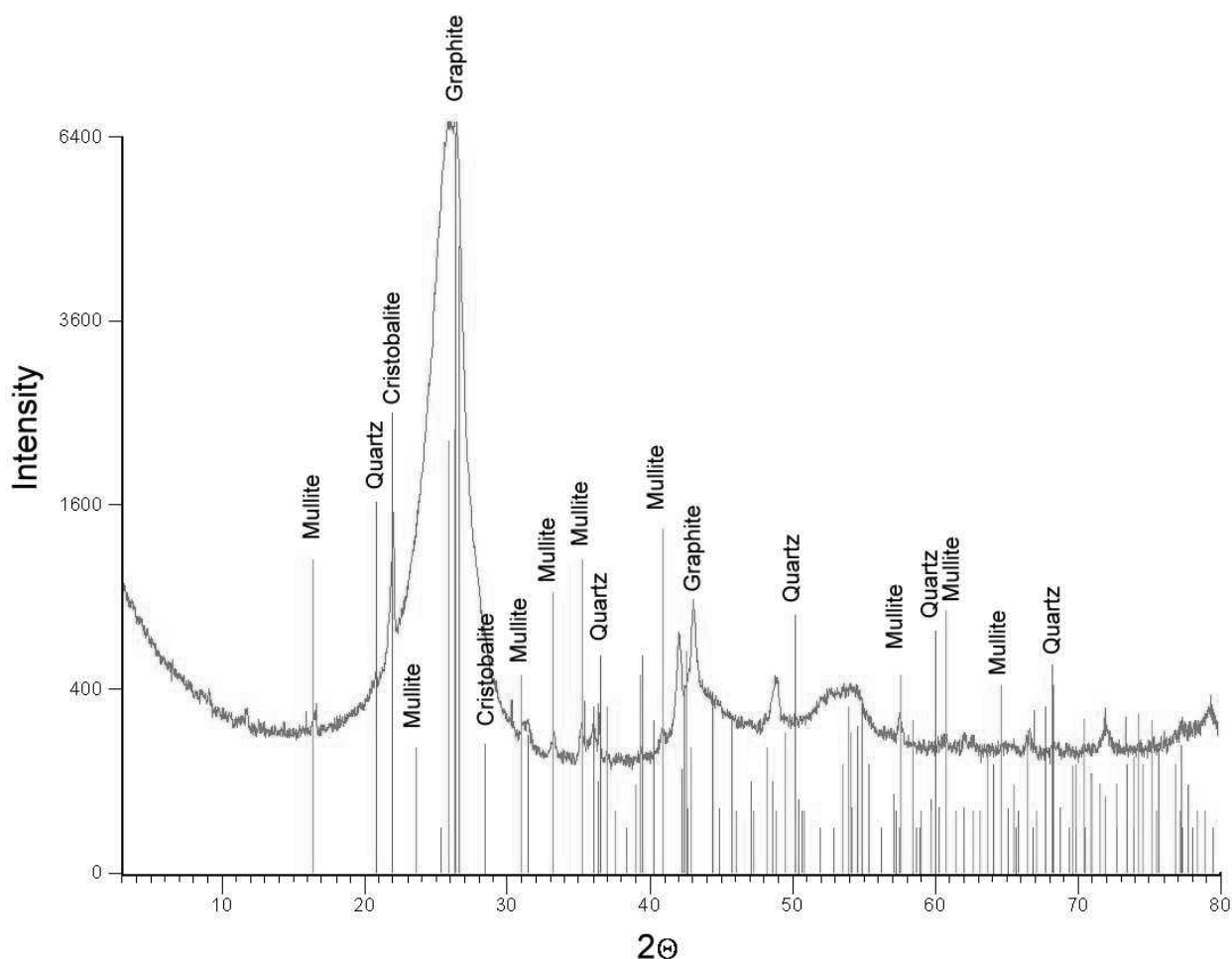


Fig. 1. XRD pattern of the CAD sample

The FTIR spectrum was obtained on spectrometer. The sample CAD (10 mg) was ground with 200 mg of KBr in a mortar pressed into 10 mm diameter disk. The FTIR spectrum was measured between 450 and 4000 cm^{-1} . Fig. 2 shows the result of this analysis. The FTIR spectrum CAD showed peaks at 3800, 3600, 2400, 1500,

1000 and 660 cm^{-1} which may be assigned to CH, OH, phenolic units, unsaturated groups like alkene, amide and aromatic group, respectively.

All experiments have been made with a fraction of particle size of 0.125 to 0.2 mm.

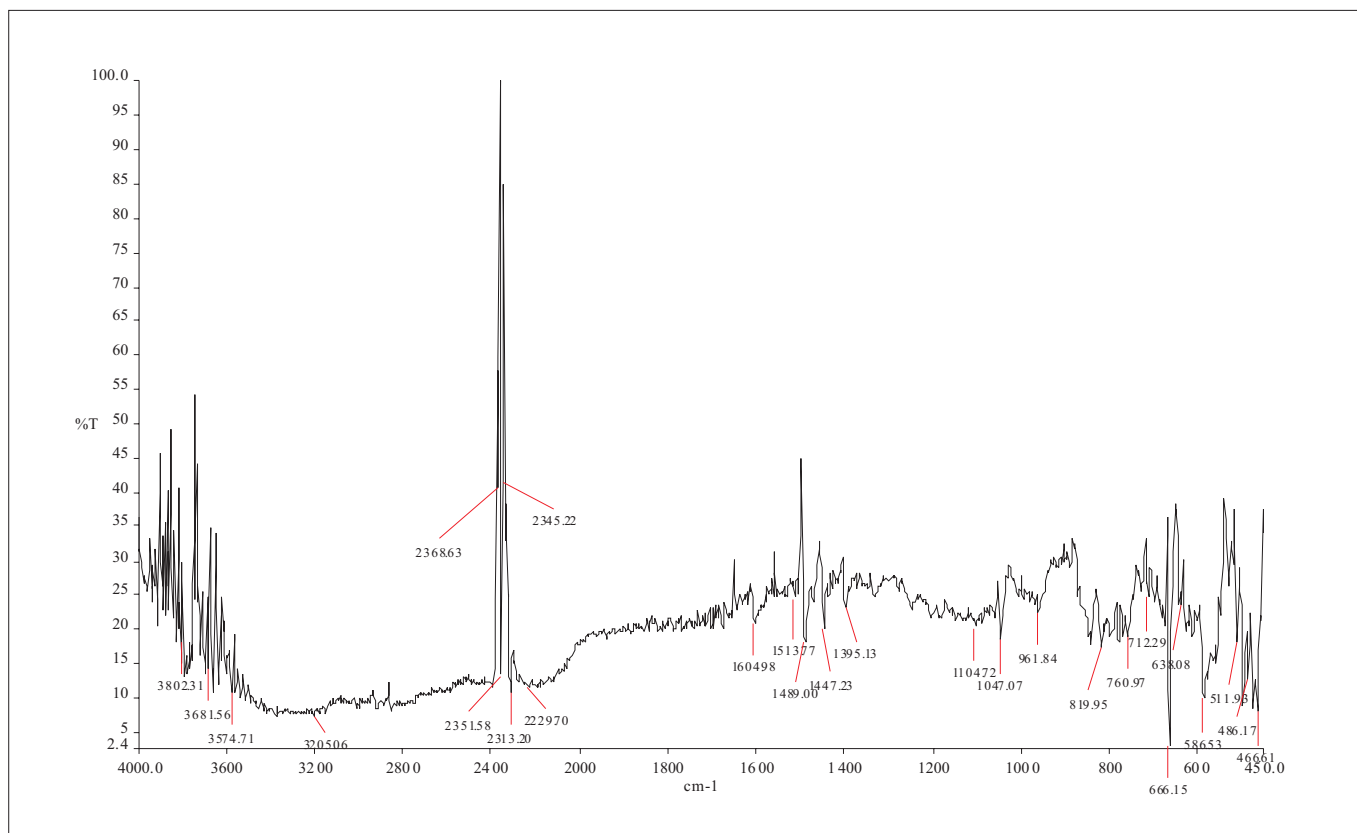


Fig. 2. FTIR spectrum of the CAD sample

2.2. Batch kinetic studies

The removal of chromium (VI) ions was studied by batch tests. A stock solution of Cr (VI) was prepared by dissolving the appropriate amount $K_2Cr_2O_7$ salt in 1000 ml deionized water. This solution was diluted as required to obtain the standard solutions. The initial concentrations of the solutions contained 50, 200 and 350 mgL^{-1} of Cr (VI) ions.

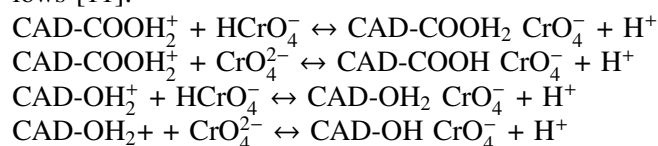
The mixtures of 0.375 g CAD sample and 25 ml of prepared chromium solutions of different initial concentrations were shaken 120 min at a temperature of 20 °C in the closed vessels. Following filtration of the suspensions, the concentration chromium ions in the filtrate was measured with a UV/VIS spectrophotometer by developing reddish-violet color with 1,5-diphenylcarbazide as a complexing agent [10].

3. Results of kinetics studies and discussion

Fig. 3 shows the results of Cr (VI) uptake per unit mass of the CAD with time. During the substitution process, exchangeable acid functional groups of CAD are replaced by chromium ions, resulting in a decrease of

chromium concentration in solution vs. time. Functional groups, such as carboxylic, hydroxyl, lactones etc. (Fig. 2) were present in the CAD. These functional groups have a high affinity for Cr (VI) ions and are the main sites for chromium ions adsorption. The acid groups reacted with H^+ ions from water solution formed positive hydronium ions such $-COOH_2^+$, $-OH_2^+$, $=C=H^+$. Based on the equilibrium constants for Cr(VI) hydrolysis, $HCrO_4^-$ and CrO_4^{2-} are the two major species in the solution [11].

Adsorption of $HCrO_4^-$ and CrO_4^{2-} on CAD were as follows [11]:



Equilibration in examined system was achieved in approximately 60 min. The optimum adsorption capacity of CAD was compared with adsorption capacity of other adsorbent reported in literature and given in Table 1. The obtained adsorption capacity for Cr (VI) ions is a good indicator of carbon anode dust potential for use in aqueous adsorption system [12].

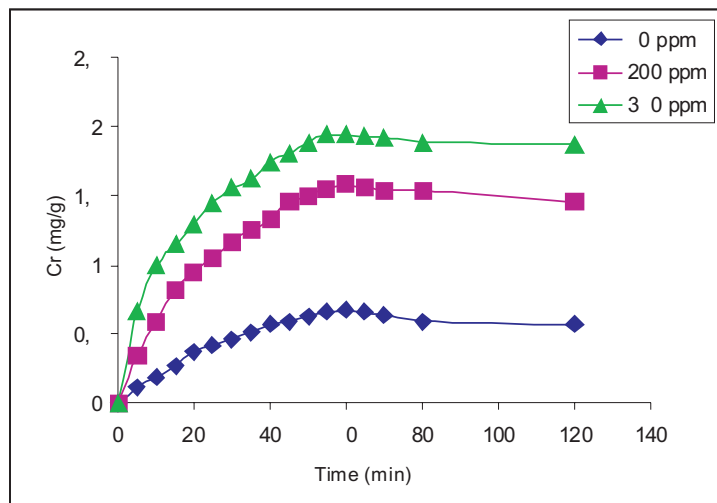


Fig. 3. The amount of chromium ions bounded versus time

TABLE 1
Comparison of adsorption capacity of different adsorbents for removal Cr (VI) ions from aqueous solutions

Adsorbents	Adsorption capacity (mg/g)	References
Commercial pure carbon	7.61	[11]
Commercial pure carbon	145.00	[13]
Soya cake	0.29	[14]
Sawdust	3.30	[15]
Coconut shell	2.00	[16]
Rise husk	45.6	[27]
Carbon anode dust	2.00	This paper

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, intraparticle diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient which will fit the experimental adsorption rate data. Generally, a process is diffusion controlled if its rate is dependent upon the rate at which components diffuse towards one another [18].

For interpretation of experimental data it is necessary to identify the steps in the adsorption process which determine the overall removal rate.

The ingenious mathematical treatment of Boyd et al [19] and Reichenberg [20] to distinguish among all diffusion models laid the foundation of significant advancement in the field of adsorption and ion exchange.

The relative film diffusion rate is the slope of the linear part of curves expressed by Eq. 1 [21]:

$$\ln(1 - F) = -\frac{3Dc}{r\delta c_a}t, \tag{1}$$

where is:

F – fraction on chromium ions bonded at time, (t), dimensionless,

D – diffusion coefficient, mg/l,

c – concentration of chromium ions in the solution, mg/l,

c_a – concentration of exchangeable chromium ions on the CAD, mg/l,

t – time, min,

r – particle radius, cm,

δ – thickness of the film, cm.

The value F is calculated from the experimental results [22]:

$$F = \frac{c_0 - c_t}{c_0 - c_e}, \tag{2}$$

where is:

c₀ – initial concentration of chromium ions in the solution, mg/l,

c_t – concentration of chromium ions in the solution at time t, mg/l,

c_e – equilibrium concentration of chromium ions in the solution, mg/l.

The rate laws for the film diffusion controlled exchange have been derived using the following assumptions: a) diffusion across the film is fast in comparison with concentration changes at film boundaries; b) the film is treated as a planar layer and its thickness is much smaller than the particle radius [23].

The heterogenous diffusion model assumes variations of the diffusion rate and can be expressed by Eq. (3) [24]:

$$F = \frac{1}{\delta} \ln t + C, \tag{3}$$

where is:

$\delta - \ln(\tau_m/\tau_i)$, dimensionless,

$\tau - s^2/D$, min,

τ_m – maximum value of τ , min,

τ_i – minimum value of τ , min,

s – maximum length of the diffusion path, m,

t - time, min,

C – integration constant.

The diffusion through the particle surface can be expressed by the relation [25]:

$$F = a + \left(\frac{D}{r^2}\right)^{1/2} t^{1/2}, \quad (4)$$

where a is the dimensionless constant.

Fig. 4 shows plot of F versus $t^{1/2}$.

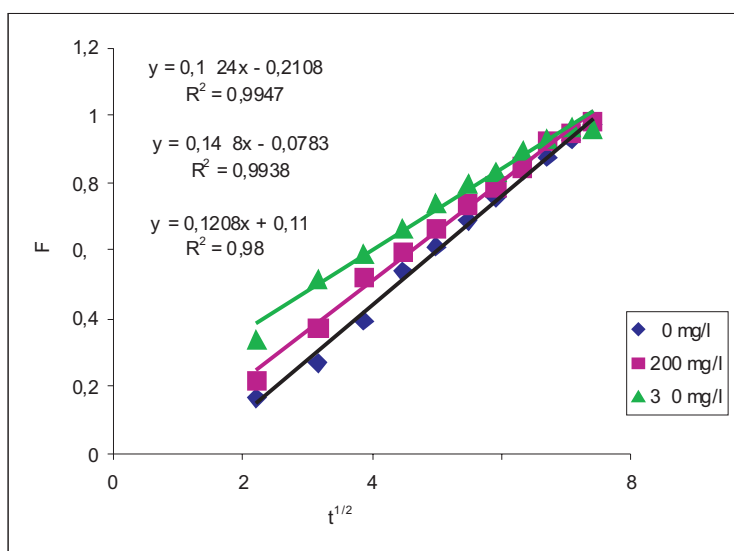


Fig. 4. The linear dependences of fraction of chromium ions bonded vs $t^{1/2}$ for the intraparticle diffusion model

The values of correlation coefficient (R^2), ranging from 0.9855 to 0.9947.

The intraparticle diffusion could involve the simultaneous adsorption in surface layers, macroporous and microporous diffusion. In adsorption process this diffusion can be accepted as a rate determining step when if the plots of F versus $t^{1/2}$ show linearity [26]. As can be seen from Fig. 4, because of the linear distribution of the plots of the curves from the origin, intraparticle diffusion can be accepted as the rate determining step for the adsorption of the chromium ions on CAD.

The pore diffusion coefficient, D , was calculated using Eq. 4 and is given in Table 2.

TABLE 2
Pore diffusion coefficient for intraparticle diffusion model

c_0 (mg/l)	$D(\text{cm}^2/\text{min})$
50	$6,97 \cdot 10^{-6}$
200	$5,69 \cdot 10^{-6}$
350	$3,85 \cdot 10^{-6}$

If the values of intraparticle diffusion rate constants were found to be in the range of 10^{-10} to 10^{-11} cm^2/s pore

diffusion is not significant [27, 28]. However, since diffusion coefficient for adsorption chromium ions on CAD is out of this range, intraparticle diffusion is significant.

4. Conclusion

- The obtained adsorption capacity for Cr (VI) ions is a good indicator of carbon anode dust potential for use in aqueous adsorption system.
- Diffusion depends on mobility and concentration chromium ions and increases with a decrease in initial concentration.
- Equilibration in examined system is achieved in approximately 60 min.
- The diffusion chromium ions were tested for film diffusion model, intraparticle diffusion model and heterogeneous diffusion model. It was found that the adsorption process controlled by intraparticle diffusion.
- Because of the linear distribution of the plots of the curves from the origin, intraparticle diffusion can be accepted as the rate determining step for the adsorption of the chromium ions studied on CAD.

- Diffusion coefficient for adsorption chromium ions on CAD is not in the range between of 10^{-10} to 10^{-11} cm^2/s and intraparticle diffusion is significant.

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