

NICKEL ADSORPTION ONTO CARBON ANODE DUST MODIFIED BY ACETIC ACID AND KOH

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Abstract

Carbon anode dust (CAD) is metallurgical waste material of aluminium production industry. The objective of this study was to convert carbon anode dust to acetic acid- modified and KOH-modified carbon adsorbat. Modified and unmodified carbon anode dust samples were characterized by SEM analysis. Pore volume, pore size and surface area were determined with BET method. The prepared carbons were evaluated for their adsorption capacity of nickel ions. The experimental data were analyzed by Freundlich and Langmuir isotherms. Changes in the surface morphology, surface area properties and obtained adsorption capacity indicate that acetic acid is a better modifier than KOH. Equilibrium results showed that acetic acid modification increased the CAD adsorption capacity for Ni (II) more than KOH modification.

Keywords: Metallurgical waste; Carbon anode dust; Ni(II) ions; Modification surface; Adsorption isotherms.

1. Introduction

In the last decades, a great interest has been developed forwards waste materials of different precursor [1-3]. Research interest into the production of alternative adsorbents

to replace the costly activated carbons has been intensified in recent years. Industrial waste is one of the potentially low-cost adsorbents for heavy metal and organic matter removal. Since these materials are locally available in large quantities, they are

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inexpensive.

Many applications of carbon materials are strongly influenced by their surface chemistry. Thus their use as adsorbents in aqueous solution, in catalysis or electrochemical process are three examples in which the surface chemistry, microporous structure, high adsorption capacity and high degree of surface reactivity can have an important relevance in the materials performance [4,5]. The carbon anode dust (CAD) originates from the baking and transport of carbon electrodes - anodes in aluminium production industry and it is not recycled [6]. This is non-toxic metallurgical waste material that has to be disposed of on the specially arranged landfill. This process is rarely applied; it is expensive and requires a lot of area. Therefore, it is necessary to find its use as a secondary raw material.

The adsorption capacities of the adsorbent depend on the characteristics of the individual adsorbents, its surface properties and the concentration of adsorbate.

The purpose of surface modification is the production of effective but not expensive adsorbents. Surface modification of carbon materials is reorganized as an attractive approach for enhancement of heavy metal removal. Different heavy metal ions have different affinities for different functional groups [25]. Modification can be performed by adsorbing foreign organic and inorganic compounds on the surfaces of carbon. It has been reported that acetic acid has a high binding affinity to Ni (II) ions [7]. It is biodegradable and widely used in the food industry. In the literature [8] we can see that there is growing interest in alkaline hydroxide activation process and KOH has

been found to be one of the most effective compounds in surface modification of carbon materials. The most important factor in KOH use are lower price and less corrosive behavior, both of which are interesting points from an industrial point of view.

Nickel is a toxic heavy metal ion present in wastewater. The main source of nickel pollution in the water derives from industrial production processes such as galvanization, smelting, mining, batteries manufacturing and metal finishing. The presence and accumulation of nickel in industrial effluents has a toxic or carcinogenic effect on living species. Thereby, it is of great importance to eliminate nickel ions from wastewaters [9].

The main objective of this paper was to compare the adsorption performance for Ni (II) ions of acetic acid- modified, KOH-modified and unmodified carbon anode dust.

2. Experimental

2.1 Preparation and characterization of carbon anode dust

Carbon anode dust, which is a solid residue of aluminium production, was used as the adsorbent. For analysis, a representative sample of CAD was obtained using a quartering technique. The sample was dried at 105°C for 4 hours and sieved to particle size ≤ 0.2 mm. The chemical composition of the ground sample was determined by atomic absorption spectroscopy (the AAS method). The mineralogical composition of the CAD sample was determined by the X-ray diffraction method (XRD method) using a

diffractometer with CuK_α radiation. The chemical composition of the examined anode dust is presented in Table 1. The mineralogical composition (XRD analysis) of anode dust is shown in Figure 1.

2.2 Modification procedure

Surface modification by inorganic agent (KOH) was carried out using the following procedure:

Four grams of CAD were mixed with a solution that contained 20 ml of water and 4 g of the modification agent. The obtained mixtures were in contact for 2 hours at 20°C and then for 2 hours at 400°C. Subsequently the samples were washed repeatedly with

distilled water. Afterwards the samples were dried for 2 hours at 110°C. The resulting mixture was carbonized in furnace under argon flow. The samples were heated for 1.5 hours from room temperature to the final heating temperature (700°C). The heating rate was 10°C/min under an argon flow of 5 l/h. The obtained products were then cooled to room temperature and washed with distilled water to remove remaining agent.

Surface modification of CAD with organic agent (acetic acid) was carried out using the following procedure:

The carbon anode dust (6.4 g) was mixed with 40 ml of acid solution concentration of 1 mol/l at 20°C by means of a mechanical shaker (for 30 minutes). The resulting

Table 1. Chemical composition of carbon anode dust

Element	C	Si	Al	S	Fe	Na	V	Ca	Ni
wt, %	94.49	1.73	1.69	1.5	0.34	0.089	0.072	0.044	0.043

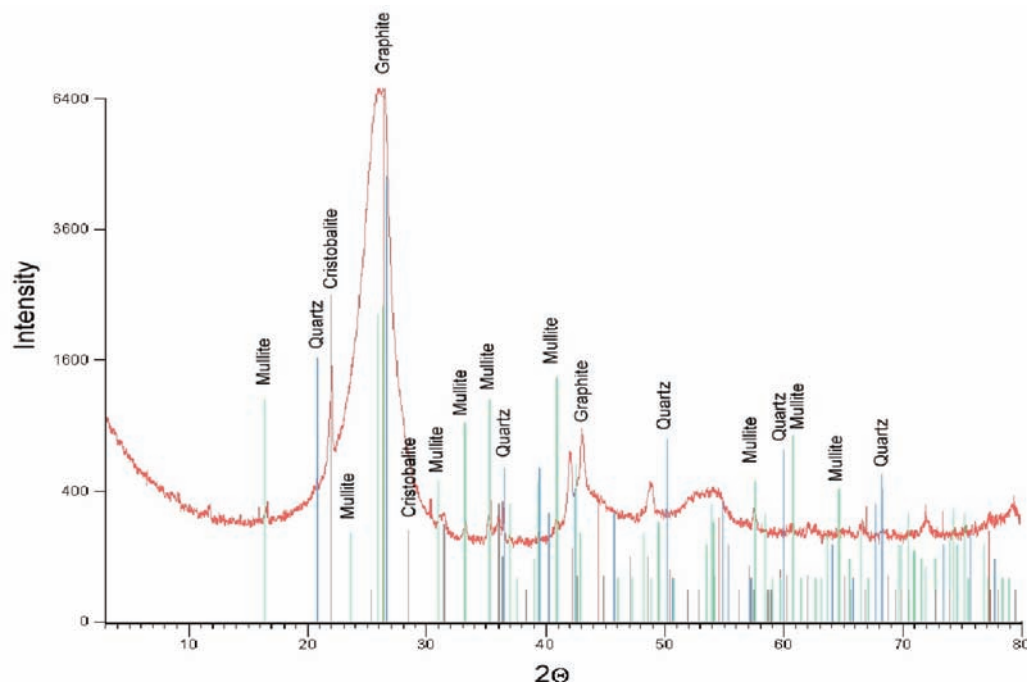


Fig. 1. XRD pattern of the CAD sample

suspension was filtered through a Whatman filterpaper No.40 to separate the carbon anode dust from the solution. The next step was washing with distilled water and drying of obtained samples at 90°C.

2.3 Analysis of surface area properties

The surface area properties were determined by the Brunauer-Emmett-Teller (BET) method. From the N₂ adsorption-desorption isotherms of the investigated samples the surface area and total pore volume were determined. The average pore diameter was calculated using the equation

$$d = \frac{4 \cdot V_p}{S_p}$$

where is V_p-specific volume and S_p-specific surface area.

2.4 Examination of surface morphology

Surface morphology of CAD samples was examined by the method of qualitative scanning electron microscopy (SEM).

2.5 Adsorption experiments

The adsorption of nickel ions from aqueous solution onto the experimental materials was performed using a batch technique. A stock solution of Ni (II) was prepared by dissolving NiCl₂·6H₂O (Merck, p.a.) in 1000 ml deionized water. This solution was diluted as required to obtain the standard solutions. The initial concentrations of the solutions contained 50-500 mg l⁻¹ of Ni (II). The batch experiments were carried out in 100 ml conical flasks by agitating 0.375 mg carbon anode dust with 25 ml of the aqueous Ni (II) solution for a period of 5-60

minutes at 20°C on a mechanical shaker. The concentration of Ni (II) ions before and after the adsorption was determined spectrophotometrically by developing yellow color with dimethylglyoxime as a complexing agent according to standard procedure [10].

2.6 Adsorption isotherm

Generally, the adsorption isotherms have been used for the design of the adsorption system. The amount of Ni (II) adsorbed at equilibrium i. e. the adsorption capacity, q_e (mg/g), was calculated according to the formula:

$$q_e = \frac{\Delta c}{m} \cdot V$$

where, q_e – adsorption capacity, mg/g; Δc - quantity of adsorbed nickel, mg/l; V - volume of solution, l; m - adsorbent mass, g.

The Langmuir and Freundlich [11] equations are commonly used for describing the adsorption isotherm. The linear equations of Langmuir and Freundlich are represented as by Eqs. (1) and (2), respectively:

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot c_e} + \frac{1}{q_m} \quad \dots(1)$$

where,

q_e – adsorption capacity, mg/g,

c_e – the equilibrium concentration of nickel ions, mg/l,

q_m – maximum adsorption capacity of the anode dust, mg/g,

K_L – Langmuir constant.

$$\ln q_e = K_F + \frac{1}{n} \ln c_e \quad \dots(2)$$

where,

q_e – adsorption capacity, mg/g,
 c_e – the equilibrium concentrations of
nickel ions, mg/l,
 K_F and n - the Freundlich constants.

3. Results and discussion

Table 2 presents the results of the surface area properties of CAD: specific surface area, average pore diameter, total pore volume (1.7-300 nm) before and after modification. The value of BET surface area for unmodified CAD is $S_B = 6.48 \text{ m}^2/\text{g}$. The BET surface area slightly increased after modification by acetic acid ($S_B = 7.69 \text{ m}^2/\text{g}$). The average pore diameter of modified samples is decreased in relating to d value of 13.22 nm for CAD sample before modification. The values of total pore volume (1.7-300 nm) of chemically modified CAD are lower ($1.95 \cdot 10^{-2} \text{ cm}^3/\text{g}^{-1}$; $1.88 \cdot 10^{-2} \text{ cm}^3/\text{g}$ respectively) than total pore volume for unmodified CAD ($V = 2,37 \cdot 10^{-2} \text{ cm}^3/\text{g}^{-1}$).

Figure 2 shows the SEM photographs of the carbon anode dust before and after modification. It can be seen from the micrographs that surface of unmodified carbon anode dust is full of cavities. Accordingly, carbon anode dust after modification by KOH maintains the original structure features of chars; i.e., holes with smooth and thick walls which are not twisted or deformed. Comparison of SEM images (Figs. 2a and 2b) shows that the modification by KOH does not significantly change the surface morphology of CAD samples.

After modification by acetic acid pore volume decreased (Table 2). This could arise from pore blockage by adsorbed acetic acid molecules. Because of its small molecular

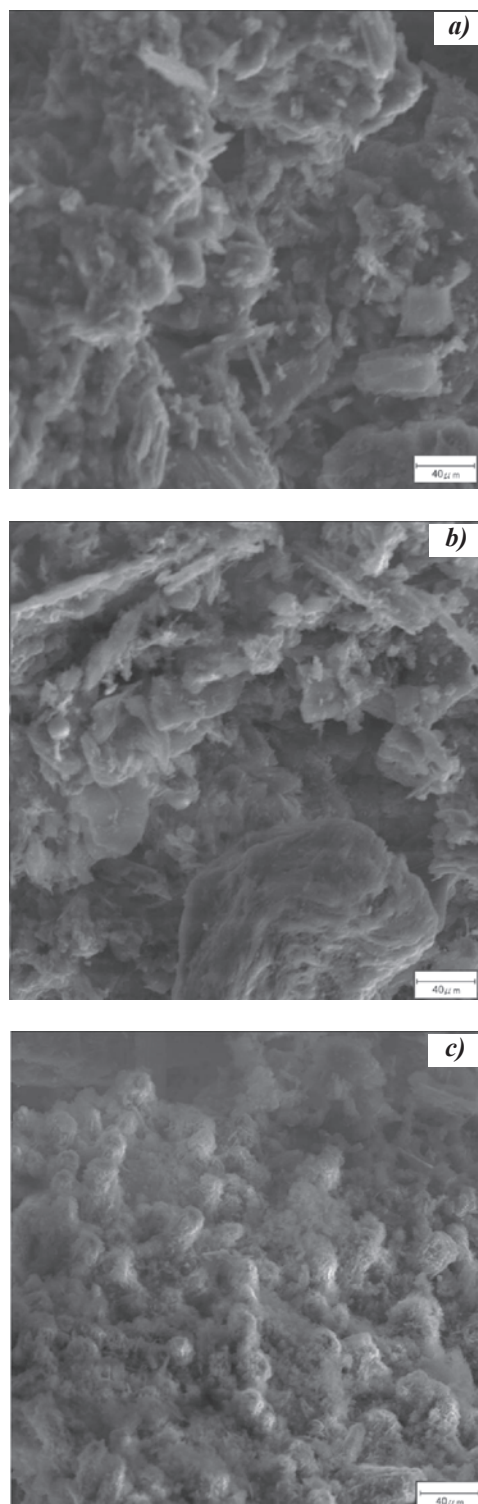


Fig. 2. SEM image of carbon anode dust: a) unmodified and modified by b) KOH and c) acetic acid

Table 2. The surface area properties of carbon anode dust before and after modification

Properties	Before modification	After modification	
		KOH	Acetic acid
Surface area, S_{BET} , m^2/g	6.48	5.87	7.69
Pore volume from 1,7 to 300 nm, V , cm^3/g	$2.37 \cdot 10^{-2}$	$1.95 \cdot 10^{-2}$	$1.88 \cdot 10^{-2}$
Average pore diameter, d , nm	13.22	11.45	9.49

size, acetic acid can easily access the pore structure of carbon material [11]. These observations were confirmed by the surface morphology of acetic acid modified CAD sample (Fig. 2c).

The equilibrium adsorption isotherm of nickel (II) ions on the carbon anode dust before and after modification is shown in Figure 3. It can be seen that the adsorption of Ni (II) ions increases with the increase of initial concentration of Ni (II) ions in aqueous solutions.

The Langmuire adsorption isotherm for Ni (II) adsorption on anode dust is shown in Figure 4. The Freundlich adsorption isotherm for Ni (II) adsorption on anode dust is shown in Figure 5. The values of Langmuir and Freundlich constants and correlation coefficients were determined,

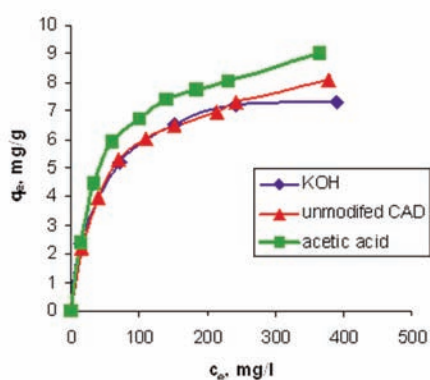


Fig. 3. The equilibrium adsorption isotherm of nickel (II) ions on the carbon anode dust before and after modification

and are shown in Table 3.

As can be seen from Table 3, maximum adsorption capacity, q_m varies from 7.96

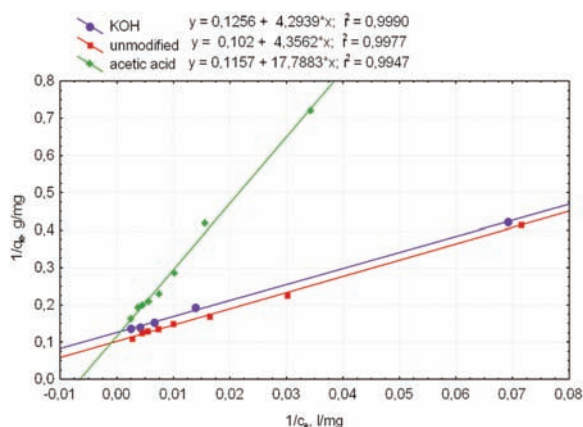


Figure 4. Langmuire isotherm for adsorption of Ni(II) on anode dust

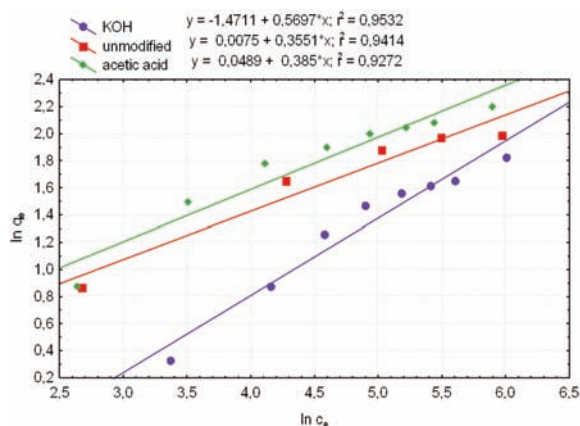


Fig. 5. Freundlich isotherm for adsorption of Ni(II) on anode dust

Table 3. Values of Langmuir/Freundlich constants and correlation coefficients

Modification agents	LAI			FAI		
	q_m , mg/g	$K_L \cdot 10^{-3}$, l/mg	r^2	n	K_F	r^2
Acetic acid	9.8	23.41	0.9994	2.6	1.05	0.9272
KOH	7.96	29.25	0.9990	2.82	1.01	0.9414
Unmodified CAD	8.64	6.5	0.9947	1.755	0.23	0.9532

mg/g to 9.80 mg/g, depending on modification agents. According to the correlation coefficients, experimental data were insignificantly better fitted to Langmuir isotherm ($r^2 = 0.9947-0.9994$). This indicates that the adsorption of Ni (II) ions from aqueous solutions probably results in monolayer.

Maximum adsorption capacity was reached on CAD modified by acetic acid ($q_m = 9.80$ mg/g). This clearly demonstrated that the acetic acid is a better modification agent than KOH.

The results of chemical analysis have shown that CAD is dominated by C (94.49 %). Then follow Si (1.73 wt %), Al (1.69 wt %), S (1.5 wt %), Fe (0.34 wt %) etc (Table 1). According to the results obtained by XRD-method, graphite, α -quartz, mullite and α -cristobalite are the major identified mineralogical components (Fig.1). Such composition of CAD can be explained by the processing conditions of the electrolytic reduction of alumina. The carbon anode is composed of the petroleum coke as a filler and coal-tar pitch as the binder. Each of these components has high content of carbon [6]. Also, the electrolyte for aluminium electrowinning is basically a solution of alumina Al_2O_3 in cryolite, Na_3AlF_6 . The presence of cryolite is essential for

dissolution of alumina as well as for lower operating temperature [12]. The adsorption capability of an adsorbent depends on chemical and mineralogical composition. Literature indicates that carbon materials with chemical and mineralogical composition similar to CAD could be considered as an effective adsorbent [13, 14]. This can be relate to high carbon content and mineralogical components (oxides and aluminosilicates) obtained in CAD sample.

4. Conclusion

The following conclusions can be drawn based on the above mentioned results:

The experimental data are analyzed by Freundlich and Langmuir adsorption isotherms and the Langmuire isotherm model showed a slightly better agreement with the equilibrium data.

Modification of CAD by KOH and acetic acid has changed CAD surface area properties and surface morphology.

After the applied modification procedure the increase of specific surface area, decrease of pore size and pore volume, as well as the change in surface morphology in CAD samples were registered.

The maximum adsorption capacity, q_m was determined in the amount of 7.96 mg/g

to 9.80 mg/g, depending on modification agents.

The obtained adsorption capacity value is promising in the use of carbon anode dust as an efficient low-cost and nonconventional adsorbent for toxic Ni (II) removal from aqueous solutions.

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