

# Study on the possibilities for the industrial water purification from heavy metal ions

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**Abstract:** Among the various methods for water purification and treatment from contaminated industrial pollutants, one of the most used is the adsorption methods based on activated carbons. The purpose of our study is to investigate the correlation between the porous texture and chemical nature of the surface and sorption capacity of the activated carbon, obtained based on lignite coal. The object of the study is also to determine its effectiveness as a sorbent for Cd-ions purification of contaminated industrial water. The obtained data from the conducted investigation show that the adsorbent based on such kind of activated carbon has good qualities for water purification from various pollutants and heavy metals.

**Keywords:** ACTIVATED CARBON, ADSORPTION, PURIFICATION, INDUSTRIAL WATER

## 1. Introduction

Nowadays the industrial water purification from heavy metals is of the basic importance due to their toxic nature and risk of potential accumulation in the food chain. This requires applying the appropriated methods of reducing the heavy metals ions concentration to the acceptable levels. By using a very promising cost-efficient technology for purifying of industrial water can be applied various adsorption methods based on carbonaceous materials, i.e. activated carbon. The activated carbons (AC) represent one of the most effective approaches to ecosystem remediation [1-7]. The most common material used for AC preparation are different carbonaceous materials like wood, peat, coal, coconut shells, wasted biomass from cellulose industry and etc. The activated carbons are widely used in water filtrating system due to its excellent adsorption capacity. They are the best way for remediation of industrial contaminated water. The ability of AC to trap and absorb various contaminations is well known but the scientists look for and develops new methods and materials for this purpose [8-10].

Uses of the AC as a sorbent is determined by its low cost and the best combination of physicochemical properties such as: developed specific surface, porous structure and presence of functional groups on the surface, as well as the high adsorption capacity to different substances. An additional requirement for AC is weak interaction of the hydrophobic carbon surface to the water molecule and good to the organic substances; well developed mesoporosity, providing good access to micro and super micropores; high selectivity and ability to be regenerated. Adsorption properties of the activated carbons can be explained by the transport pores and adsorption pores. However different AC has different surface area and porosity, depending of the kind of source of carbon and the activation process. The main parameters, allowing the specific application are the texture parameters: specific surface area, meso- and micropores volumes, their ratio and micro and mesoporous distribution. AC are defined as microporous materials, but more often as a micro- mesoporous or as a meso-microporous material. It is established that the high sorption capacity of AC to the metal ions in an aqueous medium is mainly related to the presence of oxygen functional groups on their surface [11]. Activated carbons typically contain chemically bound oxygen, which depends on the method and conditions of the production, and form the basic or acidic surface compounds [12]. The explanation of the AC adsorption capacity to the metal ions is based predominantly to the role of the surface oxygen groups, and can be given by the theory model of Grou-Chapman-Stein-Grahame (G.C.S.G) [13], the theory of ion exchange [14] and the theory of formation of surface complexes [15]. The amount and pore distribution will affect the efficiency and the adsorption capacity of the AC. The purpose of our study is to estimate the influence of the porous texture and chemical surface nature of the activated carbon, based on lignite coal and determine its sorption capacity, its effectiveness as a sorbent of Cd-ions purification of the contaminated industrial water.

## 2. Experimental

For the purpose of our investigation was used activated carbon, obtained by water vapor pyrolysis of lignite coal [16]. The ash content of the activated carbon was determined by slowly treating the sample in a muffle furnace at  $1073 \pm 50\text{K}$  and glowing of the ash residue to a constant mass. [17].

pH of the AC was performed using „Hanna instruments – 211“meter, Germany. The carbon isoelectric point was determined by Noch-Schwartz method [18]. The acidic and basic surface oxygen groups was determined by Böhm neutralization method [19].

IR analysis of the AC sample was done using a Bruker IFS 25 FTIR spectrometer in the range  $3000 - 4000\text{ cm}^{-1}$ , giving an additional information for the type of surface oxygen groups.

The characterization of the texture parameters and the specific surface area of AC were performed by low- temperature nitrogen adsorption (at  $77.4\text{ K}$ ) using conventional volumetric apparatus. Specific surface of the samples ( $A_{\text{BET}}$ ) was determined by BET method from the low temperature data of  $\text{N}_2$  ( $77\text{ K}$ ) in  $p/p_0 = 0.05 - 0.35$  relative pressure range [20]. Determining of the sample volume: total pore volume ( $V_t$ ) in accordance with the Gurvich rule at relative pressure  $p/p_0 = 0.95$  [21]. The volume of mesopores ( $V_{\text{MES}}$ ) was calculated by the formula:  $V_{\text{MES}} = V_t - W_0$ , where  $W_0$  (the limit volume of the sorption space, calculated using the simplified Dubinin - Radushkevich equation [22,23,24].  $W_0$  was determined from the  $\text{N}_2$  isotherms in the relative pressure range  $<0.1$ . The micropore volume ( $V_{\text{MI}}$ ) was determined by the t/F method [24]. The volume of super micropores ( $V_{\text{SMI}}$ ) was determined by the equation:  $V_{\text{SMI}} = W_0 - V_{\text{MI}}$ . The size distribution of micropores was done using (Simplified Equation-SE) [25]. The size distribution of mesopores was carried out by the Pierce method [26].

## 3. Results and discussion

Table 1 presents the ash content and results of the elemental analysis (wt.%) of the sample of ACVM.

**Table 1.** Ash content and elemental composition of ACVM

Sample	Ash content (%)	C, %	H, %	N, %	S, %	O, %
ACVM	10.1	91.8	1.63	0.78	0.66	5.13

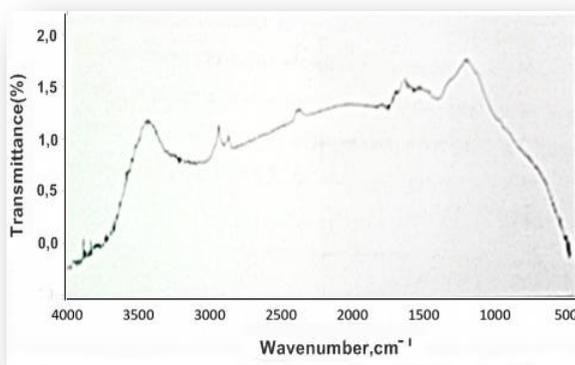
Table 1 shows that the ash content of the activated carbon is 10.1 wt.%, similar to the ash content of activated carbon based on such coal type. The elemental composition of the activated carbon is characterized by a high carbon content (91.8 wt.%) and a sulfur content in carbon of 0.66 wt. %, but it does not affect the adsorption process of the studied ions. The values of pH, IEP and the results from the Boehm neutralization method for ACVM activated carbon are presented in table 2.

**Table 2.** pH, IEP and functional group content according to Boehm neutralization method for ACVM

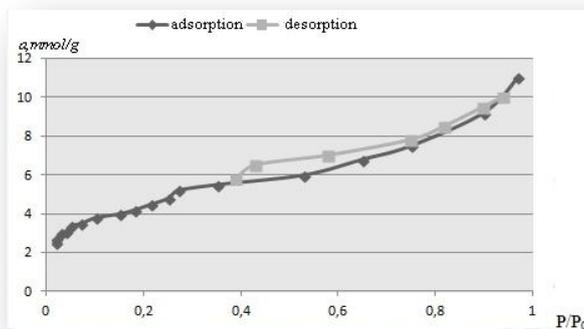
pH	IEP	Neutralized amount.10 <sup>2</sup> [meq/100 m <sup>2</sup> ]			
		NaOH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	HCl
7.8	7.5	14.43	6.93	4.99	0.8

From the results obtained for pH, IEP and functional groups content, according to the Boehm neutralization method, their values are close (7.8 and 7.5). According to the results from the Böhm neutralization method, it is obvious also, that the acidic oxygen groups prevail on the carbon surface, which is characteristic for activated carbon, obtained by vapor-gas activation. Based on the Böhm neutralization method and the results obtained for pH and IEP may be assumed that the activated carbon will adsorb metal ions which hydroxides are less basic and their salts are hydrolyzed during the experiment.

The FTIR spectrum of the studied sample is presented on figure1. It cannot be clearly identified vibrations of acidic oxide surface groups, except in the range 1600-1545 cm<sup>-1</sup>, which according to [27] is characteristic of the enol form of the dicarbonyl groups.



**Fig.1** FTIR spectra of the sample of ACVM



**Fig.2** Adsorption-desorption isotherm of the ACVM sample

The adsorption-desorption isotherm of the studied activated carbon, determined by nitrogen, is shown in figure 2, and its adsorption-texture parameters calculated on its basis are given in table 3.

It is evident from the figure that the isotherm of the sample refers to mixed type (I and IV), and has well-defined hysteresis loop of type H3, according to the IUPAC classification this is characteristic for the materials containing flat parallel pores

**Table 3.** Adsorption-desorption texture parameters of the sample of activated carbon

A <sub>BET</sub> (m <sup>2</sup> .g <sup>-1</sup> )	A <sub>MES</sub> (m <sup>2</sup> .g <sup>-1</sup> )	V <sub>t</sub> (ml.g <sup>-1</sup> )	V <sub>MI</sub> (ml.g <sup>-1</sup> )	V <sub>SMI</sub> (ml.g <sup>-1</sup> )	V <sub>MES</sub> (ml.g <sup>-1</sup> )	X <sub>0</sub> (nm)	r <sub>p</sub> (nm)
388	33	0.36	0.04	0.13	0.21	0.99	1.9

It can be seen from the texture parameter data (table 3), that AC is characterized with not so developed specific surface area (A<sub>BET</sub> = 388 m<sup>2</sup>.g<sup>-1</sup>), and slightly developed micropores volume (V<sub>MI</sub>=0.04

ml.g<sup>-1</sup>), opposing to those of super micropores (V<sub>SMI</sub> = 0.13) and well developed mesoporous transport texture, with ratio V<sub>me</sub>/V<sub>MI</sub> = 1.4

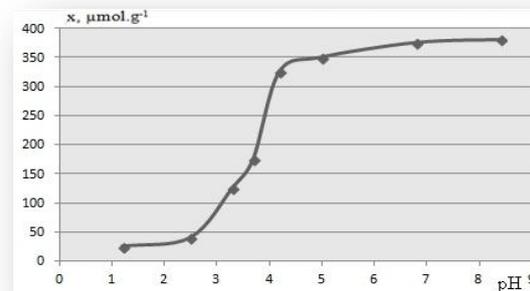
Based on the results obtained, it can be concluded that in the microporous texture of the AC super micropores dominate, and the volume of the typical micropores is four times smaller than the super micropores. All this confirm the fact that the sample ACVM carbon is obtained by high degree of activation.

The analysis of the textural parameters of the sample AC based on the lignite coals, shows that it is suitable adsorbent for organic and inorganic substances (contaminants) from aqueous medium.

As a result of meso-microporous texture developing of the sample during the activation process and the obtained favorable V<sub>ME</sub>/V<sub>MI</sub> ratio, it can be concluded that the adsorption process is facilitated for the contaminated substances to the sorption centers on the surface and in the porous texture of the AC.

**3.1. Study of the adsorption capacity of the obtained ACVM for Cd<sup>2+</sup> ions contaminated aqueous solution**

The adsorption of metal ions from aqueous solution depends on many factors, but the most important are ionic radius, ionic potential, q/r (q ionic charge, r – ionic radius), pH, chemical properties, hydrolysis and etc.



Cd<sup>2+</sup> has relatively larger hydration radius (compared to the radius of Cu, Zn, Pb ions) and hence has significantly greater access to the carbon surface area. His ionic potential is smaller than the potential of the other mentioned heavy metals ions. Therefore, the interaction forces between AC - Cd<sup>2+</sup> will be relatively weak, which means that Cd<sup>2+</sup> ions are retained only on the center of hydrocarbon surface, with a higher negative charge.

The effect of pH of the solution on the adsorption value (x, μmol.g<sup>-1</sup>) to Cd<sup>2+</sup> is given on fig. 4. At constant temperature, ion concentration, time contact and stirring rate, pH of the adsorption medium has the important influence on the adsorption process. From the presented adsorption isotherm it can be seen a sharp increase of the adsorption of Cd<sup>2+</sup> ions in region 3,2≤pH≤4,2, which reaches constant values for pH: 5÷7.

The sharp rise of pH in the range 3,2÷4,2 of X=f(pH) (fig.4) for the Cd<sup>2+</sup> ions adsorption associated with the surface charge of the activated carbon, which is extremely dependent from the solution pH value. [28]. The IEP value of the AC is 7.8 (table 2). At low value of pH, as a result of protonization of the surface oxygen groups, the electrostatic repulsion forces of Cd<sup>2+</sup> ions from the positively charged carbon surface occur, so a lower degree of adsorption is observed. The increased pH solution value leads to the amount of the protonized surface functional groups decreasing (respectively the strength of the hydrogen bonds between hydrogen cations and these groups also decreases). As a result Cd<sup>2+</sup> ions will easily displace H<sup>+</sup> from the surface oxygen groups and the adsorption of Cd<sup>2+</sup> will increase.

The results obtained show that the adsorption of Cd<sup>2+</sup> of the obtained activated carbon depends on the texture parameters (their hydration radius) and adsorption-desorption characteristics. The adsorption of Cd<sup>2+</sup> is low at low pH values (pH<3) and increases significantly in the pH range from 3,2 - 4,2, reaching constant values at pH>5.

## Conclusion

The Cd<sup>2+</sup> ions are serious environmental problem of waste water and contaminated groundwater. The obtained adsorption-texture parameters of the investigated activated carbon derived from the lignite coal show that it is a suitable adsorbent for organic and inorganic substances (contaminants) from a liquid medium.

The results obtained by studying the adsorption capacity on the obtained ACVM by static method of Cd<sup>2+</sup> ions from aqueous solution show that the adsorption of these ions depends on both the adsorption-texture parameters and the chemical nature of the carbon (in particular IEP) and as well as from the pH of the solution. The adsorption of Cd<sup>2+</sup> is low at low pH values (pH<3) and increases significantly in the pH range from 3,2 - 4,2, reaching constant values at pH>5.

However, its practical use for the purification of contaminated industrial water from Cd<sup>2+</sup> ion needs of an additional investigation on the so-called dynamic carbon adsorption capacity and on the possibility of regeneration of the sorbent.

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