Materials Research Proceedings 34 (2023) 87-94 https://doi.org/10.21741/9781644902691-11

Effect of Impregnation of Activated Carbon with Selected Transition Metal Ions on Its Adsorption Properties and Pore Size

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Keywords: Activated Carbon, Impregnation, Adsorption Isotherm, BET Method, BJH Method, Transition Metals

Abstract. Thanks to their vast surface area, activated carbons are materials of great interest. They are used as adsorbents for both liquid- and gaseous impurities. To improve their properties, impregnation with different substances is conducted. In this paper, such an impregnation was done using copper(II), manganese(II), silver(I), and zinc(II) salts. The aim was to compare the inner structure of the impregnated activated carbon with a non-impregnated one. It was done by Brunauer-Emmett-Teller (BET) adsorption-desorption isotherms that were plotted and described. Lastly, the pore size and volume were determined by Barrett-Joyner-Halenda (BJH) method. The results show that the presence of zinc(II) salts helped to develop the mesoporous structure of activated carbon and resulted in an increase in the surface area of the sorbents, while silver(I) decreased it.

Introduction

Adsorption is a process taking place at the interphase phases [1]. It can be physical and involve covalent bonds, ionic bonds, van der Waals forces, or chemical in character when adsorbate is reacting with adsorbent [2]. The efficiency of the process is highly dependent on how large the surface area of the sorbent is. Many factors may impact this parameter but one of them, more than any other is meaningful – the porosity. Pores are cavities on the surface of a sorbent which multiply its surface by manyfold. Zeolite can serve as an example here, with its surface of almost 130 m^2/g [3], or activated carbon with 2636 m^2/g [4].

Continues process of absorption can be described using graphs called isotherms, showing the relationship between the amount of adsorbed substance and its concentration in an equilibrium state. Many isotherms describe different theories and states. For example, Henry's isotherm is adequate for the process of adsorption of low-concentration fluids and gases, and the Freundlich model is describing a situation in which the surface of the adsorbent is not smooth but porous. One of the most used, thanks to its great adequacy to reality, is Brunauer-Emmett-Teller (BET) theory. Its main assumption is based on Langmuir isotherm [5] but modified, so it is describing a multilayer adsorbate on a porous sorbent's surface. The important thing here is the fact, that the greater the vapour pressure of adsorbate over adsorbent, the higher the number of adsorbed particles. BET is given by a linear equation (Eq. 1) but following further mathematical operations BET isotherms are curves.

$$\frac{1}{X(\frac{p_0}{p}-1)} = \frac{1}{X_m C} + \frac{C-1}{X_m C}(\frac{p}{p_0}) \quad \text{Eq. 1}$$

X – the total adsorbed volume of gas under pressure p

p_0 – saturated vapor pressure of an adsorbate

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X_m – monolayer capacity (volume of gas adsorbed in a single layer)
C – equilibrium adsorption state

By knowing the monolayer capacity from the equation (Eq. 1) total surface of the adsorbent can be calculated (Eq. 2):

$$S = \frac{X_m L_{Av} A_m}{M_V} \quad \text{Eq. 2}$$

S – total surface area
$L_{av.}$ – Avogadro's number
A – cross-sectional area of the adsorbate (for nitrogen 0.162 nm^2)
M_v – molar volume

Six types of isotherms can be described, according to the International Union of Pure and Applied Chemistry (IUPAC) [6]. They are depicting (Fig. 1) the adsorption process on different adsorbents with variable pore structures, divided into both pore size and pore shape. Designations (names) for pores by size are determined by IUPAC, a micropore is less than 2nm cavity, a mesopore ranges from 2 to 50 nm, and a macropore is larger than 50 nm. Pore size also affects the condensation mechanism. While there is three-dimensional condensation in micropores and capillary condensation in mesopores, there is no condensation in macropores [7].

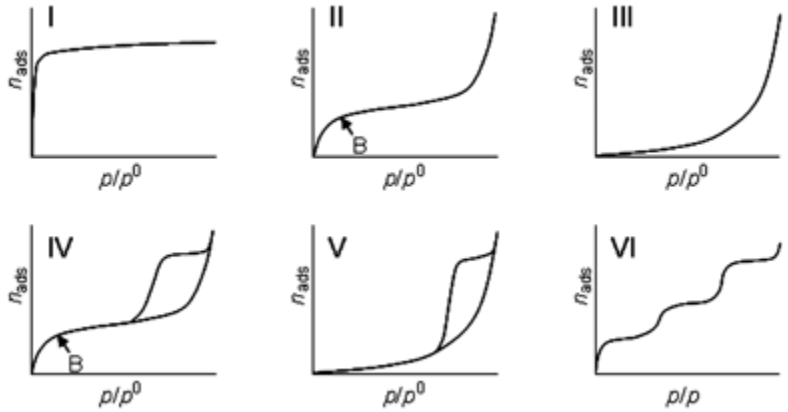

Fig.1. *Types of isotherms by adsorbent outer structure. Type I: microporous; type II: non-porous or macroporous; type III: non-porous or macroporous but with weak interactions; type IV: mesoporous; type V: mesoporous but with weak interactions; type VI: step-by-step multilayer adsorption. (source: [8]).*

Activated carbons (ACs) are being used in many fields. They are obtained from organic matter, through a process called activation. Among the most popular substrates are wood (35% of total substrates used), coal (28%), lignite (14%), peat (10%), and local organic residues such, as coconut shells or fruit stones (10%). Activation can be divided into two types: chemical one and physical one. The former involves two steps, the first step includes mixing the substrate with some reagents, e.g. zinc(II) chloride, phosphoric acid or sodium hydroxide, and the second one is heating. Activation temperature depends on the type of substance that was used. Carbon mixed with $ZnCl_2$ is heated to around 600°C, at which temperature total dehydration takes place. On the other hand, substrates containing H_3PO_4 are heated to 800°C, so that the acid is oxidizes carbon and the structure is changing [9]. Physical activation is heating conducted in two steps. In the beginning, the substrate is carbonized at 400-600°C, as in this temperature rigid carbon structure is obtained.

To get the actual, useful product oxidation has to take place. It is done by increasing the temperature to 800-950°C with the addition of water vapour or carbon dioxide to the reaction environment, which penetrates and expands pores [10]. Such products can be further modified by impregnating them with different compounds so the ACs' properties are altered or upgraded. Metal-impregnated activated carbons (MIACs) are sorbents of great interest due to their relatively simple manufacturing.

Experimental Procedure

DT0 commercially-available activated carbon (produced by Gryfskand Sp. z o.o. company in Poland) was used in this experiment. It was first oxidized in a 20% nitric acid solution and then washed until all the acid was removed. Afterwards, a washed activated carbon was kept at room temperature for 24h. At the end of the process, the product was dried in a fluid bed dryer at 120°C. The following transition metal salts were chosen for impregnation

– universal adsorbents (UA), containing zinc, copper, manganese, silver, and
– adsorbents containing zinc and silver (S-Hg/Pb) only.

The following metallic catalysts have been selected to produce UA:

– basic copper carbonate (Cu2CO3(OH)2) in aqua ammonia;
– potassium permanganate (KMnO4) in aqueous solution;
– silver nitrate (AgNO3) in aqueous solution;
– zinc nitrate (ZnNO3) in aqueous solution.

The final step leading to MIACs possessing the desired properties was drying them for 6 hours at the temperature of 120ºC and 2 hours at 180ºC.

Adsorption-desorption isotherms and inner structure tests were carried out on Autosorb-1C chemisorption - physisorption analyzer by Quantachrome Instruments.

Table 1. *Concentrations of metal ions in MIACs*

No.	Sorbent	Copper(II) [% w/w]	Manganese(II) [% w/w]	Silver(I) [% w/w]	Zinc(II) [% w/w]
1.	DT0	-	-	-	-
2.	IS-2	3.0	1.2	0.5	1.0
3.	IS-3	3.0	1.2	-	0.5
4.	IS-4	3.0	1.2	0.5	2.0
5.	IS-5	3.5	1.8	1.0	-
6.	IS-6	3.0	1.8	1.0	-
7.	IS-7	3.0	1.8	0.5	-
8.	IS-8	3.0	1.2	0.5	-
9.	IS-9	3.0	1.2	1.0	-
10.	IS-10	2.5	1.2	0.5	-

Results and Discussion

Some of the MIACs impregnated with zinc(II) and other salts contained aggregated copper-blue particles. Those carbons were observed under Keyence series VHX-7000 microscope with VH-ZST dual objective zoom lens (Fig. 2). It seems that some regions adsorbed more copper(II) salt which, during the heating process, was not reduced to copper(II) oxide. This irregularity must be linked to the presence of zinc(II) salt in the samples, but chemistry of this process is not known yet, due to insufficient amount of data.

By comparing the surface areas of DT0 and ISs we see that zinc(II) impregnated ACs have a significantly larger surface than their nonimpregnated precursor. Other adsorbents, IS-5 – IS-10, had their area decreased by 5-10%. Additionally, the highest increase, around 44%, was noted for

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IS-3 – the only sorbent which does not contain silver(I). Thus, a conclusion can be made that presence of zinc(II) salt in the impregnation mixture is promoting better performance parameters, while silver(I) presence is accomplishing the opposite.

To specify, which pores were affected the most, the BJH curve was used. It appears that zinc(II) helped to develop the mesoporous structure of activated carbon. The biggest increase is observed for IS-3 and IS-4 sorbents. This implies that the absence of silver(I) and a higher concentration of zinc(II) positively impact the efficiency of adsorption properties. As can be seen in graphs (Fig. 4 b) and c)) micropore capacity has also increased. One unusual situation was noted for IS-8 in which the mesopores disappearance almost totally.

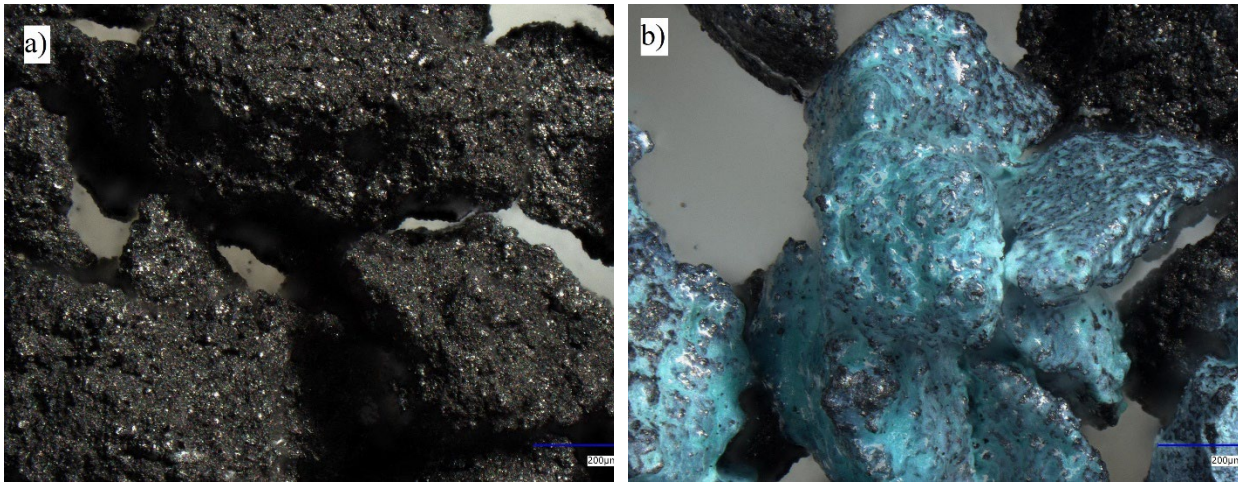


Fig.2. *a) Noncoated IS-5 vs. b) copper(II) salt coated aggregated AC IS-4*

While considering the changes to the structure of all the adsorbents, they are not as large as one could assume. This is proven by BET isotherms (Fig. 4), as all of them are type IV(a) with H4 hysteresis [11], which means that the shape of the pores remains unchanged and only the number of individual pores differentiates the MIACs.

Table 2. *Sorbents parameters*

Sample	DT0	IS-2	IS-3	IS-4	IS-5	IS-6	IS-7	IS-8	IS-9	IS-10
Surface area* [m^2/g]	555.4	796.6	804.3	592.1	523.0	507.8	491.7	498.2	482.7	519.2
Average pore size [nm]	2.100	2.139	2.346	2.296	2.117	2.106	2.076	2.114	2.115	2.112

* BJH method cumulative desorption surface area

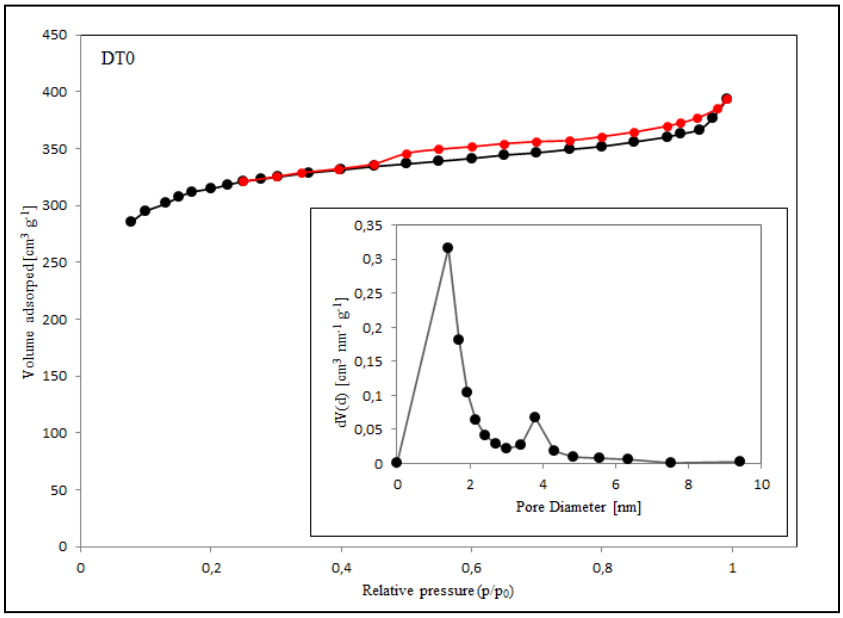
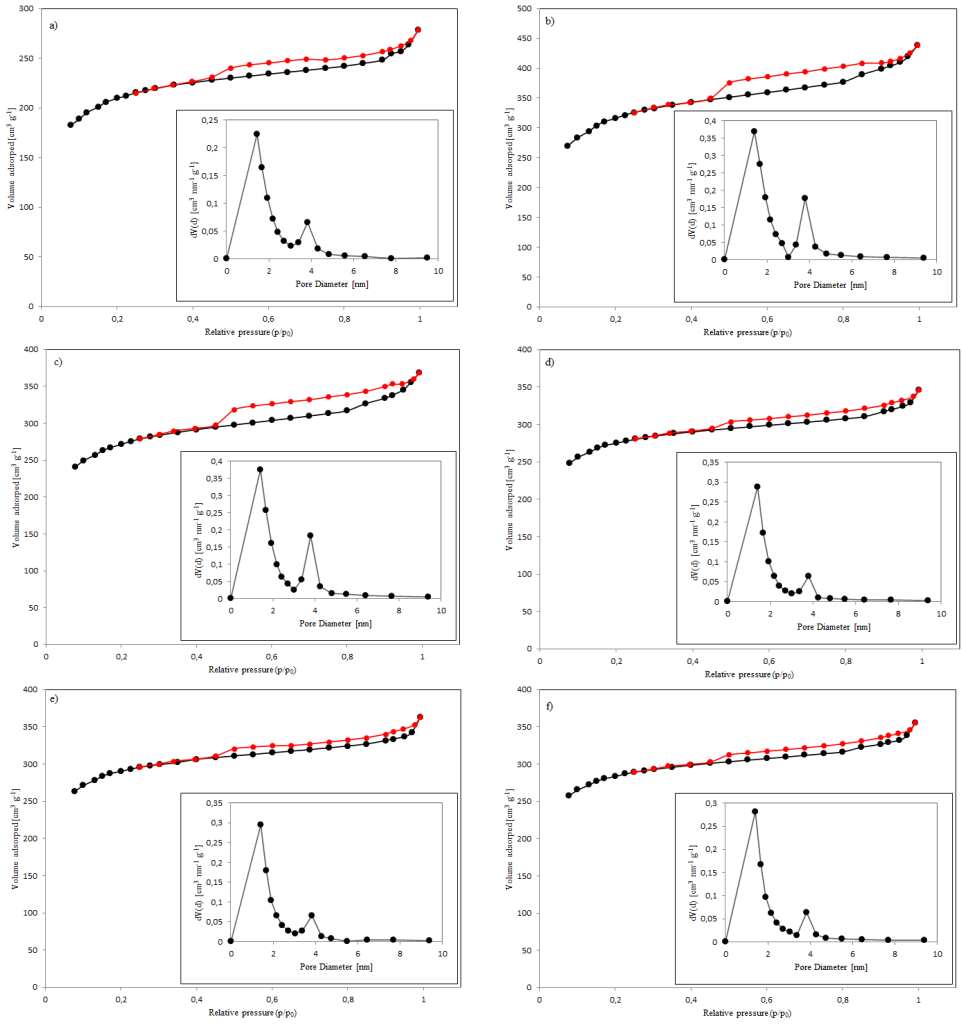


Fig.3. *BET nitrogen adsorption-desorption isotherms and BJH pore size distribution curve of DT0*



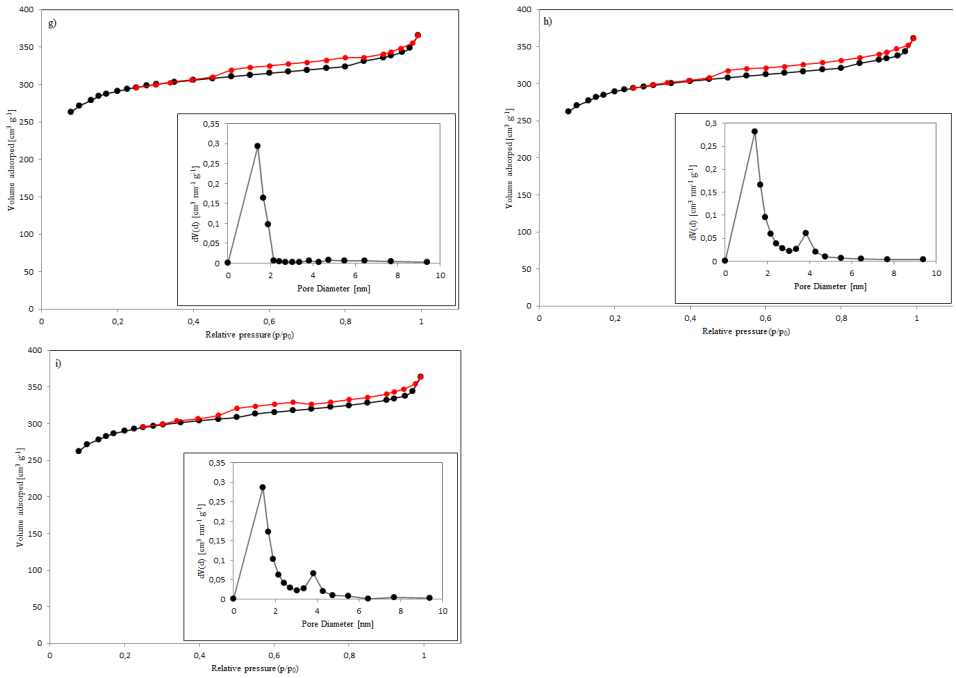


Fig.4. *BET nitrogen adsorption-desorption isotherms and BJH pore size distribution curve of: a) IS-2, b) IS-3, c) IS-4, d) IS-5, e) IS-6, f) IS-7, g) IS-8, h) IS-9, i) IS-10*

Conclusions

This paper proves that the introduction of transition metals salts is changing the inner structure of activated carbons. For example, silver(I) causes a decrease in the number of pores yielding so smaller surface area and resulting in worse adsorption properties. However, silver is an antiseptic so it would be helpful in the treatment of biologically-contaminated samples. On the opposite side, there is zinc(II), which increases the porosity of carbonaceous adsorbents by as high as 44%. Such modified carbons have more developed mesopores and micropores. More transition metal ions may have a positive impact on the adsorbent structure, however further experiments are required.

Any further work will require in-depth statistical analysis [12], especially regarding possible interactions [13-15]. In cases where the number of available measurements is too small to adequately narrow down the uncertainty range, nonparametric [16-18] and resampling [19, 20] approaches will be useful. The obtained results and the methodology of these approaches can be applicable in metal processing [21], welding [22], and coating applications [23], including special coatings [24, 25].

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