

HEAVY METAL IONS SORPTION ONTO ACTIVATED CARBON

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ABSTRACT. Heavy metal pollution is one the major problems concerning environment and water sources in particular. Their stability and mobility in natural waters mark them as a great threat for the human health. The health concern raise from the fact that their LD50 is low as well as they can be accumulated in human body. Most of the heavy metals are known to cause illnesses affecting central nervous system and known carcinogens. In this study we present sorption of different heavy metal ions (Cu²⁺, Ni²⁺) as a method for their removal from polluted water. A comparative study of the sorption of different ions of activated carbon is conducted. We have investigated the effect of different parameters (pH, temperature, ionic strength) onto sorption capacity of the activated carbon.

Key words: heavy metals, sorption, water treatment.

СОРБЦИЯ НА ТЕЖКИ МЕТАЛНИ ЙОНИ ВУРХУ АКТИВЕН ВЪГЛЕН

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РЕЗЮМЕ. Замяръсяването с тежки метали е един от основните проблеми, свързани с околната среда и водите. Тяхната стабилност и подвижност в природните води ги прави сериозна заплаха за човешкото здраве. Опасността, която те представляват се дължи на факта, че имат ниско LD50, както и това, че могат да се акумулират в човешкото тяло. Повечето йони на тежки метали причиняват заболявания, засягащи централната нервна система, а освен това са и доказани канцерогени. В това изследване е представена сорбцията на йони на различни тежки метали (Cu²⁺, Ni²⁺) върху активен въглен като метод тяхното отстраняването от замърсени води. Проведено е и сравнително изследване на сорбцията на различните видове металните йони, както и влиянието на различни параметри (pH, температура, йонна сила) върху сорбционния капацитет.

Ключови думи: тежки метали, сорбция, пречистване на води

Introduction

Releasing heavy metals in environment has been a great concern in the recent years. The development of industry, especially mining industry (Boularbah *et al.*, 2006), leads to increasing the amount of heavy metals released in the water and soil. This presents a great hazard to the human health since they are toxic and known carcinogens with tendency to bioaccumulation (Boularbah *et al.*, 2006; Megateli *et al.*, 2009; Liber *et al.*, 2011).

Sorption is one the most effective methods for removal of pollutants in water including heavy metal ions. There are a few major classes of materials used as sorbents – zeolites, ion exchange resins (synthetic and natural based polymers) and activated charcoals (AC) (Wanga *et al.*, 2009; Kandaha *et al.*, 2007). What makes AC appealing is their high sorption capacity toward metal ions, their relatively low price as well as the possibility for regeneration of the sorbent (Fu *et al.*, 2011).

Carbon based materials, in particular, have attracted attention due to their high efficiency in removal of various types of pollutant simultaneously – metal ions, the complexes they might form, as well as toxic organic substances. Their sorption properties are due to their highly developed inner surface and the various types of functional groups on their surface (Pyrzynska *et al.*, 2010).

Experimental part

Chemicals. Activated charcoal Norit® CA1 was purchased from Sigma-Aldrich and used as received (without any further treatment). Ni(NO₃)₂·6H₂O (98%) and CuCl₂·2H₂O (purum) were obtained by Valerus, Bulgaria and K₂HPO₄ (purum) and KH₂PO₄ (purum) by Teokom, Bulgaria.

Solutions. Solutions of heavy metal ions used in the experiments were prepared as it follows: about 0.5 g of Ni(NO₃)₂·6H₂O and 0.3 g CuCl₂·2H₂O were dissolved in 10ml buffers with different pH values to obtain a solution with approximate concentration 0.2 M (mol/l), respectively. The selected buffer solutions used in our experiments are with pH value of 2.2 (KCl/HCl), 4.8 (AcOH/ NaOH) and distilled water (pH 6.5). Concentration of Ni²⁺ and Cu²⁺ ion during the experiments were determined spectrophotometrically (Shimadzu UV160A).

Sorbent characterization. The morphology of the activated carbon was observed by scanning electron microscopy SEM (JEOL JSM-6390) – Figure 1 and the specific surface analysis was performed by the express method (Klichko-Gurvich) with N₂ sorption at low temperature and is determined to be 980 m²/g.

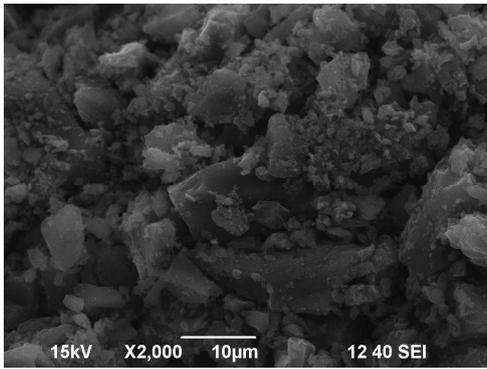


Fig. 1. SEM image of activate carbon of Norit® CA1

AC is a sorbent with highly developed inner surface. There're different types of functional groups on its surface and its activity depends on a lot of factors – material of origin, preparation and activation procedure. There are two main mechanism of interaction of AC with substances: 1) electrostatic interaction between the functional groups on its surface and 2) hydrophobic π - π interaction (Pyrzynska *et al.*, 2010).

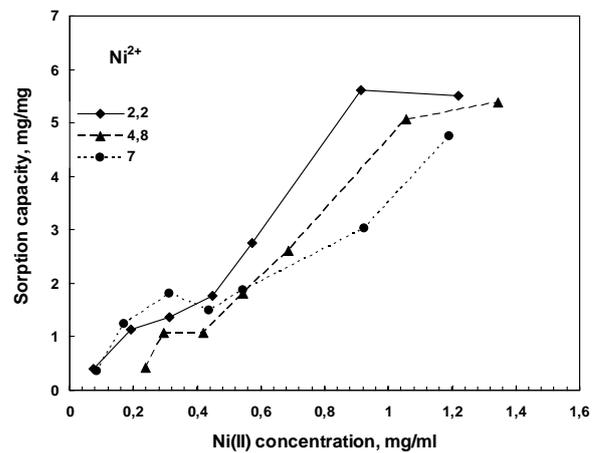
Results and discussions

pH dependence. In order to determine the influence of pH of the media onto sorption capacity of AC, a solution of Ni^{2+} and Cu^{2+} in buffers with pH value of 2,2, 4,8 and distilled water were prepared with approximate concentration of the initial solution 0.2 mol/l. Thus prepared initial solutions were use to determine the sorption isotherms for the two types of heavy metal ions onto activated carbon (AC). For this purpose a series of samples with different heavy metal ions concentrations were prepared using aliquot of the initial solution and diluting it to the same final volume. Then an activated carbon (AC) (about 5 mg) is added to each sample. Samples were left for 48 hours at room temperature and then the concentration of metal ions left in the solution was measured spectrophotometrically. Based on the Freundlich isotherm the data were presented as a relation between the mass concentration of the sorbed metal ion per mass of sorbent (q) and its concentration in the solution at equilibrium (C_M). It's more convenient to express the equation in its linear (logarithmic) form:

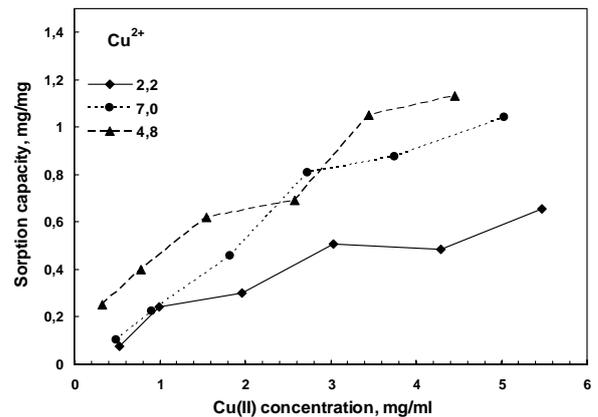
$$\log(q) = \frac{1}{n} \log C_M + \log K \quad (1)$$

where K and $1/n$ are constants describing the sorption capacity and sorption rate, respectively.

The data obtained by the linear fit are given in Table 1. We can see that the value of $1/n$ doesn't vary greatly with pH and the type of the ion, while K values for $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ differ approximately one order. Based on the data for K and $1/n$ we can assume that the rate of sorption for this two ions and pH values is practically the same but sorption capacity of AC to $\text{Ni}(\text{II})$ is greater than the one for $\text{Cu}(\text{II})$.



(a)



(b)

Fig. 2. Adsorption isotherm of Ni^{2+} (a) and Cu^{2+} (b) ions onto AC at three different pH values

In Figure 2 are shown the sorption isotherms of Ni^{2+} (a) and Cu^{2+} (b) ions at three different pH values. For the case of copper ions one can see that sorption capacity increases with pH which is in agreement with the general rule. It states that due to ionization of functional groups onto AC surface (with increasing of pH) sorption capacity increases because of the electrostatic interaction between the positive charged metal ions and negative charge functional groups. In the case of $\text{Ni}(\text{II})$ ions that dependence is not strongly pronounced and sorption capacity doesn't not significantly vary with pH at that given interval. Overall, the sorption capacity of $\text{Ni}(\text{II})$ ions onto AC is greater than one for the $\text{Cu}(\text{II})$ ion.

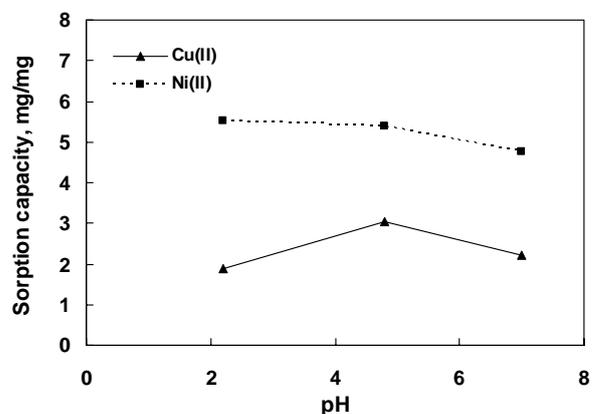


Fig. 3. Sorption capacity of $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ onto AC at three different pH values

The not so pronounced dependence of sorption capacity (Q) from pH maybe due to the fact that pH at zero value (the pH above all functional groups are deprotonated) is above or near the value of 2.2.

Table 1
Values for the parameters obtained by linear fit of Freundlich isotherm

Cu(II)			
pH	K	1/n	R ²
2.2	0.17	0.95	0.92
4.8	0.47	0.70	0.94
6.8	0.24	1.02	0.99
Ni(II)			
pH	K	1/n	R ²
2.2	4.81	0.97	0.97
4.8	4.15	1.40	0.95
6.8	3.64	0.83	0.90

We can assume that varying the pH above that value doesn't affect Q greatly. Other factor that may contribute to the sorption capacity (Q) of Ni(II) and Cu(II) ions onto activated carbon is the fact that they can form stable complexes with chloride and acetate anions from the buffer solutions and thus making them more stable in solution and lower their affinity toward the AC surface.

Conclusions

In this study we have investigated the sorption capacity of nickel and copper ions onto activated carbon, its dependence from pH and ionic strength of the media. It was shown that AC has a high sorption capacity in regard of these ions, as well as the complexes they form. It was established that pH doesn't significantly change the sorption capacity, which is very useful given the fact that AC can be applied in wide range of wastewater treatment processes. AC can be used as an effective and economically profitable sorbent for a wide range of heavy metal ions and the fact that its sorption capacity remains high regardless of the media conditions – pH, ionic strength and complex forming reagents present in the wastewater.

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