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THE SORPTION OF CYANIDES FROM THE WATER ONTO ACTIVATED CARBON

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Abstract. *Activated carbon is very often used as an efficient and economic adsorbent for waters refining from organic and anorganic chemical reagents. The aim of the whole research is to analyze the sorption process as well as the possibility of predicting exit parameters of the system for cyanide chemisorption onto activated carbon impregnated by copper (II) acetate monohydrate from the water's medium. Specific surface of granulated activated carbon, granulation of activated carbon, mass of the substance for impregnation per unit mass of activated carbon, initial concentration of cyanides and temperature of the solution are used as initial parameters. Realization of experiment and data processing of obtained results has been done by methods of mathematical planning of experiment, regression and correlation analysis. This paper presents the results of investigation of bonded cyanides relative mass reliability to time,* $m_{CN} = f(\tau)$ *for three samples with different contents of impregnant per unit mass of activated carbon. Three complex exponential regression equations formed as* $Y = a \cdot x^{b_1} e^{b_2 \cdot X}$ *were obtained and they are suitable for representation of experimental data for examined time interval (*$\tau < 30$ *min) with correlation coefficient which is more than 0.99 and medium relative error of experiment less than 2.64%.*

Key Words: *Activated Carbon, Impregnation, Adsorption, Chemisorption, Regression Analysis, Correlation Analysis*

INTRODUCTION

The same name "cyanides" is used for the compounds having cyanide ions, CN^-, formed as free or complex ion (1) in their structure. They belong to the group of non specific pollutants of the natural waters in which they come from industries such as ones for manufacturing coke, refining ores and metals, galvanizing, etc. There are a great number

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of methods developed for removing cyanides from water and they are mostly based on chemical change of cyanides (*CN*) to the less toxic and untoxic compounds. Few attempts have been made for removing CN from water by ionic changing (2-4) but they have not had commercial significance. For the last twenty years granulated activated carbon (*AC)* has been having a wider application in chemical engineering particularly for removing impurities from the wastewater and drinking waters; this is confirmed by the emergence of a great number of papers from this domain of study (5,12). An attempt to discharge cyanide wastewater onto AC by physical adsorption has not been successful (6). For those reasons there are used AC impregnated by salts which form stable complexes with cyanide ions. Copper, silver and nickel salts are the most often used for chemisorption onto AC. Ferric salts, which have the most stable complexes with CN, can be used only in the cases where the conditions for photolysis are impossible because in that case, complex decomposes and toxic HCN are formed (1).

Systems for chemisorption of CN from water can be most generally classified into the charged and the current ones. In order to design them, the kinetic and other parameters of AC should be known. Since single sorption of CN onto AC presents a complex process which includes chemical reaction and physical sorption at the same time, application only of known kinetic laws for chemical reaction and physical sorption independent of one another, for determination of chemisorption, is not enough for satisfactory results. Mass of bonded CN per unit mass of AC during the testing time (m_{CN}) is a complex function of specific surface AC (*S*), impregnant mass per unit mass of AC – impregnation index (*I*), temperature (*t*), granulating composition of AC (*G*), nature of impregnant, initial concentration of CN in to water (C_0), mass of AC per unit volume of cyanide solution (*M*), medium pH, in other words $m_{\mathrm{CN}}=f(S,I,t,g,C_0,M,pH)$. Bonding of a greater number of those parameters into a mathematical model could have great practical importance for designing of the system for water refining of the CN.

Mathematical description of chemical processes, using experimental statistic methods and multivariable statistic had much larger application through the past years. The reason for this is in the fact that statistic methods allow the acquisition of the mathematical model including all known variables, even at the low level of the theoretical knowledge about process mechanism (7).

This paper presents a segment of the authors' complete research work about the possibility of predicting sorption parameters of CN from the water onto AC impregnated by copper (II) acetate monohydrate (ACCuAc), forming mathematical model, using methods of mathematical planning of experiment, and regression and correlation analysis including all existed variables.

EXPERIMENTAL

Materials

All the chemicals used in paper were of analytical grade (p.a). Copper (II)-acetate monohydrate (CuAc) was produced by Kemika Zagreb, Croatia. Solution for impregnation of AC was prepared by immersing it in the solution prepared by dissolving CuAc in distilled water with conductivity < 1 µS. Basic CN solution was prepared by dissolving the appropriate mass of KCN, produced by Zorka, Šabac, Yugoslavia, in distilled water with the same quality. The basic adsorbent for impregnation was coconut granular AC (using steam at 950 °C), type KRF-H, produced by Trayal Corporation, Krusevac, Yugoslavia. The characteristic of the used non impregnated (I_0) and impregnated (I_{42}, I_{59}, I_{72}) AC are listed in Table 1. The pH values of CN solution were adjusted to pH = 12 with KOH and HCl p.a quality and either acid and base were produced by Zorka, Šabac, Yugoslavia.

Table 1. Characteristic of impregnated and nonimpregnated AC

CHARACTERISTIC OF AC	VALUE			
	I_0	I_{42}	I_{59}	I_{72}
Specific surface area BET (m^2/g)	1436	1357	1327	1297
Adsorption of C_6H_6, (%)	48.28	45.9	44.3	43.2
Iodine number (mg/g AC)	1419			
Methylen blue index (cm^3)	17			
pH value	9.35			
ASH (%)	7.90	11.9	13.6	14.8
DAMP (%)	7.81			
	> 1.6 mm		5.1%	
Granular structure	0.425-1,6 mm		96.9%	
(DIN 4188)	< 0.425 mm		0.6%	
	< 0.355 mm		0.3%	

ANALYSIS

Experimental research in this paper could be separated into three totalities: impregnation of AC, examining of the sorption kinetic of CN onto ACCuAc and data processing of the obtained results. ACCuAc with three different impregnation indices was prepared by immersing 10 g AC dried at 110 °C to constant mass into the 250 cm^3 solution of CuAc during 24 hours.

In order to get ACCuAc with approximate needed impregnation index, initial concentrations of CuAc were determined on the basis of the previously defined Freundlich isotherm. Initial concentrations of CuAc solution for impregnation were 0.05; 0.10 and 0.25 mol/dm^3. In that way, ACCuAc with impregnation indices 42.0; 59.0 and 72.0 mgCu/gAC, respectively, were done. Deposit mass of copper per unit mass of AC (m_{Cu}) was determined on the basis of the volume of the solution for impregnation (V), initial concentration of copper (C_0), concentration of copper after immersing (C_1) and mass of the immersed AC (m_{AC}) according to equation 1 (8):

$$m_{Cu} = V(C_o - C_1)/m_{AC} \tag{1}$$

The determination of the copper concentrations in the solution for impregnation before and after immersing was done by an atomic adsorption spectrometer (*AAS*) Perkin Elmer 1100B and by iodometric titration method. The basic CN solution in water (3.80×10^{-2} mol/dm^3) was prepared by dissolving 3.80×10^{-2} mol KCN into the 1 dm^3 of distilled water. The concentration of CN in such prepared solution (basic solution) was determined by the Liebig method with 0,01 mol/dm^3 $AgNO_3$ titration. Susceptibility of method was 3.85×10^{-5} mol/dm^3 (9). Working solution (3.85×10^{-3} molCN/dm^3) was prepared by measuring of aliquot part of the basic solution and dissolving to working volume. Since the kinetic of process is greatly present in the starting period and since more than half of maximum capacity of ACCuAc is reached for less than 30 minutes, observation of the CN concentration in the solution during sorption process at AC by classic method is not practical. For those reasons an electroanalytic method of direct potentiometry with ion selective electrode (*ISE*) for cyanide has been applied (Radiometer, model F1042CN-0, Copenhagen, Denmark). In the area of applied concentrations ($0–3.85 \times 10^{-3}$ mol/dm^3), electrode is agreed to Nernst law. The saturated Calomel electrode was used as referent electrode. Continual observation, numeric and graphic notes of experimental data were realized by AD converter type MAS 345 and by program package Mas View Software Version 1.1, produced by Mastech. Temperature of working solution ($\pm 0.1\ ^0$C) was kept by Thermostat U1, produced by VMP VERK, GDR. Fig. 1 shows scheme of aparature which was used for observation of sorption kinetic of CN onto ACCuAc.

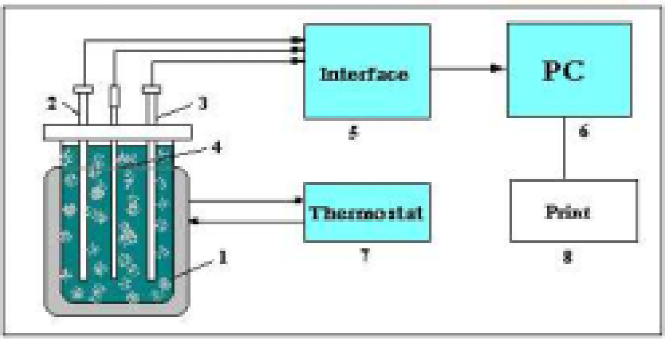

Fig. 1. Scheme of aparature used for observation of sorption cinetic of CN onto ACCuAc
1) Reactor; 2) Ion selective electrode; 3) Referent electrode; 4) Temperature sonde; 5) Interface; 6) PC; 7) Thermostat; 8) Writer

RESULTS AND DISCUSSION

Impregnation of AC gives better selectivity and capacity of chemisorption. Deposited impregnant causes partial change of pore structure of AC which is consequence of its depositing in macropores and transitional pores. At the same time, there is a blockade of one part of the micropores. The investigated results of deposing of impregnant (CuAc) onto AC are presented in Table 1. Partial reduce of specific surface of AC caused by increase of impregnation index appears, and its consequence is reduction of physical sorption effect compared with chemisorption. The results (Table 1) confirm the reduction of benzole sorption from 48.28% at nonimpregnated AC (I_0) to 43.20% at AC with impregnation index 72.0 mgCu/gAc (I_{72}). This result is caused by fact which shows that benzole is bonded for AC only by physical sorption under the given experimental conditions.

Bonding process of chemical reagents onto impregnated AC is a complex process which depends on many factors. This fact is a consequence of complex phenomena, which appear in the structure of impregnated AC (chemical reaction, physical sorption, diffusion). Chemisorption process of CN bonding takes part in two phases (10):

$$Cu^{2+}_{(aq)} + 2CN^{-}_{(aq)} \leftrightarrow Cu(CN)_{2(s)} \quad (2)$$

$$2Cu(CN)_{2(s)} + 6CN^{-}{}_{(aq)} \leftrightarrow 2[(Cu(CN)_4)]^{3-}_{(aq)} + (CN)_2 \quad (2)$$

Results from investigation of temperature influence on sorption kinetic of CN onto ACCuAC are listed in Fig. 2. It can be noticed that process of CN bonding is relatively slow considering that final equilibrium appears after few hours and that it has diffusion control (reliability C/Co has exponential character) (11). The kinetic influence at the start (3 min) is less expressed and it has more significant appearance in the later process phase. In the starting phase when the reactants` concentrations (Cu^{2+}; CN^{-}) are the biggest, in other words, ions of Cu^{2+} are the most available and since it happens to be a ionic reaction which takes part in a very short time interval (max 2 s), the diffusion processes of this phase have less importance. In later phase when ions of Cu^{2+} are less available, for some of them it is impossible to reach because of the blockade for input at the micropores made by the already formed sediment of $Cu(CN)_{2(s)}$ and $[Cu(CN)_4]^{3-}{}_{(aq)}$,,their diffusion processes became more expressed and their dependence on temperature, too. Velocity progress of CN sorption onto ACCuAc with temperature increasing shows dominance of chemisorption process and absence of cyanide physical sorption onto AC which happen to be reduced with the temperature increasing

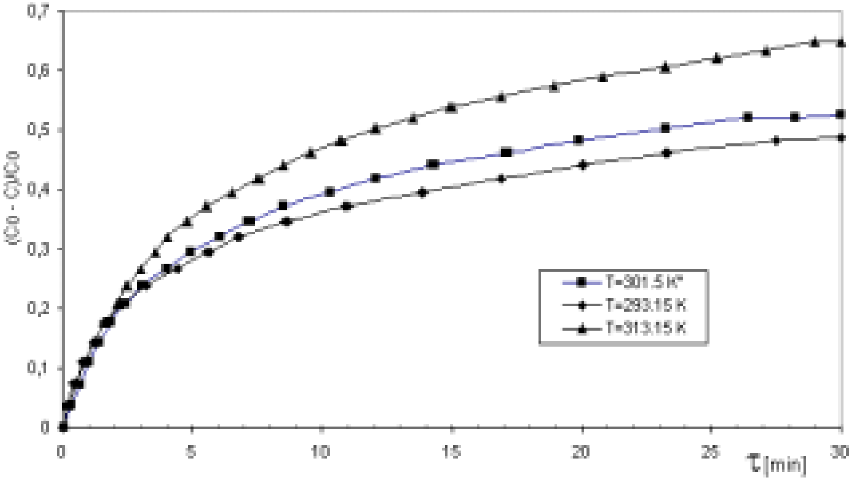

Fig. 2 Cyanides sorption reliability on temperature of solution
(Initial concentration of CN, $C^0_{CN} = 0.100$ g/dm^3; mass of ACCuAc, $m_{ACCuAc} = 1.00$ g; volume of working solution of CN, V = 0.100 dm^3; used AC with 42.0 mgCu/gAC; pH=12.0)

Mass of the covered impregnant, approximately per unit mass of AC, considering the fact that we are dealing with the diffusion controlled special chemisorption process, has important influence on velocity of CN sorption onto ACCuAc in all the phases of the process. Investigation results of the impregnation index influence on the kinetic of CN sorption onto ACCuAc are shown in Figure 3. It is noticed that difference of process velocity in the starting period is more expressed on the samples with lower impregnation index since the increasing of impregnation index slightly causes difference between the velocities at the starting period. Equilibrium conditions are clearly expressed and equilibrium concentration of bonded CN per unit mass of AC are expanded with increasing of impregnation index which is in accordance with the well-known dependence of reaction velocity on reactant concentrations.

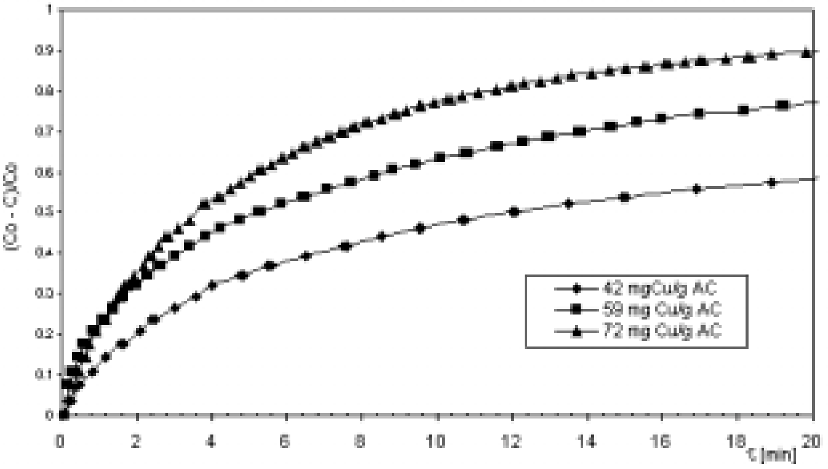

Fig. 3 Cyanides sorption reliability on mass of Cu^{2+} deposed by impregnation (Initial concentration of CN, $C^0_{CN} = 0.100$ g/dm^3; mass of ACCuAc, $m_{ACCuAc} = 1.00$g; volume of working solution of CN, V = 0.100 dm^3; t = 40 ^{0}C; pH = 12.0)

At the mathematical modeling the biggest problem is the choice of adequate type of starting equation. Considering that there is, in certain cases, a process with dominant role of chemical reaction, as the most probable form of the mathematical model there have been tested models with complex exponential form.

$$Y = a \cdot x^{b_1} e^{b_2 X} \tag{4}$$

There have been tasted experimental data caused by CN sorption onto ACCuAc impregnated by 42.0 mgCu/gAC at t = 40 ^{0}C and pH = 12, at charged system with intensive mixing: Volume of the working solution was 0.100 dm^3 and mass of the ACCuAc was $m_{AC} = 1.00$ g. There were three regression equations for three cases of impregnant contens per unit mass of AC:

$$[(c_o - c)/c_o]_{I_{42}} = 0.137 \cdot \tau^{0.631} e^{-0.0211 \cdot \tau} \tag{5}$$

$$[(c_o - c)/c_o]_{I_{59}} = 0.246 \cdot \tau^{0.465} e^{-0.0122 \cdot \tau} \tag{6}$$

$$[(c_o - c)/c_o]_{I_{72}} = 0.244\ \tau^{0.625} e^{-0.0278 \cdot \tau} \tag{7}$$

Figure 4 graphically gives experimental data and data from regression equations 5, 6 and 7

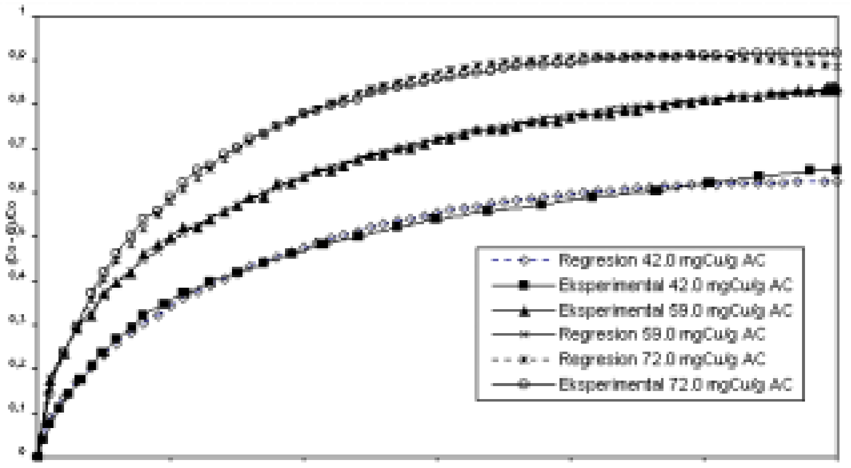

Fig. 4.Experimental and regression curves of CN sorption cinetic onto AC with different contens of impregnans
(Initial concetracion of CN, $C^0_{CN} = 0.100$ g/dm^3; mass of ACCuAc, $m_{ACCuAc} = 1.00$ g; volume of working solution of CN, V = 0.100 dm^3; t = 40 ^{0}C; pH = 12.0)

It can be noticed that given equations satisfactorily correspond to the description of the examined process kinetic which is confirmed by correlation coeficient $R_{I_{42}} = 0.996$, $R_{I_{59}} = 0.999$ and $R_{I_{72}} = 0.998$, as well as data of medium relative error of experiment $\overline{\alpha}_{I_{42}\,rel} = 2.64\%$, $\overline{\alpha}_{I_{59}\,rel} = 0.884\%$ and $\overline{\alpha}_{I_{72}\,rel} = 1.616\%$ respectively.

CONCLUSION

The aim of this paper was to study the impregnation process of AC and CN chemisorption onto AC impregnated with CuAc. This was a part of the author's larger research of the possibilities of predicting parameters of CN sorption onto the AC, as well as describing kinetic of this process by the mathematical model using methods of regression and correlation analysis, all limited with practical use (for $\tau < 30$ min). Results which will be obtained could have practical significance for designing the systems for removing pollution from wastewaters and drinking waters.

Based on the theoretical knowledge and experimental data obtained from this paper, the following can be concluded:

1. Impregnation of AC by CuAc makes possible CN sorption onto AC with the reduction of specific surface per 10%, at the same time.
2. Working temperature has significant influence on kinetics of CN sorption and it is less expressed in the process starting phase.
3. Increasing of AC impregnation index has positive influence on velocity of the CN bonding process which is more expressed in the starting phase (τ<5 min), and it confirms specific chemisorption nature of this process.

4. Equilibrium mass of bonded CN per unit mass of AC expands with increasing of impregnation index.
5. Effective continual observing of kinetics of CN sorption onto ACCuAc is possible using ISE for CN, AD converters and software package used in this paper.
6. Constructed mathematical models adequately represent experimental data considering that correlation coefficient is R > 0.99 for all of three cases of AC impregnation index.

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SORPCIJA CIJANIDA IZ VODE U AKTIVNI UGALJ

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Aktivni ugalj se veoma često koristi kao efikasan i ekonomičan adsorbens za prečišćavanje vode od hemijskih agenasa organskog i neorganskog porekla. Impregnacijom aktivnog uglja postiže se veća selektivnost i kapacitet. Cilj ukupnih istraživanja je analiza sorpcionog procesa i mogućnost predvidjanja izlaznih parametara sistema za hemisorpciju cijanida na aktivnom uglju impregnisanom bakar(II) acetatom monohidratom iz vodene sredine. Kao polazni parametri koriste se specifična površina granulisanog aktivnog uglja, granulometrijski sastav, masa supstance za impregnaciju po jedinici mase aktivnog uglja, polazna koncentracija cijanida i temperatura rastvora. Realizacija eksperimenta i obrada dobijenih rezultata vršena je metodama matematičkog planiranja eksperimenta, regresione i korelacione analize. U ovom radu prikazani su rezultati istraživanja zavisnosti relativne mase vezanih cijanida, od vremena, , $m_{CN} = f(\tau)$*, za tri uzorka sa različitim sadržajem impregnansa po jedinici mase aktivnog uglja. Ustanovljene su tri složeno eksponencijalne regresione jednačine oblika* $Y = a \cdot x^{b_1} e^{b_2 \cdot X}$ *koje dobro reprezentuju eksperimentalne podatke u posmatranom vremenskom intervalu (*$\tau<30$ *min) sa koeficijentima korelacije većim od 0,99 i srednjom relativnom greškom eksperimenta manjom od 2,64%.*

Ključne reči: *Aktivni ugalj, impregnacija, adsorpcija, hemisorpcija, regresiona analiza, korelaciona analiza*