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Adsorption of Sodium Cyanide on Activated Carbon

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1. Introduction

Disasters and chemical breakdowns have many times been the cause of environmental pollution, the poisoning and death of people.

The breakdowns and disasters can be caused by pouring out or evaporation of toxic industrial compounds (TIC) and poisons into the environment. Toxic compounds can escape from chemical and industrial plants as a result of damage of the storage areas, tanks, cisterns, installations, etc. containing the substrates or final products. There are 37 chemical, petrochemical and paper-cellulose plants in Poland which can be the cause of extreme dangers to the environment. According to the State Inspection of the Environmental Protection, there are 1700 potential sources of great industrial disasters in the country. These include storage areas and industrial plants. The most hazardous ones as to the possibility of air, water and soil pollution are gas substances (ammonia, chlorine, sulfur dioxide, Freon, propylene, carbon dioxide and acrylonitrile), liquid substances (nitric acid, sulfuric acid, hydrochloric acid, formic acid) and solids (caustic soda and hydrogen cyanide) [3, 15, 20, 40, 41].

The hazards of pollution and poisoning of people and the natural environment can be looked at in four aspects [5–7, 16, 23–27, 43, 44]:

- poisoning of people and contamination of plants using cyanides in the technological processes,
- chemical breakdowns and disasters,
- terrorist actions using poisonous substances for sabotage and diversive purposes,
- military actions using toxic substances or military actions resulting in the damaging of plants or installations using sodium cyanide in their technological processes.

Hydrogen cyanide is a member of a group of generally toxic substances and can cause immediate death when administered in certain doses. Poisoning under industrial conditions happens rarely and may be a result of breathing in the fumes or by absorption through skin. Hydrogen cyanide poisoning can incidentally occur among people as a result of eating plant products containing this substance. Hydrogen cyanide and its salts are frequently used for suicidal, criminal as well as sabotage and diversion purposes. Hydrogen cyanide is quickly absorbed by lungs, undamaged skin and a digestive system. The cyanides are absorbed in the form of fogs and dust through a respiratory tract. They also easily penetrate a skin and are quickly resorbed by a digestive system. Sodium cyanide and potassium cyanide are more toxic than other cyanides. The lethal dose of NaCN for a human being is 0.10 g and 0.12 g of KCN. However, sometimes even much larger doses do not cause death. The following symptoms are observed during the poisoning: loss of body weight, decrease in potency, anemia, weakening of eyesight and hearing and others [2, 5, 13, 14, 40].

The performed research makes it possible to determine the amount and type of activated carbon needed in order to purify water for people as well as for the purposes of agriculture, and of the agricultural and food industry.

2. Materials and Methods

2.1. The properties of sodium cyanide

Sodium cyanide (NaCN) forms colorless crystals of faint hydrogen cyanide aroma. Sodium cyanide dissolves in ethanol and methanol. The basic properties of sodium cyanide [2, 12, 15, 44]:

– molecular weight: 49.01

– density: 1.596 g/cm^3

– solubility in water: 48.15 g/100 cm^3 (10°C), 58.2 g/100 cm^3 (20°C)
63.7 g/100 cm^3 (25°C), 71.5 g/100 cm^3 (30°C)
81.8 g/100 cm^3 (35°C), 82.5 g/100 cm^3 (55°C)

2.2. Adsorption from water solutions

Seven activated carbons were selected for the studies. These carbons are produced on a technical scale at the Hajnowka Company of Dry Wood Destillation and are as follows: ML, CWZ-3, Cf, AG-5, AG-2u, N, AHD and author's made laboratory examples: WP/W, WS-10, WS-11, WS-12, WS-13, WS-14, WS-15, WS-16. The activated dusty carbons medicinalis ligni (ML) and carbopol CWZ-3 as well as the granulated Cf (carboferrogel), AG-5, AG-2u, N, AHD and WP/W, WS-10, WS-11, WS-12, WS-13, WS-14, WS-15, WS-16 were crushed and sifted through a sieve with the holes of 0.075 mm a in diameter. The isotherms for sodium cyanide were marked for a range of dilutions from 10.0 mg/dm^3 to 1000.0 mg/dm^3 (ML, CWZ-3, Cf, AG-5, AG-2u, N, AHD) and from 10.0 mg/dm^3 to 1500.0 mg/dm^3 (WP/W, WS-10, WS-11, WS-12, WS-13, WS-14, WS-15, WS-16) and the weighed amount of carbon is equal to 500.0 mg. The isotherms were obtained in the temperature 20.0^{o}C under the conditions of an established sorption equilibrium. A generally used research methodology referring to adsorption in static conditions was used [16, 17, 19, 42]. The activated carbons were flooded with destilled water and left aside for 24 hours at room temperature. Next, after filtration, they were dried in temperature of 130.0^{o}C. The weighed amounts of the sorbent equal to 500.0 mg were dropped into round flasks with glass plugs. The volume of each flask was 250.0 cm^3. Next, 50.0 cm^3 of a water solution of sodium cyanide was poured into the flasks, the concentration of the solution was increased consecutively: 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0, 200.0, 300.0, 400.0, 500.0, 600.0, 700.0, 800.0, 900.0, 1000.0 mg/dm^3 (and 1100.0, 1200.0, 1300.0, 1400.0, 1500.0 mg/dm^3). The flasks with the samples prepared in the described manner were shaken manually ensuring full soaking of the crushed carbon sorbent. The contact of the solution with the adsorbent was ensured by intensive mixing of the samples on the shaker with the shaking speed of 250 and the amplitude of 8. After having achieved a sorption equilibrium, the suspended matter was filtered through a hard paper filter in order to separate the active carbon. The cyanide concentration as well as the chemical oxygen demand and permanganate value were marked in the filtrate. For each carbon and for the separate equilibrium concentrations, adsorption volumes were established [15, 18, 21].

The concentration of sodium cyanide was marked colorimetrically on a spectrophotometer by means of the barbiture method [15, 44].

For the purpose of description of the adsorption of chemical compounds from water solutions with the use of activated carbons, usually the Freundlich, Langmuir, BET and Dubinin-Astachov (DA) equations of isotherm adsorption are used [10, 21, 27, 30, 36, 38, 39].

Most frequently, for the evaluation of the adsorption processes of water and sewage technology, the Freundlich equation of the adsorption isotherm is used (1) [4, 28]:

$$a = kC_e^{1/n} \tag{1}$$

where: a – the extent of the adsorption; k, $1/n$ – equations constants, C_e – equilibrium concentration.

In order to establish the volume of the adsorption level a_m, $a_{m'}$ as well as the specific surface of the sorbents S_L, S_{BET} the Langmuir's (2) equation for adsorption isotherm and BET (3) was used [8, 9]:

$$a = \frac{a_m K C_e}{1 + K C_e} \tag{2}$$

where: a_m – volume of the adsorption monolayer, K – adsorption equilibrium constant, a, C_e – as above.

The equation for the adsorption isotherm BET (3) is presented in the following form [1, 11, 29]:

$$a = \frac{a_m C \frac{C_e}{C_n}}{(1 - C_e)\left[1 + \left(C - 1\frac{C_e}{C_n}\right)\right]} \tag{3}$$

where: C_n – concentration of the saturated solution, C – the BET equation constant, $a_{m'}$ – the volume of the adsorption layer, a, C_e – as above.

For the purpose of the analysis of the adsorption process from water solutions, taking into consideration the energy parameters (E), the border adsorption volume (V_a) and the microporous structure (B), the Dubinin-Astachov equation was used (4,5) [31÷35, 37]:

$$\lg a = \lg a_0 - 2.303\frac{R^n T^n}{E^n}\left(\lg\frac{C_n}{C_e}\right)^n \tag{4}$$

or

$$\lg(aV^*) = \lg V_a - 2.303\frac{R^n T^n}{E^n}\left(\lg\frac{C_n}{C_e}\right)^n \tag{5}$$

where: a_o – the border adsorption amount, V^* – the molar volume of the adsorbate, V_a – the border adsorption volume, E – characteristic adsorption energy, C_n – concentration of the saturated solution, R – gas constant, T – temperature [K]; a, C_e – as above.

3. Results and Discussion

Being a non-organic compound, sodium cyanide is adsorbed by carbon sorbents rather poorly in comparison to water soluble organics. The carried out research helped to establish the extent of adsorption of sodium cyanide on activated carbon produced in the country at an industrial scale as the contamination of surface waters or the water supply systems by cyanides cannot be excluded. In such case, the answer to the question regarding the extent of cyanide adsorption on activated carbon discussed in the present work would be of significance in the protection of people's health as well as effective purification of water.

Studies have been carried out on the adsorption of sodium cyanide on active carbon from water solution for a range of concentrations from 10.0 to 1000.0 mg/dm^3. For the initial concentration of sodium cyanide equal to 100.0 mg/dm^3, under the conditions of sorption equilibrium, the following values of the extent of the adsorption a (in mg/g) were obtained:

ML=WP/W=WS-10=WS-11=WS-12=WS-13=WS-14=WS-15
=WS-16=10.0 > Cf=9.6 > CWZ-3=7.7 > AG-5=4.0 > AHD=3.7 >
AG-2u=3.5 > N=1.0

For the initial cyanide concentration of 100.0 mg/dm^3 the highest sorption volume approximately 10 mg/g activated carbons ML (medicinalis ligni), WS-11–WS-16 and Cf (carboferrogel) have demonstrated.

For the initial sodium cyanide concentration of 1000.0 mg/dm^3 under the conditions of sorption equilibrium, the following values of adsorption *a* were obtained:

WS-15=90.1 > WS-14=88,8 > Cf=84.0 > WS-12=75.6 > WS-10=71.9 > WS-11=71.7 > WP/W=71.2 > WS-13=70.2 > WS-16=69.9 > ML = 68.5 > CWZ-3 = 22.0 > AHD = 7.1 > AG-5 = 7.0 > AG-2u = 5.0 > N=1.5

The highest sorption volumes for the initial concentration of cyanide of 1000.0 mg/dm^3 belong to activated carbons WS-15 and WS-14 and are respectively 90.1 mg/g and 88.8 mg/g. The high adsorption of sodium cyanide on activated carbon Cf (*a*=84.0 mg/g) is related to the saturation of its surface with sodium hydroxide.

Equation factors for the Freundlich, Langmuir, BET and Dubinin-Astachov equations were established (tables 1, 2, 3, 4).

The extent of the adsorption of sodium cyanide on the chosen activated carbon depends on the value of the *k* and *n* factors of the Freundlich equation. The higher value of the *k* factor, the bigger the adsorption volume of the activated carbon. For sodium cyanide, the values of factor *k* (in m^2/g) for the studied carbons can be put in order ranging from the highest to the lowest value as follows:

WS-15=32.3 > WS-14=30.3 > WS-15=32.3 > WS-12=29.7 >
WS-13=25.2 > ML=22.9 > W-10=21.9 > WS-11=21.6 > WP/W=20.9 > WS-16=20.0 > Cf=4.0 > CWZ-3=2.6 > AG-5=1.8 > AG-2u=1.5 >
AHD=0.8 > N=0.6

As seen in the above formula, the best activated carbons are WS-15 and WS-14, the worst ones are AHD and N.

The values of the Freundlich equation factors (*k, 1/n*) allow to establish the amount of sorbent being inevitable for decreasing the concentration of sodium cyanide in water from the level of its detectable concentration (toxic) C_o to the permissible (unharmful) concentration C_e. The examplificatory calculations of the reduction of sodium cyanide concentrations from 100.0 mg/dm^3 to 50.0, 25.0, 10.0, 5.0, 2.0, 1.5, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.01, 0.001 mg/dm^3 and from 10.0 mg/dm^3 to 5.0, 2.0, 1.5, 0.5, 0.1, 0.01, 0.001 mg/dm^3 are shown in table 5. The *k* factor significantly influences the extent of the cyanide adsorption in the range of concentrations from 100.0 mg/dm^3 to 1.0 mg/dm^3 with the *1/n* value having no significant influence. When reducing the initial concentrations of cyanide C_o to the nontoxic C_e being the hundredth (thousandth) fractions of mg/dm^3, the *k* and *1/n* factors competitively affect the weight amounts of the active carbon.

For example, the reduction of the concentration of cyanide from 100.0 mg/dm^3 to 10.0 mg/dm^3 requires 2.538 g/dm^3 of carbon ML, however in the case of AG-5 carbon, this value is 32.732 g/dm^3. Conducting the process in two stages reduces the amount of carbon inevitable for purifying water from pollution. The one-stage reduction of sodium cyanide concentration from 100.0 mg/dm^3 to 0.01 mg/dm^3 requires 10.474 g/dm^3 of active ML carbon and 129.622 g/dm^3 of AG-5 carbon. Decreasing the cyanide concentration in two stages, for example from the concentration of 100.0 mg/dm^3 to 10.0 mg/dm^3 in the first stage and from 10.0 mg/dm^3 to 0.01 mg/dm^3 in the second stage, can be obtained by dosing into the water solution of sodium cyanide 2.538 g/dm^3 of ML carbon in the first stage and 1.047 g/dm^3 in the second and 32.732 g/dm^3 of AG-5 carbon in the first stage and in the second 12.951 g/dm^3. For the case described above, the reduction of the cyanide concentration in two stages requires 3.585 g/dm^3 of ML carbon and 45.683 g/dm^3 of AG-5 carbon, i.e., in comparison to the one-stage process 6.889 g/dm^3 less of ML carbon and 83.939 g/dm^3 less of AG-5 carbon need (tables 5).

The specific surfaces of activated carbon in m^2/g (table 1) established on the basis of the Langmuir and BET equations are parallel (excluding AG-5 carbon); they can be placed in order according to their decreasing values:

ML=119.6 > Cf=101.2 > CWZ-3=42.5 > AHD=15.3 > AG-5=11.8 >
AG-2u=10.2 > N=3.1

The above order is very similar to the evaluation of the quality of the activated carbons in reference to their adsorption value *a* as well as the *k* factor of the Freundlich equation. The calculated specific surfaces of the activated carbons on the basis of the sodium cyanide adsorption represent the values of the surface which can be engaged by cyanide and not the real surfaces of the studied carbons, which are several times larger. The specific surfaces in m^2/g of the studied activated carbons were established by means of the porosymetric method are as follows:

ML=784.7 > N=673.4 > AHD=615.9 > AG-2u=495.8 > AG-5=454.7 >
CWZ-3=425.4 > Cf=330.5

As it results from the presented data, there is no relationship between the real specific surfaces of the activated carbons established by means of the porosymetric method, which are from 330.5 m^2/g to 784.7 m^2/g, and the values of the specific surfaces established on the basis of the sodium cyanide adsorption.

The value of the *K* constant in the adsorption process in the Langmuir equation is correlated with the extent of the adsorption. Higher value of the *K* constant generally corresponds with an increased adsorption ability of sodium cyanide on the studied carbons. The decreasing order of *K* values are as follows:

WS-15=0.622 > WS-14=0.544 > WS-13=0.501 > WS-12=0.254
> ML=0.250 > WS-10=0.206 > WS-11=0.193 > WP/W=0.163 >
WS-16=0.150 > AG-2u=0.042 > AG-5=0.032 > Cf=0.031 >
CWZ-3=0.028 >AHD=0.022>N=0.018

The order of the activated carbons according to the *K* constant which characterizes the intensity of the reaction of sodium cyanide with the carbon surface gives an approximate evaluation of the quality of the activated carbons. The product of $K \cdot a_m$ potential affinity between the adsorbate and the adsorbent correlates in relation to the surface which it is to be filled. The order of $K{\cdot}a_m$ values informs directly about the order of the active carbons with regard to their adsorption volume:

WS-15=49.487 > WS-14=41.688 > WS-13=32.806 > WS-12=16.458 > ML=16.450 > WS-10=14.099 > WS-11=13.163 > WP/W=11.237 >
WS-16=10.116 > Cf=2.750 > CWZ-3=0.655 > AG-2u=0.235 >
AG-5=0.208 > AHD=0.185 > N=0.031

Analyzing the value of the *C* constant of the BET equation (3) can lead to an observation that the highest value for ML carbon corresponds with the highest *k* value of the Freundlich equation, the lowest values *C* for the AHD and N carbons correspond with the lowest value of *k* for AHD and N carbons:

ML=154908 > AG-2u=26272 > AG-5=19806 > Cf=19373 >
CWZ-3=17514 > AHD=13600 > N=11467

The analysis of the equations (1) and (4,5) allows to establish a relationship between the value of the *B* constant of the Dubinin-Astachov equation (exponent n=1) and the *1/n* factor of the Freundlich equation. Putting in order the values of the $B=(2.303{\cdot}R/E)^2$ constant from the lowest value to the highest one as well as the *1/n* factors, the following has been obtained:

Activated carbon	$B{\cdot}10^2$	*1/n*	*n*
N	0.116	0.148	6.757
AG-5	0.145	0.184	5.435
ML	0.149	0.190	5.263
AG-2u	0.161	0.205	4.878
CWZ-3	0.270	0.343	2.916
AHD	0.296	0.376	2.660
Cf	0.471	0.599	1.670

From the thermodynamic perspective, the *n* factor of the Freundlich equation is taken as a constant of reaction between the adsorbed molecules. Usually *n* is larger than one which means that the adsorbed molecules push each other away. The *B* constant (5) for n=1 can therefore be treated as the value defining the mutual pushing away of the molecules. The higher the *n* value of the Freundlich equation the lower the value of the B constant. Therefore, the lower the B value (for n=1 and for the given carbon) the more intensive the reaction of adsorbate molecules upon each other. For sodium cyanide adsorption on the researched carbons, the dependence of the B constant of the Dubinin-Astachov equation from the *1/n* constant of the Freundlich equation can be described by means of the following formula:

$$B\cdot 10^2 = 1.27/n$$

The characteristic adsorption energies marked on the basis of the Dubinin-Astachov equation (4,5) for the purpose of analyzing the active carbons with n=1 range from 4.07 kJ/mol for the Cf carbon to 16.50 kJ/mol (N) (for n=2; E=15.17 kJ/mol (Cf) – 27.29 kJ/mol (N) and for n=3; E=21.57 kJ/mol (AHD) – 30.18 kJ/mol (ML). Theoretically, for n=1 a loss of one degree of freedom of the adsorbed molecules takes place which is equilibrium to E=9.65 kJ/mol. In the case of microporous adsorbents, adsorption is connected with the loss of two degrees of freedom and E=20.2 kJ/mol (n=2). In the case of ultramicroporous adsorbents with the pore radius r=1.0-1.5 nm and n=3, the adsorption of molecules leads to a loss of 3 degrees of freedom: E=26.8 kJ/mol. The values of the characteristic adsorption energy established for sodium cyanide adsorption oscillate around the theoretical values.

The border value of adsorption a_o and the border adsorption volume V_a decreases parallelly to the increase of the exponent of the equation (4,5), and that leads to a conclusion that the number of moles (i.e. a_o) needed for filling of the micropores of 1.0 gram of adsorbent with the liquid adsorbate decreases with the increase of the equation exponent (4, 5).

The correlation factors for all of the analyzed isotherms of adsorption are high and close to one (table 1, 3). This proves that there is high agreement between the data referring to the experimental sodium cyanide adsorption from the water solution and the equations (1–5) presented above.

Table 1. Calculations of the adsorption isotherm factors of sodium cyanide from water solutions on activated carbon
(m = 500 mg, C_o = 10.0–1000.0 mg/dm^3)

Tabela 1. Obliczenia współczynników izoterm adsorpcji cyjanku sodu z roztworów wodnych na węglach aktywnych
(m = 500 mg, C_o = 10.0–1000.0 mg/dm^3)

Adsorption Isotherms	Equation Factors	Activated carbon						
		ML	CWZ-3	Cf	AG-5	AG-2u	N	AHD
Freundlich	k mg/g	22.9	2.6	4.0	1.8	1.5	0.6	0.8
	$1/n$	0.190	0.343	0.599	0.184	0.205	0.148	0.376
	R'	1.000	0.998	1.000	0.992	0.988	0.848	0.969
Langmuir	a_m mg/g	65.8	23.4	88.7	6.5	5.6	1.7	8.4
	K	0.250	0.028	0.031	0.032	0.042	0.018	0.022
	S_L m^2/g	119.6	42.5	101.2	11.8	10.2	3.1	15.3
	R'	0.996	0.992	0.951	0.994	0.993	0.965	0.983
BET	a'_m mg/g	65.8	23.4	88.7	6.4	5.6	1.7	8.4
	C	154908	17514	19373	19806	26272	11467	13600
	S_{BET} m^2/g	119.6	42.5	101.2	11.6	10.2	3.1	15.3
	R'	0.996	0.992	0.951	0.994	0.993	0.966	0.983

Table 2. Calculations of the adsorption isotherm factors of sodium cyanide
from water solutions on activated carbon
(m = 500 mg, C_o = 10.0–1500.0 mg/dm^3)

Tabela 2. Obliczenia współczynników izoterm adsorpcji cyjanku sodu
z roztworów wodnych na węglach aktywnych
(m = 500 mg, C_o = 10.0–1500.0 mg/dm^3)

Adsorption Isotherms	Equation Factors	Activated carbon			
		WP/W	WS-10	WS-11	WS-12
Freundlicha	k mg/g	20.85	21.91	21.55	29.73
	$1/n$	0.208	0.201	0.203	0.153
Langmuira	a_m mg/g	68.95	68.32	68.20	64.80
	K	0.163	0.206	0.193	0.254
	$a_m K$	11.24	14.10	13.163	16.26

Adsorption Isotherms	Equation Factors	Activated carbon			
		WS-13	WS-14	WS-15	WS-16
Freundlicha	k mg/g	25.16	30.26	32.33	19.98
	$1/n$	0.174	0.220	0.216	0.214
Langmuira	a_m mg/g	65.45	76.57	79.60	67.53
	K	0.501	0.544	0.622	0.150
	$a_m K$	32.81	41.69	49.49	10.12

Table 3. Calculations of the sodium cyanide adsorption isotherm factors from water solution on activated carbon according to the Dubinin-Astachov (DA) equation (m = 500 mg, C_o = 10.0–1000.0 mg/dm^3)

Tabela 3. Obliczenia współczynników izoterm adsorpcji cyjanku sodu z roztworów wodnych na węglach aktywnych według równania Dubinina-Astachowa (DA) (m = 500 mg, C_o = 10.0–1000.0 mg/dm^3)

Equation exponent	DA equation factors	Activated carbon			
		ML	CWZ-3	Cf	AG-5
$n = 1$	ao mg/g	287.2	254.1	119.8	21.4
	E kJ/mol	12.86	7.11	4.07	13.24
	$B \cdot 10^2$ 1/K	0.149	0.270	0.471	0.145
	Va cm^3/g	0.180	0.159	7.488	0.013
	-R'	1.000	0.998	0.996	0.992
$n = 2$	ao mg/g	108.7	46.0	419.2	9.2
	E kJ/mol	25.95	19.23	15.17	24.85
	$B \cdot 10^6$ 1/K^2	0.544	0.991	1.593	0.594
	Va cm^3/g	0.068	0.029	0.262	0.006
	-R'	0.996	0.996	0.996	0.983
$n = 3$	ao mg/g	79.1	25.8	136.5	7.0
	E kJ/mol	30.18	24.92	21.65	28.38
	$B \cdot 10^9$ 1/K^3	0.255	0.454	0.692	0.307
	Va cm^3/g	0.049	0.016	0.085	0.004
	-R'	0.986	0.981	0.985	0.962

Table 3. cont.
Tabela 3. cd.

Equation exponent	DA equation factors	Activated carbon		
		AG-2u	N	AHD
$n = 1$	ao mg/g	22.7	4.0	116.5
	E kJ/mol	11.90	16.50	6.48
	$B \cdot 10^2$ 1/K	0.161	0.116	0.296
	Va cm^3/g	0.014	0.003	0.073
	-R'	0.989	0.848	0.969
$n = 2$	ao mg/g	8.4	2.1	22.3
	E kJ/mol	24.42	27.29	16.98
	$B \cdot 10^6$ 1/K^2	0.615	0.492	1.272
	Va cm^3/g	0.005	0.001	0.014
	-R'	0.983	0.823	0.976
$n = 3$	ao mg/g	6.0	1.7	12.8
	E kJ/mol	28.94	29.76	21.57
	$B \cdot 10^9$ 1/K^3	0.290	0.267	0.700
	Va cm^3/g	0.004	0.001	0.007
	-R'	0.960	0.755	0.975

Table 4. Calculations of the sodium cyanide adsorption isotherm factors from water solution on activated carbon according to the Dubinin-Astachov (DA) equation (m = 500 mg, C_o = 10.0–1500.0 mg/dm^3)

Tabela 4. Obliczenia współczynników izoterm adsorpcji cyjanku sodu z roztworów wodnych na węglach aktywnych według równania Dubinina-Astachowa (DA) (m = 500 mg, C_o = 10.0–1500.0 mg/dm^3)

Equation exponent	DA equation factors	Activated carbon			
		WP/W	WS-10	WS-11	WS-12
$n = 1$	V_a cm^3/g	0.208	0.198	0.200	0.142
	E kJ/mol	11.71	12.15	12.01	12.98
$n = 2$	V_a cm^3/g	0.082	0.080	0.081	0.068
	E kJ/mol	23.20	23.77	23.60	23.60
$n = 3$	V_a cm^3/g	0.061	0.060	0.060	0.054
	E kJ/mol	26.75	27.32	27.15	27.09

Equation exponent	DA equation factors	Activated carbon			
		WS-13	WS-14	WS-15	WS-16
$n = 1$	V_a cm^3/g	0.157	0.345	0.350	0.209
	E kJ/mol	13.99	11.09	11.28	11.42
$n = 2$	V_a cm^3/g	0.070	0.110	0.114	0.082
	E kJ/mol	26.00	24.54	24.57	22.71
$n = 3$	V_a cm^3/g	0.055	0.074	0.078	0.061
	E kJ/mol	29.44	29.39	29.40	26.24

Table 5. Calculations of the amounts of activated carbon *m* in g/dm^3 inevitable for reducing the concentration of sodium cyanide in water from the initial C_o being 10.0 mg/dm^3 and 100.0 mg/dm^3 to the equilibrium concentration C_e from 50.0 mg/dm^3 to 0.001 mg/dm^3

Tabela 5. Obliczenia ilości węgli aktywnych *m* w g/dm^3 niezbędnych do obniżenia stężenia cyjanku sodu w wodzie z początkowego C_o wynoszącego 10.0 mg/dm^3 i 100.0 mg/dm^3 do stężenia równowagowego C_e od 50.0 mg/dm^3 do 0.001mg/dm^3

C_o mg/dm^3	C_e mg/dm^3	Activated carbon			
		ML *m* g/dm^3	CWZ-3 *m* g/dm^3	Cf *m* g/dm^3	AG-5 *m* g/dm^3
10.0	5.0	0.161	1.107	0.477	2.066
	2.0	0.306	2.426	1.320	3.912
	1.5	0.344	2.845	1.667	4.383
	1.0	0.393	3.461	2.250	5.000
	0.5	0.473	4.636	3.597	5.996
	0.1	0.670	8.388	9.830	8.402
	0.01	1.047	18.645	39.393	12.951
	0.001	1.622	41.114	156.724	19.800
100.0	50.0	1.038	5.026	1.200	13.523
	25.0	1.780	9.563	2.727	23.044
	10.0	2.538	15.713	5.665	32.732
	5.0	3.056	21.038	9.057	39.250
	2.0	3.751	29.717	16.175	47.924
	1.5	3.982	32.965	19.315	50.789
	1.0	4.323	38.077	24.750	55.000
	0.9	4.415	39.518	26.389	56.135
	0.8	4.520	41.189	28.347	57.421
	0.7	4.640	43.163	30.738	58.907
	0.6	4.767	45.553	33.746	60.665
	0.5	4.957	48.541	37.677	62.796
	0.4	5.176	52.454	43.109	65.496
	0.3	5.473	57.952	51.268	69.126
	0.2	5.917	66.667	65.426	74.556
	0.1	6.757	84.640	98.401	84.104
	0.01	10.474	186.618	394.282	129.622
	0.001	16.224	411.180	1567.382	198.018

Table 5. cont.
Tabela 5. cd.

C_o mg/dm^3	C_e mg/dm^3	Activated carbon		
		AG-2u m g/dm^3	N m g/dm^3	AHD m g/dm^3
10.0	5.0	2.397	6.567	3.413
	2.0	4.627	12.034	7.706
	1.5	5.215	13.342	9.122
	1.0	6.000	15.000	11.250
	0.5	7.300	17.544	15.410
	0.1	10.582	23.201	29.412
	0.01	17.118	32.916	70.551
	0.001	27.445	46.313	167.769
100.0	50.0	14.948	46.707	14.357
	25.0	25.846	77.624	27.948
	10.0	37.424	106.686	47.331
	5.0	45.535	124.770	64.838
	2.0	56.680	147.413	94.394
	1.5	60.430	154.607	105.709
	1.0	66.000	165.000	123.750
	0.9	67.507	167.767	128.885
	0.8	69.230	170.887	134.856
	0.7	71.224	174.455	141.938
	0.6	73.581	175.525	150.560
	0.5	76.462	183.749	161.395
	0.4	80.122	190.113	175.692
	0.3	85.076	198.566	195.990
	0.2	92.536	211.083	228.480
	0.1	106.776	234.122	296.791
	0.01	171.333	329.456	706.144
	0.001	274.723	463.173	1677.84

C_o – initial concentration of the sodium cyanide solution, mg/dm^3
C_e – equilibrium concentration of the sodium cyanide solution C_e mg/dm^3

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Adsorpcja cyjanku sodu na węglach aktywnych

Streszczenie

Katastrofy i awarie chemiczne spowodowały wielokrotnie skażenie środowiska przyrodniczego, zatrucia i śmierć ludzi. Zagrożenie skażeniami ludności i środowiska naturalnego można rozpatrywać w czterech aspektach:

- zatruć ludzi i skażeń w zakładach stosujących cyjanki w procesach technologicznych,
- awarii i katastrof chemicznych,
- akcji terrorystycznych i dywersyjnych z zastosowaniem trucizn sabotażowo-dywersyjnych,
- działań wojennych z zastosowaniem środków trujących lub w wyniku których zostaną uszkodzone zakłady i instalacje stosujące cyjanki w procesach technologicznych.

Zbadano adsorpcję cyjanku sodu z roztworów wodnych na polskich przemysłowych węglach aktywnych ML, CWZ-3, Cf, AG-5, AG-2u, N, AHD oraz węglach aktywnych otrzymanych przez autora w warunkach laboratoryjnych WP/W, WS-10, WS-11, WS-12, WS-13, WS-14, WS-15, WS-16.

Izotermy adsorpcji cyjanku sodu dla wyżej wymienionych węgli aktywnych wyznaczono dla szeregu stężeń początkowych od 10 mg/dm^3 do 1000 mg/dm^3 (ML, CWZ-3, Cf, AG-5, AG-2u, N, AHD) oraz dla stężeń początkowych od 10 mg/dm^3 do 1500 mg/dm^3 (WP/W, WS-10, WS-11, WS-12, WS-13, WS-14, WS-15, WS-16) dla ustalonej równowagi sorpcyjnej.

Do opisów procesu adsorpcji cyjanku sodu z roztworów wodnych z wykorzystaniem węgli aktywnych zastosowano równania izoterm adsorpcji Freundlicha, Langmuira, BET, Dubinina-Astachowa – wyznaczono współczynniki wymienionych równań.

W oparciu o równania izotermy adsorpcji Langmuira i BET wyznaczono pojemności warstwy adsorpcyjnej oraz powierzchnie właściwe sorbentów. Stwierdzono, że najwyższe pojemności sorpcyjne w stosunku do cyjanku sodu posiadają węgle aktywne WS-14, WS-15, WS-12 i ML, najniższe zaś węgle AHD oraz N. Wykazano, że wielkość adsorpcji cyjanku sodu na badanych węglach aktywnych zależna jest od wartości współczynników k oraz n równania Freundlicha. Większa wartość współczynnika k odpowiadała większej pojemności adsorpcyjnej węgla aktywnego.

W ujęciu termodynamicznym współczynnik n równania Freundlicha jest przyjmowany jako stała oddziaływania między adsorbowanymi cząsteczkami. Zwykle n jest większe od jedności, co oznacza, że adsorbowane molekuły

odpychają się. Stała B równania Dubinina-Astachowa (dla $n = 1$) może więc zostać przyjęta jako wielkość określająca siłę wzajemnego odpychania się adsorbowanych cząsteczek.

Do analizy procesu adsorpcji cyjanku sodu z roztworów wodnych z uwzględnieniem parametrów energetycznych (E), granicznej pojemności adsorpcyjnej (V_a) i struktury mikroporowatej (B) zastosowano równanie Dubinina-Astachowa:

$$lg\, a = lg\, a_o - 2{,}303 \frac{R^n T^n}{E^n} \left(lg \frac{C_n}{C_r} \right)^n$$

lub

$$lg(aV^*) = lg V_a - 2{,}303 \frac{R^n T^n}{E^n} \left(lg \frac{C_n}{C_r} \right)^n$$

Ustalono zależności pomiędzy wartością stałej $B = (2{,}303R/E)^n$ równania Dubinina-Astachowa (dla wykładnika potęgowego $n = 1$) a współczynnikiem $1/n$ równania Freundlicha.

Stwierdzono, że większej wartości współczynnika n równania Freundlicha odpowiada mniejsza wartość stałej B. Im więc jest mniejsza wartość stałej B (dla $n = 1$ i danego węgla) tym wzajemne oddziaływania cząsteczek adsorbatu jest intensywniejsze. Zależność stałej B równania Dubinina-Astachowa od stałej $1/n$ równania Freundlicha może być opisana wzorem: $B \cdot 10^2 = 1{,}27/n$.

Wyznaczono według równania Dubnina-Astachowa, charakterystyczną energię adsorpcji E dla analizowanych węgli aktywnych. Dla wykładnika potęgowego $n = 1$ równania DA wynoszą one od 4,07 kJ/mol dla węgla Cf do 12,86 dla węgla ML i 13,99 dla węgla WS-13, dla $n = 2$ wartości parametru energetycznego E wynoszą od 15,17 kJ/mol do 27,29 kJ/mol, zaś dla $n = 3$ wartość E zawiera się w granicach od 21,57 kJ/mol do 30,18 kJ/mol.

Graniczna wielkość adsorpcji a_O i graniczna objętość adsorpcyjna V_a wraz ze wzrostem wykładnika potęgowego równania Dubinina-Astachowa zmniejsza się, co prowadzi do wniosku, że liczba moli (tj. a_o) potrzebna do zapełnienia ciekłym adsorbatem mikroporów 1 grama adsorbenta zmniejsza się wraz ze wzrostem wykładnika potęgowego równania Dubinina-Astachowa.

Współczynniki korelacji dla wszystkich analizowanych izoterm adsorpcji jest wysoki i bliski jedności. Świadczy to o wysokiej zgodności danych eksperymentalnych adsorpcji cyjanku sodu z roztworów wodnych z równaniami Freundlicha, Langmuira, BET i Dubinina-Astachowa.