Empirical Formulae for Efficiency of DOM Removal by Adsorption Determined on the Basis of Bench-Scale Results

M. Szlachta*, W. Adamski

Wrocław University of Technology, Institute of Environmental Protection Engineering, Wybrzeże S. Wyspianskiego 27, 50-370 Wrocław, Poland

Received: 9 July 2008
Accepted: 27 December 2008

Abstract

The adsorption process of dissolved organic matter (DOM) from natural water, using the commercial powdered activated carbon (PAC) Norit SA Super, was studied in two variants. In one of the variants adsorption was conducted as a separate process. In the second, adsorption onto PAC was regarded as a process that supports coagulation. In both instances the efficiency of organic matter removal was expressed as the ratio of dissolved organic carbon (DOC) concentration (persisting in the water upon the termination of the process) to the initial DOC concentration in raw water. Experimental results were used to derive parameters of empirical formulae describing the efficiency of DOM removal by PAC adsorption.

Keywords: adsorption, coagulation, mathematical modelling, powdered activated carbon, water treatment

Introduction

Recent years have witnessed a growing tendency to toughen legal regulations regarding the quality of potable water. Such trends are being observed all over the world, including Poland. Owing to continued advances in science and technology, as well as the availability of advanced analytical techniques, the list of standard water quality parameters is being extended with further substances that might adversely affect human health.

Typical surface waters contain anthropogenic pollutants classified as nuisance compounds. These include inter alia, polycyclic aromatic hydrocarbons, surfactants, phenols, pesticides, radionuclides and heavy metals. The issues with these substances are that they exert an unfavourable influence on living organisms and disturb the biological equilibrium of the aquatic environment. They make the water treatment process difficult when occurring seasonally or in trace amounts. Some of the anthropogenic pollutants (e.g. benzene and its derivatives, naphthalene and toluene), as well as some of the substances synthesized by microorganisms (such as geosmin or methylisoborneol), are blamed for unpleasant taste and smell [1-2].

In addition to the pollutants mentioned above, surface waters also include natural dissolved organic substances. Dissolved organic matter is a complex, heterogeneous mixture of organic compounds displaying various physical and chemical properties [3]. Since the DOM is, on the one hand, ubiquitous in natural waters and, on the other hand, the main component of DOC, it is not surprising that the majority of disinfection by-product (DBP) control strategies focus on DOM removal from water prior to the application of disinfectants [4-6].

An effective means of removal of the organic compounds that are DBP precursors is feasible through inclu-
sion of PAC adsorption into the water treatment train. The process can be conducted either simultaneously with conventional coagulation or in separate contact reactors. The results of PAC application and the factors that exert a limiting effect on the adsorption process have been reported by other investigators [7-10]. They have demonstrated that the extent of reduction in organic pollutants depends primarily on the properties of the adsorbent applied and on the nature of the pollutants to be removed, the process conditions (pH, contact time, reagent dosage, etc.) being basically of equal importance.

The propensity of natural organic compounds for adsorption varies considerably. In natural water those substances generally occur in great diversity, which seriously complicates the description of their adsorption. What adds further complication to such description is the heterogeneous pore size of the adsorbents used and also the difficulty in separating the diverse interactions observed in a water treatment train. A reliable description and modelling of the phenomena involved will offer the chance of defining not only the applicability criteria for the process itself, but also the major parameters that are of significance to the course of the process.

The study reported in this paper addresses the problem of the efficiency of dissolved organic matter removal from natural water by adsorption onto powdered activated carbon, conducted in two variants: as a separate process and in combination with conventional coagulation. Furthermore, a mathematical model has been formulated, which relates the efficiency of the PAC-based adsorption process to the varying quantity of the adsorbent dosed and to the time of contact between the adsorbent and the water being treated. When adsorption was combined with the coagulation process, an additional parameter, the coagulant dose, was incorporated into the model.

Materials and Methods

The extent of dissolved organic compound removal was determined on the basis of a test series performed using natural water samples collected from the Odra River. DOC concentrations in the riverine water varied from 3.1 to approximately 4.0 mgC/L. They were measured in water samples upon passage through a membrane filter of a 0.45 μm pore diameter, using a Shimadzu TOC-5050 analyzer.

The tests were conducted in square reactors (Velp Scientifica Jar-tester) and the volume of the water sample in each reactor equalled 2 L.

The PAC adsorption process was carried out for 1 h, with samples being collected upon termination and in the course of the process. Powdered activated carbon marketed under the brand name of Norit SA Super was used, produced from selected vegetable materials and steam activated [11]. The doses of the adsorbent (which was added in the form of a suspension prepared on the basis of distilled water) ranged from 5 to 75 mg/L.

Coagulation-adsorption tests were performed using the process parameters established in a previous study [12]. The tests were conducted at a pH adjusted to 6.0, with alum (Al₂(SO₄)₃·18H₂O) as a coagulant, using doses of 2.15, 2.46 and 3.07 mgAl/L. PAC doses were the same as those used in the tests of adsorption performed as a separate process. Adsorbent and coagulant were dosed simultaneously.

Adsorbent particle size was measured with a Mastersizer 2000 (Malvern) analyzer of a measuring capacity which varied from 0.02 to 2000 μm, using the laser diffraction method.

Results and Discussion

The test results were used to determine the extent of DOC removal obtained by two methods of PAC adsorption, namely with and without coagulation. In both methods, removal efficiency was expressed as the ratio of the DOC concentration persisting in the water upon termination of the process (Cₑ) to the initial DOC concentration (C₀). Fig. 1 depicts the variations in the efficiency of adsorption with time for the PAC doses tested, while Fig. 2 relates the efficiency of DOC removal by coagulation-adsorption to the quantity of the coagulant dose used.

![Fig. 1. Efficiency of DOC removal by the adsorption method, related to the duration of the process; Dₚ₉₃₅ = 5, 10, 30 and 75 mg/L.](image1)

![Fig. 2. Efficiency of DOC removal by the coagulation-adsorption method, related to the coagulant dose applied; Dₚ₉₃₅ = 5, 10, 30 and 75 mg/L.](image2)
As shown by the relations in Fig. 1, the efficiency of adsorption increases with the time of contact between water and adsorbent. Over the entire range of the PAC doses tested, adsorption was effective up to a certain point in time; after several minutes, adsorption rate decreased, the process ran at a noticeably slower rate, and its continuation had an insignificant effect on the extent of removal. But adsorption efficiency also depends on the adsorbent dose applied; higher doses result in greater overall removal. The differences in efficiency between particular PAC doses indicate that the internal surface of the porous structure has been effectively utilized.

When adsorption was combined with coagulation, the efficiency of the process for particular coagulant doses varied with the adsorbent dose applied (Fig. 2). As the PAC dose increased, so did the efficiency of adsorption-coagulation, which is to be attributed to the increased availability of the surface for adsorption. Upon closer analysis of the effect of the coagulant dose it became apparent that the increase in the quantity of the alum added was paralleled by the increase in the efficiency of DOC removal. For example, with the alum dose of 2.15 mgAl/L, the Ce/C0 ratio amounted to 0.54 and 0.21 for the PAC dose of 5 mg/L and 75 mg/L, respectively. Greatest effects were achieved with the highest coagulant dose (Dc = 3.07 mgAl/L), for which the relative values of the adsorbate concentrations varied between 0.52 and 0.17 within the range of the PAC doses applied.

The experimental results were used for the verification of the proposed mathematical model describing the efficiency of adsorption onto PAC.

In the model, a single grain of the activated carbon is considered as a specific system where the process occurs in a defined liquid volume. It has been assumed that the adsorbent particles and the water volume per single grain are spherical in shape. Furthermore, it has been assumed that the adsorbent particle has a central position in water volume.

The diameter \( d_{50} = 15.8 \times 10^{-6} \text{ m} \) determined from the measured values of the adsorbent particle size has been adopted as the equivalent diameter of the carbon grain (\( d_{\text{PAC}} \)).

The grains of the PAC examined varied widely in size, ranging between 0.6 μm and 250 μm (Fig. 3). Particles falling in the range of 5-10 μm and 10-25 μm were in the majority, accounting for 23.7% and 24.1%, respectively; particles larger than 150 μm were not numerous, constituting approximately 2.8%.

For the assumed spherical shape of the adsorbent particle, the volume of a single carbon grain and its mass in air-dry state were determined. The calculated results are:

\[
V_{\text{PAC}} = \frac{4}{3} \pi \cdot \left( \frac{d_{\text{PAC}}}{2} \right)^3 = 2.065 \times 10^{-15} \text{ m}^3
\]

\[
m_{\text{PAC,ad}} = V_{\text{PAC}} \cdot \rho_{\text{PAC}} = 5.16 \times 10^{-10} \text{ g}
\]

...where \( V_{\text{PAC}} \) denotes the volume of a single carbon grain \( [\text{m}^3] \), \( m_{\text{PAC,ad}} \) stands for the adsorbent particle mass in air-dry state \( [\text{g}] \), and \( \rho_{\text{PAC}} \) is the bulk density of the carbon in air-dry state \( [250 \text{ kg/m}^3] \) [11].

The mass of a single carbon grain in hydrated state was calculated in terms of the following formula:

\[
m_{\text{PAC,h}} = m_{\text{PAC,ad}} + m_{\text{H2O}} = 8.87 \times 10^{-10} \text{ g}
\]

...where \( m_{\text{H2O}} \) stands for the mass of the water filling up the pores of a single PAC particle, determined on the basis of total carbon pore volume (\( V_{\text{total}} = 0.719 \text{ cm}^3/\text{g} \)) for water density at 20ºC.

According to the amount of PAC applied, the quantity of the adsorbent grains in 2 L of the water being treated was calculated, and subsequently the volume of the water being treated per single particle of the adsorbent in hydrated state (\( V_{\text{H2O}} \)) [13]. On this basis, the radius of the water volume enclosing a single PAC grain \( (r_{\text{H2O}}) \) was calculated, which varied from 2.911×10⁻⁴ m to 1.180×10⁻⁴ m for the adsorbent dose ranging between 5 and 75 mg/L.

When analyzing the adsorption process in a batch reactor, it seems advisable to consider not only the kinetic factors that affect the adsorbate flow outside the adsorbent particle and the saturation of the adsorbent particles, but also the static factors that influence the state of adsorption equilibrium. The basic equations describing the kinetics of diffusion processes in a homogeneous environment are Fick's laws. In the mathematical model proposed for the description of the efficiency of PAC adsorption, use was made of Fick's first law [14-15]:

\[
\frac{dm}{dt} = -D_m \cdot F \cdot \frac{dC}{dr}
\]

...where \( m \) is adsorbate mass \( [\text{g}] \), \( t \) stands for diffusion time \( [\text{s}] \), \( C \) denotes adsorbate concentration \( [\text{g/m}^3] \), \( r \) indicates diffusion length \( [\text{m}] \), \( F \) refers to the surface of the field of diffusion flux \( [\text{m}^2] \), and \( D_m \) is the molecular diffusion coefficient \( [\text{m}^2/\text{h}] \).
If the adsorbate mass is defined as:

$$m = (C_e - C_i) \cdot V$$  \hspace{1cm} (5)

...where $m$ denotes adsorbate mass [g], $C_e$ indicates final concentration of adsorbate [g/m³], $C_i$ is adsorbate concentration in boundary film [g/m³], and $V$ stands for volume [m³], then Fick’s equation (4) will take the form:

$$\frac{d}{dt}(C_e - C_i) \cdot V = -D_m \cdot F \cdot \frac{dC_i}{dr}$$  \hspace{1cm} (6)

$$\frac{4}{3} r \cdot \frac{d}{dr}(C_e - C_i)dr = -D_m dC_i$$  \hspace{1cm} (7)

In equation (7) the variables were separated and the left-hand side was integrated over the range of $r_{H2O}$ to $r_{PA C}$, where $r_{PA C}$ is the radius of the adsorbent grain which has been determined using the diameter $d_{PA C} = d_{50}$ adopted for the calculations. The right-hand side of equation (7) was integrated over the range of $C_e$ to $C_i$. It has been, furthermore, assumed that the adsorbate concentration in the boundary film is constant ($C_i =$ const). Thus, the following relation has been obtained:

$$\frac{dC_i}{dt} = -K(C_e - C_i)$$  \hspace{1cm} (8)

When the quotient of the molecular diffusion coefficient ($D_m$) and the difference of the squares of the radii ($r_{H2O}^2 - r_{PA C}^2$) is defined as the coefficient of the adsorbate mass transfer rate ($K$), equation (8) will take the form:

$$\frac{dC_i}{dt} = -K(C_e - C_i)$$  \hspace{1cm} (9)

Considering the final concentration of the adsorbate ($C_e$) as the difference between its initial and adsorbed concentration ($C_0 - C_a$), and using $\delta$ to denote the quotient of adsorbed and equilibrium concentration ($C_a/C_R$), the relation of (9) has been transformed as follows:

$$\frac{d\delta}{dt} = K \left( \frac{C_0}{C_R} - \delta \right) \frac{C_a}{C_R}$$  \hspace{1cm} (10)

Assuming that the extent of desorption is negligibly small, which means that adsorbate concentration in the boundary film is notably lower than the equilibrium concentration ($C_i << C_R$), we obtain:

$$\frac{C_a}{C_0} \cdot \frac{d\delta}{dt} = K \left( 1 - \frac{C_a}{C_0} \right) \delta$$  \hspace{1cm} (11)

Subsequently, separating the variables and integrating both sides of the equation (11) we have:
Kinetic analysis of the adsorption process (Fig. 1) makes it clear that within the first several minutes the majority of the organic fractions have been adsorbed. In subsequent minutes the efficiency of the process declined. The increment in the efficiency of DOC removal between the 15th and 60th minute varied from approximately 2.2% to slightly more than 10% for the PAC doses that ranged between 5 and 75 mg/L. The observed pattern is to be attributed, inter alia, to the type of the pollutants being removed, as the natural water samples used in this study contained both low- and high-molecular-weight organic substances [12]. The smaller organic fractions, which are characterized by a higher diffusivity, took less time to reach the active sites of the adsorbent as compared to the compounds of a higher molecular-weight, which diffuse to the interfacial surface and in the porous structure of the PAC particles at a slower rate.

As for the combined coagulation-adsorption process, the coefficient of adsorbate mass transfer rate, which defines the diffusivity and geometry of the system, depended not only on access to the internal PAC structure available for adsorption, but on the coagulant dose as well. Over the entire range of the PAC doses tested, the value of $K$ increased with the quantity of the coagulant added (Table 2); the increment, however, was relatively low for each of the PAC doses and failed to exceed 0.45 h$^{-1}$. When adsorption was combined with coagulation, the viscosity of the medium increased gradually, owing to the presence of the flocs that had formed during flocculation. It is worth noting that the reduction in the diffusivity of the particles in the medium had no negative effect on the efficiency of the combined process; on the contrary, the increase in the coagulant dose brought about a higher extent of DOC removal. An explanation for this is to be sought in the superposition of the efficiency of colloid destabilization, flocculation and adsorption both onto the flocs and the PAC grains.

From the statistical analysis of the relationship between the values of $K$, $D_{PAC}$, and $D_c$, it follows that these parameters can be approximated using an exponential function of the generalized form $y = a \cdot \exp(b \cdot x)$. The results of regression analysis enabled the following to be established: the empirical formulae that describe the coefficients of the adsorbate mass transfer rate for the system involving PAC adsorption alone and for the system combining coagulation and PAC adsorption, as well as the equations that describe the final adsorbate concentration ($C_e$) for both systems (Table 3).

The relations obtained retain their accuracy for the raw water DOC of 3.0 to 4.0 mgC/L, contact time of 0 to 1 h, as well as for the adsorbent and coagulant doses resulting from the ranges applied in the technological investigations that were performed for the purpose of the study: $D_{PAC} = 5$ to 75 mg/L and $D_c = 2.0$ to 3.0 mgAl/L, respectively.

The mathematical models describing the efficiency of PAC adsorption were verified on the basis of experimental data. Their analysis made it clear that in the case of adsor-
tion as a separate process the $C/C_0$ ratio depended on two factors: the time of PAC contact with the water being treated and the adsorbent dose, whereas in the case of coagulation-adsorption there was one more factor that affected the efficiency of the process, namely the coagulant dose applied.

In Figs. 4 and 5, the experimental efficiencies of organic matter removal ($C/C_0$) are compared with those calculated on the basis of the models proposed.

For both the adsorption systems under study, the consistency of calculated and experimental data is high, as can be inferred from the values of the coefficients of determination. The observations made in the course of the study, as well as the results obtained, can be of practical use in the optimization of water treatment trains where PAC adsorption is combined with coagulation or conducted as a separate process. Moreover, the presented mathematical models may optimize the control of the process and thus enhance the extent of dissolved organic matter removal from natural water.

**Conclusions**

The study addressed the problem of the efficiency of dissolved organic fraction removal by the method of PAC adsorption conducted separately (as a single process) and simultaneously with coagulation (as a combined process). During adsorption tests the efficiency of the process varied as a function of the time of PAC-water contact. In the first minutes of the test, adsorption proceeded at a very fast rate and within that period the majority of low-molecular particles were adsorbed. The larger fractions, whose adsorption was difficult and poor, took a longer time to reach the interfacial surface. Analysis of the effect of the PAC dose (which ranged from 5 to 75 mg/L) has revealed that the efficiency of adsorption increased with the quantity of the adsorbent dosed. The variations in the efficiency of organic fraction removal observed in the course of the combined coagulation-adsorption process also depended on the size of the adsorbent dose: as the dosage increased, so did the extent of DOC removal. For particular PAC doses, the efficiency of the coagulation-adsorption process increased with the increase in the coagulant dose.

The empirical formulae for the value of the coefficient of the adsorbate mass transfer rate ($K$) derived within the scope of the study apply to the ranges of contact times, coagulant and adsorbent doses resulting from the ranges of the technological investigations performed. The mathematical models proposed for the description of adsorption conducted in two examined variants relate the variations in the efficiency of dissolved organic matter removal. The verification of the models by experiments has revealed a high consistence of experimental and calculated data.

Broadening the applicability of the models is an important issue. Therefore in the authors’ future research of water sources differing from the Odra River, both activated carbons and coagulants will be used.

**Acknowledgements**

Funding for this study was provided by a grant from the Polish Ministry of Science and Higher Education in 2005-07 (Grant No. 3 T09D 026 28).

**References**

11. NORIT DATASHEET: Manufacturer’s Specification for Powdered Activated Carbon Norit SA Super.