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Adsorption of selected nitrophenols on activated carbon in the presence of nicotinamide

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1. Introduction

Nitrophenols are widely used in industry and agriculture. Since they are water soluble and resistant to biological treatment, they can easily enter the environment through industrial wastewater and runoff from agricultural farms. Once nitrophenols reach surface water, they pose a threat to aquatic ecosystems due to their toxicity. Therefore, development of efficient methods for their removal from water matrices is very important in regions where contamination can occur.

So far, multiple approaches to the removal of nitrophenols have been proposed, including adsorption [1–4], photocatalytic degradation [5] and different ways of oxidative degradation using oxygen radical species [6–8]. Although degradation methods reduce pollutants to small molecules and thus completely remove them from the environment, they require special conditions to work efficiently. Necessary materials can be expensive to produce, and can only be applied to limited portions of contaminated water at a time. Adsorption on activated carbon (AC) is one of the most frequently used practices in water treatment for the removal of nitrophenols [9–12]. In real systems, part of the adsorption capacity of AC can be occupied by organic molecules that are naturally occurring in the environment (Natural organic matter - NOM). Most studies concerning adsorption of pollutants focus only on single-component systems. It is essential to dedicate more effort to investigation of combined adsorption and adsorption in systems with interfering molecules [13], so that more realistic models for water treatment can be made.

Factors that influence adsorption of phenols have been extensively researched, but little is still known about the mechanism of phenol adsorption itself. Papers on adsorption of phenols and chloro-substituted phenols have reported that with increase in the number of chloro groups, increase in adsorption of these molecules has been observed [14–16]. Authors have implied that the driving force of the adsorption process is hydrophobicity. On the other hand, adsorption capacity of phenol derivatives with different substituents is connected to the electron withdrawing property of the substituent [17]. Higher ability of the substituent to shift electrons from the phenol aromatic ring has shown to raise relative adsorption affinity of the phenol derivative. In the same study, increase in relative adsorption affinity has also been observed with increase in available surface area and porosity of activated carbon. Charge transfer interactions between phenol aromatic ring and the π-electrons of the basal plane of activated carbon have been singled out as one of the main causes that lead to phenol derivative adsorption on activated carbon. The stronger electron withdrawing property the substituent on aromatic ring has, the greater electron acceptor capability the aromatic ring will possess, which will lead to stronger attractive forces with the basal plane of activated carbon.

It has been shown that the presence of more voluminous amides lowers the adsorption capacity of 4-nitrophenol (PNP) on AC [18]. In the present work adsorption of PNP, dinitrophenol (DNP) and picric acid (TNP) on AC in the presence of nicotinamide (NCA) has been investigated. Single component systems (nitrophenols only) were investigated so that the substituent influence on adsorption can be assessed. Effect of interfering molecule (NCA) on nitrophenols adsorption has been observed in two component systems. Mechanism of adsorption in these bicomponent systems will be estimated through obtained kinetic and equilibrium parameters.

The aim of this paper is to contribute to better understanding of the influence of nitro substituent on adsorption of nitrophenols as well as influences of NCA as interfering NOM molecule on adsorption of nitrophenols. Results obtained from this study will be of use to both researchers interested in the mechanism of adsorption of organic molecules, and also to researchers investigating the influence of interfering compounds present in water on pollutant adsorption. With the limited supply of drinking water becoming one of tomorrow's primary concerns, compounded by increasing difficulty and complexity of treating polluted systems due to continuous industrial development, there is a clear necessity for widening the knowledge related to these areas.

2. Material and methods

2.1. Adsorbates and sorbent

Adsorbates, 4-nitrophenol (PNP), 2,4-dinitrophenol (DNP) and picric acid (2,4,6-trinitrophenol, TNP), used in this study were purchased from Fluka (≥99.5%). Nicotinamide (NCA) was acquired from Sigma Aldrich (≥99.5%). Physical-chemical properties of the studied molecules are given in Table 1. Dipole moment and volume of the molecules and their anions were determined using Gaussian 03 software at model B3LYP/6-31 g* [19]. Stock and work solutions of studied nitrophenols and nicotinamide were prepared in organic carbon free water (<0.2 mg TOC/L) with phosphate buffer (pH 7.4).

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Table 1
Physical-chemical properties of PNP, DNP, TNP and NCA.

	Molecular mass [g/mol]	Water solubility (20 °C)	pK_a (25 °C)	Dipole moment [Debye]		Volume [cm^3/mol]	
		[mg/cm^3]		Molecule	Ion	Molecule	Ion
PNP	412.61	11.6	7.15	5.34	0.88	83.1	87.0
DNP	462.43	2.8	4.11	3.41	2.58	93.8	97.6
TNP	521.59	12.7	0.38	1.77	2.25	128.3	133.2
NCA	404.97	50.1	3.35[a]	4.89	6.24	84.1	82.7

[a] Value refers to conjugated acid.

Powdered activated carbon (PAC) Norit SA 2 (Cabot Norit Nederland B·V) was used as the adsorbent. The adsorbent was prepared for adsorption experiments by drying at 378 K for 24 h. Measurements of the average pore radius, the total pore volume and micropore test were performed in the previous study [18]. The physical-chemical characteristics of the PAC used are listed in Table 2.

Fourier-transform infrared spectroscopy (FTIR) spectrum of the adsorbent was collected using a Thermo-Nicolet Nexus 670 instrument. Resolution was set to 4 cm^{-1}, and 60 scans were collected. The sample was prepared using KBr pellet technique. The spectrum was afterwards processed using the Savitzky-Golay smoothing filter.

The measurement of the point of zero charge (PZC) of activated carbon was performed following the method described by Noh and Schwarz [20]. The procedure was as follows: three aqueous $NaNO_3$ (0.01 M) solutions of different pH (3, 6 and 11) were prepared using HNO_3 (0.1 M) and NaOH (0.1 M). The adsorbent was then added to the solutions at different mass ratios (0.05%, 0.10%, 0.5%, 1.0%, 5.0% and 10%). The final pH of the mixture was measured after 24 h of shaking at 298 ± 1 K. PZC was determined as the converging pH value from the pH vs. sample mass curves.

2.2. Adsorption experiments

All adsorption experiments were performed at room temperature (298 ± 1 K). All of the experiments were run in duplicate. Tests were performed on equilibrium and kinetics of the adsorption of single-solute systems for nitrophenols and nicotinamide. In all single-solute systems starting concentration of adsorbate was 5 mg/dm^3. Afterwards, binary systems were investigated in which starting concentration of the nitrophenol remained 5 mg/dm^3, and its adsorption was followed in the presence of NCA at three concentration levels (5, 50 and 100 mg/dm^3). Synthetic pH adjusted (7.4) organic carbon free water (<0.2 mg/dm^3) was prepared from deionized water with addition of phosphate buffer. Synthetic water was used as a blank. For all investigated systems the initial pH value and the pH value after addition of the activated carbon suspension were in the range of 7.4–8.2 and did not change during the experiment. Batch equilibrium experiments were performed on a rotary shaker using 250 cm^3-shaking flasks, at 180 rpm. PAC was added to starting solutions in the form of a suspension, and probes with following mass to volume ratio were obtained: 0, 20, 30, 40, 50, 60, 70 mg/dm^3.

Table 2
The physical-chemical properties of the adsorbent.

Property	
Iodine number	850
SSA BET [m^2/g]	664
Average pore radius [Å]	18.5
Total pore volume [cm^3/g]	0.39
Micropores	32.3
Mesopores	58.6
Macropores	9.1
Average particle diameter [m]	$2{\cdot}10^{-5}$
PZC [pH units]	11.28

All values except PZC are from previous study [18].

The kinetic experiments were carried out in 1 dm^3 reaction vessel placed on a magnetic stirrer. The experiment was started by addition of the PAC suspension until a concentration of 17.5 mg/dm^3 was achieved. Samples were taken at defined time intervals over a period of 180 min. After reaching certain time, the adsorbent was removed for the purpose of determining p-nitrophenol concentrations. All samples were filtered through 0.45 μm glass fiber filters before measuring the remaining adsorbate concentrations. Adsorbates were analyzed by UV–VIS spectrometry (Shimadzu UV 1800) at characteristic wavelengths, i.e. for PNF at 400 nm, for DNF and TNF at 365 nm, and at 245 nm for NCA.

2.3. Adsorption data analysis

The amount of adsorbed adsorbent was calculated per mass unit of activated carbon using the following formula:

$$q_e = \frac{C_0 - C_e}{m} \tag{1}$$

where q_e is adsorbent loading (mg/g), i.e. the amount of adsorbed adsorbate per unit weight of adsorbent at equilibrium, C_0 (mg/dm^3) is the starting concentration of adsorbate, C_e (mg/dm^3) concentration of adsorbate in solution at equilibrium, and m (mg) is the mass of PAC.

Adsorption data were further analyzed by two reaction kinetic models: pseudofirst-order and pseudosecond-order, and two diffusion models: external (film) diffusion model, and Boyd's model. Also, three equilibrium adsorption models were investigated: Freundlich, Dubinin-Radushkevich, and Redlich-Peterson isotherm.

2.3.1. Kinetic models

Kinetic of adsorption on porous materials is frequently being described by two simple models based on chemical reaction kinetics. These models are known as pseudofirst-order and pseudosecond-order rate laws. Prefix pseudo comes from the fact that instead of concentration which is used in the classical reaction kinetic equations, adsorption capacity change is being followed in adsorption kinetics. Both of these models have weak theoretical background and good correlation with experimental results should be taken with caution.

2.3.1.1. Pseudofirst-order rate law. Pseudofirst-order describes adsorption rate primarily based on the adsorption capacity, neglecting the diffusion processes. It is given by equation:

$$\ln(q_e - q(t)) = \ln q_e - k_1 t \tag{2}$$

here $q(t)$ (mg/g) is the adsorption capacitie at time t (min), and k_1 is the rate constant (1/min).

2.3.1.2. Pseudosecond-order rate law. Pseudosecond-order rate law is given:

$$\frac{t}{q(t)} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{3}$$

where k_2 represents rate constant (mg/g min).

Pseudosecond-order is often being appreciated for obtaining exceptionally good values of coefficient of determination. Although it was originally used for describing chemisorptions of metal ions, it has been reported that it also fits well wide range of sorption processes from water systems [21,22]. Recent study pointed out on possibility of over fitting of experimental data in the case of pseudosecond-order model [23]. As stated in this study, more accurate results are obtained by fitting only starting part of the kinetic curve for both pseudofirst and pseudosecond-orde models, before plateau has been reached. Because of this only data for fractional uptake below 85% were used for model fitting.