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Dedicated to professor Gh. Marcu at his 80th anniversary

ADSORPTION AND ELECTROCHEMICAL DATA FOR p-NITROPHENOL REMOVAL FROM SYNTHETIC WASTEWATERS

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ABSTRACT. There are three main results reported in this paper refer to: (*i*) the equilibrium adsorption experiments of recalcitrant toxic p-nitrophenol (p-NP) on natural zeolites from Balkan area; (*ii*)voltamperommetric data on the electrochemical behavior of p-nitrophenol, depending on the electrode nature and working conditions (pH, electrolyte composition, hydrodynamic parameters (*iii*) and electrochemical oxidation to remove the remaining p-nitrophenol on different electrodes after the adsorption.

The zeolite from Mirsid, Romania (zeolite-2) seems to have the best adsorption properties for p-nitro phenol, comparing to classical sorbent, active carbon powder. The synthetic waste waters containing 0.01p-NP have been treated by adsorption on (zeolite-2) and the decrease of the p-NF concentration up to 0.01 mM has been obtained. The remaining p-NP was treated by electrochemical way (electro-oxidation). Applying the combined adsorptive-electrochemical oxidation procedure we have been obtained the decrease of COT up to 98%, on $SnO_2/IrO_2/Ti$ (Modified Oxides Electrode- MOE). These results could be explained by the catalytic effect of the zeolite for the chemical phenol oxidation.

Key words: nitrophenols, adsorption, zeolites, electrochemical oxidation

Introduction

Due to the recognized toxicity of nitrophenols, the International Programme on Chemical Safety (IPCS), established in 1980, as a joint venture of the United Nations Environment Programme (UNEP) and the World Health Organization (WHO) elaborate the authoritative document, Concise International Chemical Assessment Document (CICAD 20), on the risk assessment of nitrophenols.

During the past decade, extensive research has been conducted to develop innovative, effective, inexpensive and promising adsorbent materials that are regenerated easily for dealing with the problem of the treatment of contaminated wastewater. Organically modified benthonites and zeolites, produced

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by replacing exchangeable inorganic cations with quaternary alkyl ammonium cations, have been reported as strong adsorbents for non-ionic organic pollutants.

The monosubstituted 4-nitrophenol is found in wastewaters discharged from various industrial activities such as pulp and paper industries, textile mills, steel plants, oil refineries, etc. [1]. This compound is also associated with agricultural activities as an intermediate for the production of pesticides, herbicides and insecticides [2].

Attempts have been made to remove mononitrophenols from wastewater by a number of methods: oxidation with strong oxidizing agents as H_2O_2 [3], biodegradation [4], biosorption [5], photocatalytic degradation [6], etc. With respect to adsorption of nitrophenols, activated carbon is one of the most commonly used adsorbents due to its high surface area and well developed pore structure [7-11]. As activated carbon is relatively costly, attempts have been directed to the utilization of low-cost and abundant natural materials as alternative adsorbents for nitrophenols removal from aqueous phase.

Electrochemical processes offer useful possibilities for *in situ* and local treatment of industrial waste-waters at anodes for destructive removal or modification of noxious solutes (especially organics) [9]. For this latter type of impurity solutes, the overall process most desirable is that of so-called "mineralization", *i.e.*, complete anodic oxidation to CO_2 and H_2O, or additionally to N_2 or NO_3^-, or to SO_4^{2-} in the case of N or S containing organics, respectively. The use of electrode processes has the advantage that no added oxidizing or reducing agent needs to be provided since electrons (at cathodes) or their vacancy states (at anodes) are direct reagents, so that no other undesired exogenous products will arise. The oxidation of phenols on different types of modified oxides anodes, including the DSA commercial anodes has been studied, by cyclic voltammetry, polarization measurements, and electrochemical impedance spectroscopy and potentiostatic transients in different aqueous solutions [11-14]. The formation of a phenoxy radical in a diffusion-controlled irreversible process is the initial step. In the concentrated phenols solution, the polymerization of phenoxy radicals leads to the formation of porous polyoxyphenylene film, strongly adherent to the electrode surface; this film inhibits partially the further oxidation [3].

Continuing our previous research focus on the electrochemical investigation of the phenols and other organic pollutants oxidation [12, 13], this paper presents the results obtained by combining two procedures in order to eliminate the nitrophenols: adsorption of nitrophenols from the quasi concentrated solution (10^{-2}M) and the electrochemical oxidation of the remaining nitrophenols.

Experimental

Nitrophenols are sparingly soluble in water and therefore, both the adsorption and electrochemical properties have been investigated from their hydro alcoholic solutions (1/1 water/n-propyle alcohol mixture). For the electrochemical measurements the 0.1 M Britton-Robinson buffer electrolytes was used. The voltamperommetric and spectrophotometric control of nitrophenols has been achieved using a common three electrodes cell (WE: glassy carbon and; RE: $Ag/Ag^+/AgCl$; AE: Pt wire).

The reactor setup used for adsorption measurement contains magnetic stirred and thermostated saturation vessel equipped with a reflux condenser. In a typical adsorption experiments, 0.5 mg of zeolites were been added to a glass reactor followed

by the addition of known quantity of nitrophenols in 1/1 water/i-propanol mixture. Initial sample was taken before starting the experiment. Each experiment was carried out at the constant temperature. The experiment was continued until analysis of two successive samples was constant, which confirmed the adsorption equilibrium stage.

The concentration of the remaining nitrophenols, after their adsorption on zeolites has been reduced by electrochemical way (oxidation or/and reduction), using a modified PRIAM reactor [12]. The intermittent samples were taken out at certain time intervals during both adsorption and electrochemical experiments and analyzed by UV-VIS (Pye UNICAM Heliosβ) and cyclic voltammetry (ECOCHEMIE-BAS100W).

The yellow benthonite used for the investigations was taken from deposits in the southern part of Bulgaria. The zeolites were taken from deposits in different regions in Romania: zeolite 1- from the region Marsid, zeolite 2- from Macicas and zeolite 3- from Sacaramb.

Results and discussion

Adsorptive properties of the investigated sorbents

The chemical composition and physical properties of the zeolite 1, zeolite 2 and yellow benthonite are presented in Table 1. Specific surface area and pore volume of the natural materials were determined using Sorptomatic 1990, Fisons instruments.

The adsorption isotherms, Figure 1 (plots of q - the quantity of adsorbed solute per unit weight of adsorbent, versus C_e- equilibrium concentration):

$$q= V (C_0- C_e)/w$$

suggested that the isotherms of p-nitrophenols on zeolites are similar to Langmuir isotherms.

Table 1

Characteristics of zeolites

Content, %	Zeolite 1	Zeolite 2	Yellow bentonite
SiO_2	65.43	63.905	59-75
TiO_2	0.29	0.385	0.1-0.8
Al_2O_3	13.94	14.455	12-16
Fe_2O_3	1.31	1.74	1-6
CaO	3.98	5.335	1.8-5
MgO	0.41	0.30	0.9-3
Na_2O	0.28	1.02	0.5-1
K_2O	2.06	0.86	0.5-1
Loss at ignition	12.3	12.00	-
Specific surface area $m^2 g^{-1}$	44.56	27.33	57.99
Pore volume at p/p^0 0.99, $cm^3 g^{-1}$	0.133	0.132	0.169
Monolayer volume, $cm^3 g^{-1}$	8.8704	8.5030	13.3204

The Langmuir adsorption isotherm has been successfully applied to many adsorption processes. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogenous sites within the absorbent. It is then assumed that once an organic molecule occupies a site, no further adsorption can taken place at that site. Theoretically, therefore, a situation value is reached beyond which

no further sorption can take place. The values of the calculated Langmuir constants (K_L, a_L) and the correlation coefficient (R^2) are listed in Table 2.

The adsorption of p-nitrophenol on zeolites was compared with the data on activated carbon indicating that the adsorption is quite similar, in both cases could be attributed to the physisorption.

The adsorbed quantity of monolayer, q_m was found to vary with temperature. The adsorption equilibrium constant, K, decreased with increase in temperature, which was also consistent with the Langmuir theory.

Form the comparative analysis of the experimentally obtained adsorption capacity of the studied natural materials it was established that zeolite 2 and yellow bentonite exhibited the highest affinity to 4-NP. The values of the equilibrium and monolayer adsorption capacity of the sorbents to 4-NP follow the order:

Yellow bentonite = zeolite 2 > zeolite 1

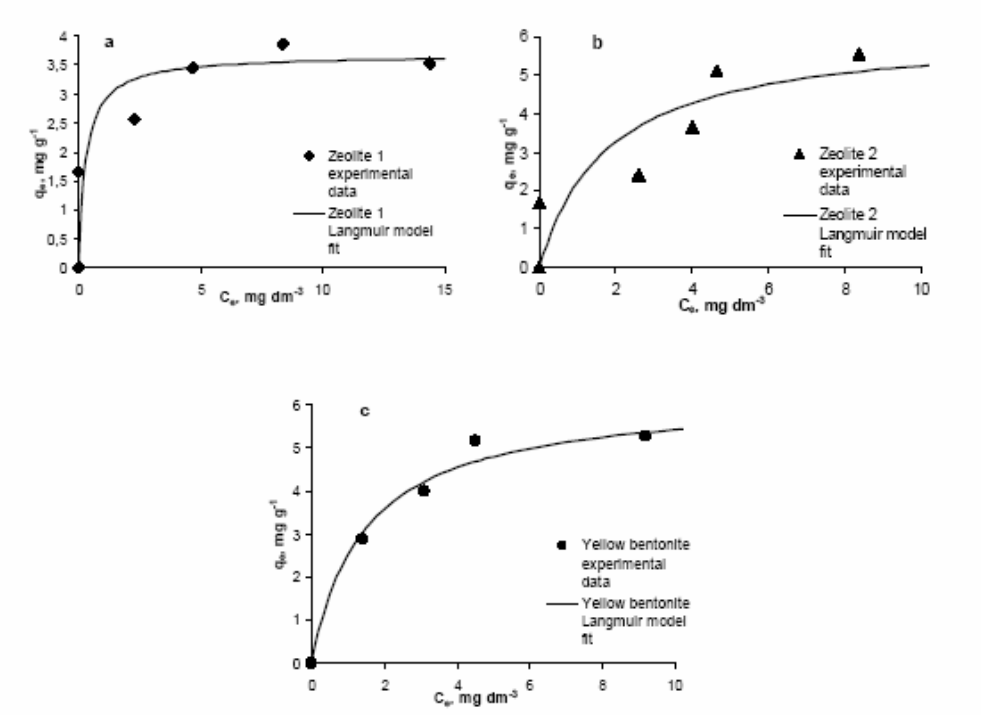

Figure 1. The adsorption isotherms comparing with Langmuir model

Table 2

Value of the calculated constants in the Langmuir and Freundlich models.

Sorbent	Langmuir			Freundlich		
	K_L	a_L	R^2	K_F	n_f	R^2
Zeolite 1	12.5313	3.4097	0.9911	2.3911	0.1827	0.6694
Zeolite 2	3.4435	0.5557	0.7642	1.3270	0.7259	0.8076
Yellow bentonite	4.2212	0.6809	0.9875	2.7077	0.3385	0.8787

Adsorption experiments of p-nitrophenol on Zeolite-2

During the adsorption of p-NP on Zeolite-2 the change of color has been observed, as can see in UV-spectrum, Figure 2 (λ=400nm);

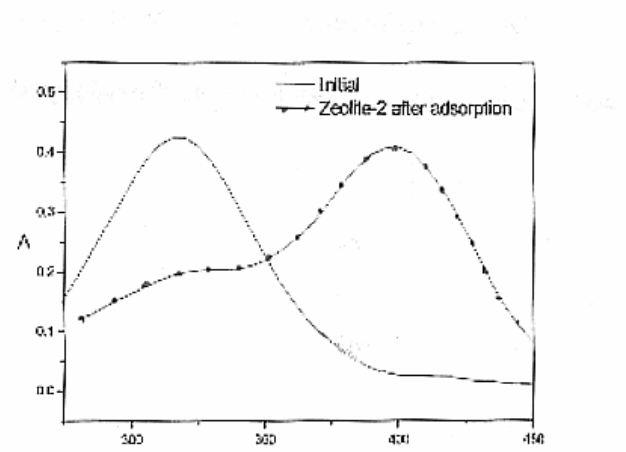

Figure 2. Evidence for p-NF oxidation after the adsorption on Zeolite-2, after 20 min of adsorption (see Fig.3).

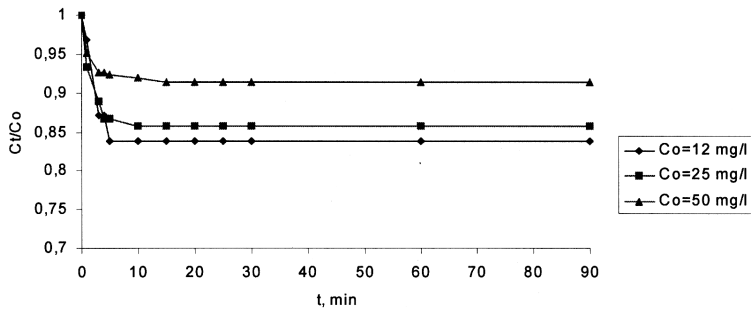

Figure 3. Effect of the initial concentration on adsorption of p-NP on benthonite. P=300 rpm; W=2 g

The surface of sorbent has been totally covered after 10-20 min, depending on the initial concentration.

This behavior (Figure 2) could be explained by the catalytic activity of the Zeolite-2 for p-NP oxidation. The most important results of p-NP adsorption are: decrease of p-NP concentration with (5-18) %, depending on the zeolite nature and conditions and partial oxidation of p-NP to the quinone structure, easier to oxidize by electrochemical way.

Decrease of nitrophenols concentration by electrochemical oxidation

According to our previous results the decrease of p-NF concentration could be realized both by reduction and oxidation [12].

The oxidation potential of 4-nitro phenol slowly decrease at the same time with increasing of phenols concentration, due the increasing of the coverage degree, Fig. 3

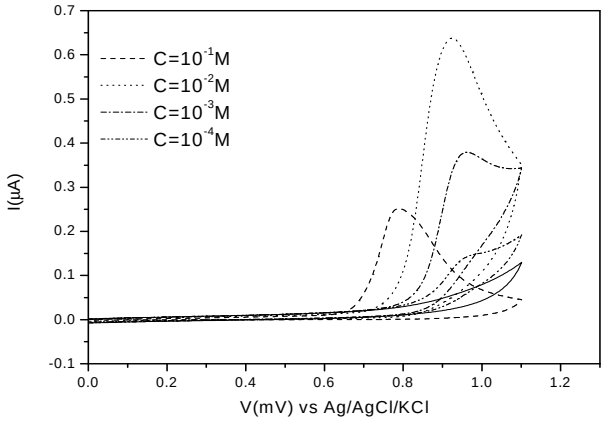

Figure 3. Dependence of oxidation potential of p-NP on concentration on GC.

Because each type of electrode shows a different behavior depending on its superficial characteristics and properties, by electrochemical oxidation on (MOE) and GC (glassy carbon electrode) the total mineralization takes place with different yields.

To make the comparison between these types of electrodes (GC and MOE), the oxidation of aqueous synthetic phenolic water was chosen.

As can be seen in figure 4, on (MOE) [16] an almost complete mineralization of the p-NP achieves and the mineralization rate is higher than those obtained on GC. The electrochemical total oxidation of the remaining p-NP, on (MOE) from about 1 mM to 10–50 μM.

On the other hand the analysis of the answer after multiples scans shows that polymerization is an important secondary reaction pathway on GC, Figure 5.

Preliminary data by the GPC liquid chromatography have demonstrated that the polymeric material developed in the process was a mixture of the various polymers with low molecular weight (ranging from 200 to 500 mg/mmol). Conversely, the oxidation of the phenol waste using (MOE) electrode deals to the sequential formation of aromatic compounds, carboxylic acids and carbon dioxide, Table 3.

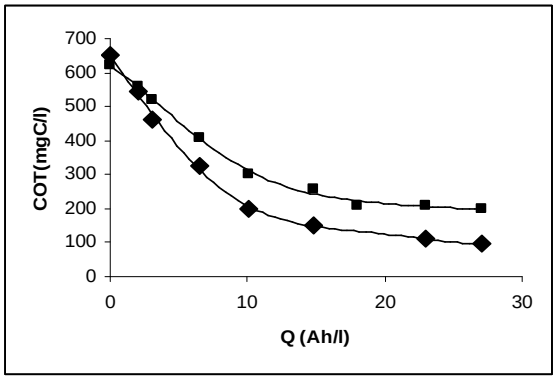

Figure 4. Decrease of COT on GC (■) and on MOE (◆)
$[Phenol]_O$: 1000 ppm; $[Na_2SO_4]$: 5000 ppm; pH: 2; Current density: 10 mA/cm^2

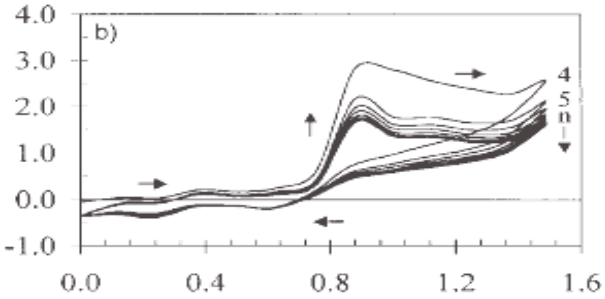

Figure 5. Polymers formation on GC.

Table 3

Preliminary data concerning the intermediates and final products of electro-oxidation (mg/l)

Compound	GC	MOE
Quinones	1.6	1.1
C_4 acids+C_2 acids	2.8	2.5
Polymers	38.5	0.0
Carbon dioxide	30.0	90.3
Unidentified compounds	26.6	6.1

Results obtained in this work could be explained in the terms of the oxidations of phenol to phenoxy radicals (first step of the process). The oxidation performed in (MOE) is stronger dealing whit the quick formation of benzoquinone and to the split of the aromatic ring. On the contrary the softer oxidation performed in GC electrode.

Conclusion

The combined procedure proposed in this paper is the adsorption of p-NP on zeolite in order to reduce the pollutant concentration up to 1 mM, followed by the electrochemical oxidation of remaining p-NP, up to 10–50 μM. The electrochemical mineralization of the remaining p-NP on (MOE) could be realized at accessible temperatures and pH≈2, when the competitive oxygen formation diminishes. The preliminary data on the nature and distribution of the oxidation intermediates and products has to be confirmed by future experiments.

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