Sorption of different phenol derivatives on a functionalized macroporous nanocomposite of poly(glycidyl methacrylate-*co*--ethylene glycol dimethacrylate) and acid modified bentonite

SANJA R. MARINOVIĆ[1]*, ALEKSANDRA D. MILUTINOVIĆ-NIKOLIĆ[1#],
ALEKSANDRA B. NASTASOVIĆ[2], MARIJA J. ŽUNIĆ[1], ZORICA M. VUKOVIĆ[1],
DUŠAN G. ANTONOVIĆ[3] and DUŠAN M. JOVANOVIĆ[1]

[1]*University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Center for Catalysis and Chemical Engineering, Njegoševa 12, Belgrade, Serbia,* [2]*University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoševa 12, Belgrade and* [3]*University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Republic of Serbia*

Abstract: Macroporous nanocomposite of poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) and acid modified bentonite was prepared by radical suspension copolymerization. Nanocomposite was functionalized with diethylenetriamine (DETA), by ring-opening reaction of the pendant epoxy groups. Functionalization was performed in order to enable phenol derivatives sorption. This new, not sufficiently investigated material, with developed porous structure was denoted CP–S$_A$–DETA. In this study, the influence of temperature on 4-nitrophenol (4NP) sorption on CP–S$_A$–DETA was investigated. The chemisorption was estimated as dominant process since activation energy of sorption of 4NP of 54.8 kJ mol^{-1} was obtained. After determining the optimal sorption conditions for 4NP, the sorption of 2-nitrophenol (2NP) and 2-chloro-4-nitrophenol (2Cl4NP) on CP–S$_A$–DETA was investigated with respect to pH, initial concentration and contact time. The 2NP sorption was seldom tested, while according to our knowledge, the 2Cl4NP sorption was not investigated. The isotherm data were best fitted with Langmuir model, while the sorption dynamics obeyed the pseudo-second-order kinetic model for all derivatives.

Keywords: functionalized nanocomposite; wastewater sorbent; 4-nitrophenol; 2-nitrophenol; 2-chloro-4-nitrophenol.

---

* Corresponding author. E-mail: sanja@nanosys.ihtm.bg.ac.rs
# Serbian Chemical Society member.

1249

INTRODUCTION

Phenol and its derivatives are harmful to organisms even at low concentrations,[1,2] which qualifies them as priority pollutants. Many have been classified as hazardous pollutants because of their potential harm to human health.[3,4] The US Environmental Protection Agency (EPA) limited the quantity of phenols in wastewater to 1 mg dm^{-3}.[1,2,5] The removal of phenolic compounds from wastewater before discharge into water bodies is a necessity in order to reduce their side effects on the environment and human health.[6,7]

Phenolic compounds are widely found in the wastewaters from pesticide, pharmaceutical, petroleum, petrochemical and other industries.[2,8]

The available concentration data regarding industrial wastewaters are generally expressed as the total concentration of phenols and they depend on the plant potentiality and operating conditions. The total concentrations of phenols in the wastewaters of some chemical industries were as follows: phenolic resin production, ≈400 mg dm^{-3}; refineries, < 50 mg dm^{-3}; naphthalenic acid production, 12 mg dm^{-3} and shale dry distillation, ≈200 mg dm^{-3}.[9,10]

Conventional processes that are used for the removal of phenol and its derivatives from wastewaters are biodegradation,[11,12] liquid membrane processes,[13–15] electrochemical oxidation,[16] photocatalytic degradation[17] and adsorption.[18–20]

Adsorption is being employed extensively for the removal of phenol and its derivatives from aqueous solutions.[18–20] Activated carbons as adsorbents for the removal of phenolic compounds are the most widely used method for water treatment.[21] However, the use of effective commercial activated carbons based on relatively expensive starting materials, such as wood and coal, lead to limitation in their application the pollution sector.[5] Other adsorbents used for the removal of phenols from wastewaters are: zeolites,[2] bentonites,[3,22] organo-modified bentonites,[23] synthetic resins,[24] and different polymeric materials.[25–27] In the past few decades, polymeric adsorbents have been used as an alternative to activated carbon in terms of high surface area and improved mechanical rigidity. Macroporous poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate)s have been used for the removal of organic pollutants,[28–30] due to their chemical resistance, regenerability and reuse in adsorption processes.

In the present study, a functionalized nanocomposite obtained by incurporation of acid-modified bentonite into a poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) matrix was investigated as a sorbent for phenol derivatives. The incorporation of the acid modified bentonite into the copolymer matrix led to an increase of porosity, total pore volume and, particularly, the specific surface area.[31] Further amino functionalization of the nanocomposite with diethylenetriamine (DETA) enabled the sorption of phenol derivatives.[29] The obtained composite CP–S$_A$–DETA was used for an investigation of 4-nitrophenol (4NP), 2-nitrophenol (2NP) and 2-chloro-4-nitro phenol (2Cl4NP) sorption

from aqueous solutions. The starting concentrations of the phenol derivatives in the presented experiments were in range of 0.05 to 0.30 mmol dm^{-3} (7.0 to 41.7 mg dm^{-3}), which is comparable to reported industrial wastewater concentrations of phenols.[9,10] The influence of temperature, pH, sorption time and initial sorbent concentration on the sorption efficiency of CP–S$_A$–DETA were studied in order to evaluate this material as a wastewater sorbent.

EXPERIMENTAL

Materials

Bentonite clay was obtained from the coal and bentonite mine "Bogovina", Serbia. It was crushed, ground and sieved through a 74-µm sieve and acid modified.[29] The chemical and the textural properties of the acid-modified bentonite were reported previously.[32,33] All the chemicals used for the synthesis of the composite were analytical grade products and used as received. Glycidyl methacrylate, GMA, and ethylene glycol dimethacrylate, EGDMA, were obtained from Fluka and Merck, respectively. Poly(*N*-vinyl pyrrolidone), PVP, (BASF with $\bar{M}_w = 1\times10^6$ g mol^{-1}) was used as the stabilizer in the suspension copolymerization and 2,2′--azobisisobutyronitrile, AIBN (Merck), was used as the reaction initiator. Cyclohexanol (Merck) and 1-tetradecanol (Merck) were used as an inert component in the polymerization. For the sorption experiments, 4-nitrophenol (4NP, Ciba, solubility in water 16 g dm^{-3} at 25 °C), 2-nitrophenol (2NP, Alfa Aesar, solubility in water 2 g dm^{-3} at 25 °C) and 2-chloro-4--nitrophenol (2Cl4NP, Alfa Aesar, solubility in water – slightly soluble) were used as received.

Synthesis and functionalization of nanocomposite

Macroporous nanocomposite of poly(glycidyl methacrylate–*co*–ethylene glycol dimethacrylate) and acid modified bentonite was prepared by the radical suspension copolymerization of GMA and EGDMA in the presence of the acid–modified bentonite (S$_A$) and an inert component. The synthesis procedure was previously reported.[29,31]

The obtained sample was denoted as CP–S$_A$. TEM analysis confirmed the CP–S$_A$ was a nanocomposite.[34] The functionalization was realized as follows. A mixture of 3.6 g of CP–S$_A$ and 15.7 g of diethylenetriamine (DETA) and 100 cm^3 of toluene was left at room temperature for 24 h, and then heated at 80 °C for 6 h. The modified sample was filtered, washed with ethanol, dried and labeled as CP–S$_A$–DETA.[35]

Sorption experiments

Batch-type sorption experiments were conducted in aqueous suspensions in a temperature-controlled shaker water bath (Memmert WNE 14 and SV 1422). Aliquots were withdrawn from the shaker at regular time intervals and the suspension was centrifuged at 17000 rpm for 6 min (Hettich EBA-21) in order to separate the sorbent from the dispersion. The absorbance of the supernatant solution was measured. The spectra were obtained using a Thermo Electron Nicolet Evolution 500 UV–Vis instrument. Since the UV-Vis spectra of all phenol derivatives vary with pH, the pH of the supernatant solution was adjusted to pH 11 before every UV–Vis measurement. The calibration curves at λ_{max} of 227, 417 and 399 nm for 4NP, 2NP and 2Cl4NP, respectively, were obtained with coefficients of determination $R^2 > > 0.9999$. A pH value of 11 was chosen to keep the phenol derivatives in their ionic state.[36]

Sorption of phenol derivatives by CP–S$_A$–DETA was investigated with respect to temperature, pH, initial concentration and contact time. The mass of sorbent and solution volume were kept constant (m_{sorb} = 25 mg, v = 50.0 cm^3) in all experiments.

The effect of temperature was studied at 25, 40, 50 and 60 °C. For these experiments, the solute concentration was kept constant at 2×10^{-4} mol dm^{-3} and pH was unadjusted (pH 5.1).[29]

The amount of sorbed derivative at time t, q_t / mmol g^{-1}, was calculated from the following mass balance relationship:

$$q_t = \frac{(c_0 - c_t)v}{m_{\text{sorb}}} \tag{1}$$

where: c_0 and c_t in mol dm^{-3} are the initial and the solution concentrations after sorption time t, respectively.

The pH of the solution was monitored using a Jenway 3320 pH meter.

RESULTS AND DISCUSSION

The characterization of functionalized macroporous nanocomposite was previously reported.[29] Textural properties determined by mercury intrusion porosimetry were as follows: specific surface area (S_{Hg}= 90 m^2 g^{-1}), total pore volume per mass of sample (the specific pore volume, V_{p} =1.09 cm^3 g^{-1}), porosity (P= 64 %), and the pore diameter that corresponds to half of the pore volume ($d_{\text{V/2}}$ = 62 nm). Amino group content was estimated to be 2.7 mmol g^{-1}.[29]

The sorption of 4NP on CP–S$_A$–DETA was previously investigated with respect to contact time, pH and initial concentration.[29] These experiments were complemented with new experiments where the effect of temperature on sorption efficiency was investigated. The effect of temperature was studied at 25, 40, 50 and 60 °C and the results are presented in Fig. 1.
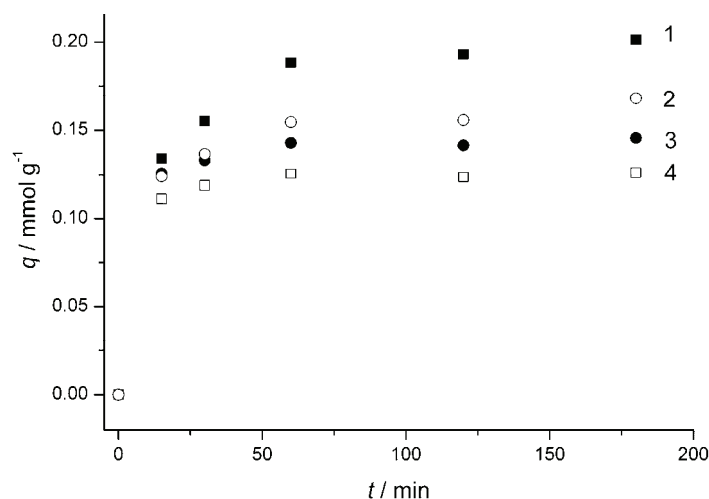

Fig. 1. The effect of temperature on the sorption of 4NP on CP–S$_A$–DETA: 1) 25, 2) 40, 3) 50 and 4) 60 °C ($c_0 = 2\times10^{-4}$ mol dm^{-3}, pH 5.1).

The sorption efficiency decreased with increasing temperature. The decrease in the sorption efficiency indicates an exothermic process. This effect may be

ascribed to the increasing trend of desorption of 4NP from the interface into the solution at elevated temperatures.[4]

Kinetic analysis of temperature effect for 4NP sorption was performed using the data given in Fig. 1. The pseudo-first-order and the pseudo-second-order kinetic models were tested.[37] The integrated rate laws for pseudo-first-order and pseudo-second-order reactions in linear form are presented by Eqs. (2) and (3), respectively:

$$\log (q_e-q_t) = \log q_e - k_1 t/2.303 \qquad (2)$$
$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (3)$$

where q_t is the amount of sorbed sorbate (mmol g^{-1}) at any time t, q_e is the amount of sorbed sorbate at equilibrium (mmol g^{-1}), k_1 is the pseudo-first-order rate constant (min^{-1}), k_2 is the pseudo-second-order rate constant (g mmol^{-1} min^{-1}).

The kinetic results were also analyzed using the intraparticle diffusion model[38] in order to determine the rate-controlling step of the sorption process. The rate of intraparticle diffusion can be calculated according to the equation:

$$q_t = C_{id} + k_{id}t^{0.5} \qquad (4)$$

where k_{id} (mmol g^{-1} min$^{-0.5}$) is the intraparticle diffusion rate constant and C_{id} is the intercept, which is proportional to the boundary layer thickness.

Parameters for pseudo-first-order, pseudo-second-order kinetics model as well as intraparticle diffusion kinetic model are presented in Table I.

TABLE I. Kinetic parameters for sorption of 4NP on CP–S$_A$–DETA at different temperatures

Parameter	Temperature, °C			
	25	40	50	60
q_e^{exp} / mmol g^{-1}	0.201	0.169	0.146	0.126
Pseudo-first-order				
q_e^{calc} / mmol g^{-1}	0.324	0.254	0.169	0.130
$k_1 \times 10^2$ / min^{-1}	2.00	1.19	1.49	1.66
R^2	0.866	0.770	0.554	0.303
Pseudo-second-order				
q_e^{calc} / mmol g^{-1}	0.210	0.172	0.147	0.126
k_2 / g mmol^{-1} min^{-1}	0.51	0.77	3.04	7.96
R^2	0.999	0.998	0.999	0.999
Intraparticle diffusion				
$k_{id} \times 10^2$ / mmol g^{-1} min$^{-0.5}$	1.41	0.79	0.45	0.36
C_{id} / mmol g^{-1}	0.079	0.093	0.108	0.098
R^2	0.999	0.999	0.999	0.982

The coefficients of determination (R^2) for the pseudo-second-order kinetics model are closer to unity in comparison to the corresponding R^2 for the pseudo--first-order kinetics. Furthermore, the experimentally obtained values for the equilibrium amount (q_e^{exp}) were almost identical to the values calculated (q_e^{calc})

using the pseudo-second-order kinetics model. Therefore, it could be stated that the adsorption of 4NP on CP–S$_A$–DETA obeyed pseudo-second-order kinetics model, which is in accordance with finding of other authors for 4NP for similar systems.[25,39,40]

The obtained $R^2 \geq 0.982$ for the intraparticle diffusion model for all investigated temperatures showed that this model was applicable for the investigated system. The linear plot of q_t *vs*. $t^{0.5}$ did not pass through the origin, indicating that both intraparticle diffusion and external mass transfer were rate-controlling steps.[41,42]

The Arrhenius Equation was used to evaluate the activation energy of sorption:

$$\ln k_2 = \ln A - E_a/RT \tag{5}$$

where E_a is activation energy of sorption (kJ mol^{-1}), A is the Arrhenius factor, R is the universal gas constant ($R = 8.314$ J K^{-1} mol^{-1}), T is thermodynamic temperature (K) and k_2 is the equilibrium rate constant of the pseudo-second-order reaction (g mmol^{-1} min^{-1}) given in Table I.

The magnitude of E_a indicates the dominant type of sorption, *i.e.*, either physisorption (E_a in range of 5–40 kJ mol^{-1}) or chemisorption (E_a in range of 40–800 kJ mol^{-1}).[43] E_a was found to be 54.8 kJ mol^{-1}, indicating that chemisorption was the dominant sorption process.

In order to evaluate the synthesized sorbent as sorbent of various phenol derivatives, sorption experiments were performed using 2NP and 2Cl4NP in addition to 4NP. Considering that the investigation of the influence of temperature on 4NP sorption showed that the best sorption was achieved at 25 °C, the experiments with 2NP and 2Cl4NP were performed at this temperature.

The effect of initial pH on the sorption of 2NP and 2Cl4NP was determined within the pH range of 2–11 and the results are presented in Fig. 2, together with the pH behavior of CP–S$_A$–DETA that was previously reported.[29] The diagram shows initial pH of suspension of CP–S$_A$–DETA in 0.01 M NaCl (pH$_i$) *vs*. pH after 24 h of shaking (pH$_f$). A plateau in the pH value between 4 and 9 was observed and the pH at the point of zero charge, pH$_{PZC}$, was estimated to be 7.8.

It was observed that sorption of both derivatives significantly depended on the initial pH value. Sorption capacity was very low in extremely acidic and alkaline environments. The maximal sorption of 2NP of 35.3 % was determined at pH 7.2 and 79.7 % for 2Cl4NP at pH 3.9. The sorption efficiency for both derivatives at unadjusted pH 5.8 for 2NP and pH 4.8 for 2Cl4NP were close to the maximal values. Further experiments were performed at the unadjusted pH values. Additional pH adjustment would increase the purification costs and would be ecologically unjustified.

The effect of contact time on the amount of sorbed 2NP and 2Cl4NP on CP––S_A–DETA was investigated in the range of initial concentrations (0.5×10^{-4}––2×10^{-4} mol dm^{-3}, Fig. 3a and b). Due to significant removal of 2Cl4NP on CP––S_A–DETA, experiments were also conducted at the higher initial concentration of 3×10^{-4} mol dm^{-3}.
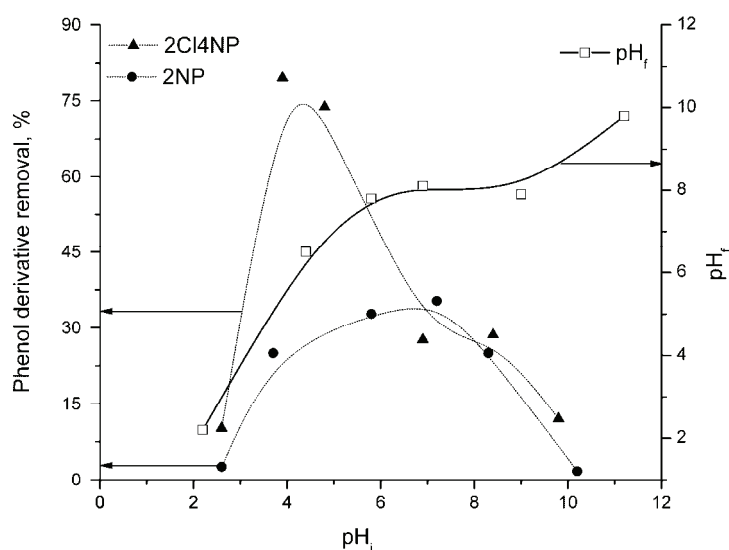

Fig. 2. The pH behavior of CP–S_A–DETA in the sorption 2NP and 2Cl4NP and the pH$_i$ *vs.* pH$_f$ diagram.

The rate of removal of both phenol derivatives was initially high. The initial rapid phase may be due to increased number of vacant surface sites available during the initial stage. Therefore, there was an increased concentration gradient between sorbate in the solution and sorbate on the sorbent.[44,45] Subsequently, the remaining vacant surface sites were difficult to occupy due to repulsive forces between already sorbed phenol derivative molecules and these molecules in solution.[46]

For initial concentrations of sorbate, for both phenols, the equilibrium was reached after 60 min. The time when half of total sorption capacity was reached ($t_{1/2}$) was in the range 8–14 min and 13–24 min for all initial concentration of 2NP and 2Cl4NP, respectively.

Pseudo-first-order and pseudo-second-order kinetic models were applied (Table II) in order to predict the adsorption kinetics.

The coefficients of determination R^2 for pseudo-first order kinetic were low showing that this model was not applicable for the investigated sorption systems. On the other hand, a linear correlation was obtained for pseudo-second-order

kinetics with $R^2>0.990$ and the q_e^{calc} calculated from the pseudo-second order kinetic model were in good agreement with q_e^{exp}.

In order to illustrate different sorption efficiencies of CP–S$_A$–DETA toward 4NP, 2NP and 2Cl4NP, the results of sorption experiments realized under the same experimental conditions ($c_0 = 2\times10^{-4}$ mol dm^{-3}, for 3 h at 25 °C and unadjusted pH) are presented in Fig. 4.
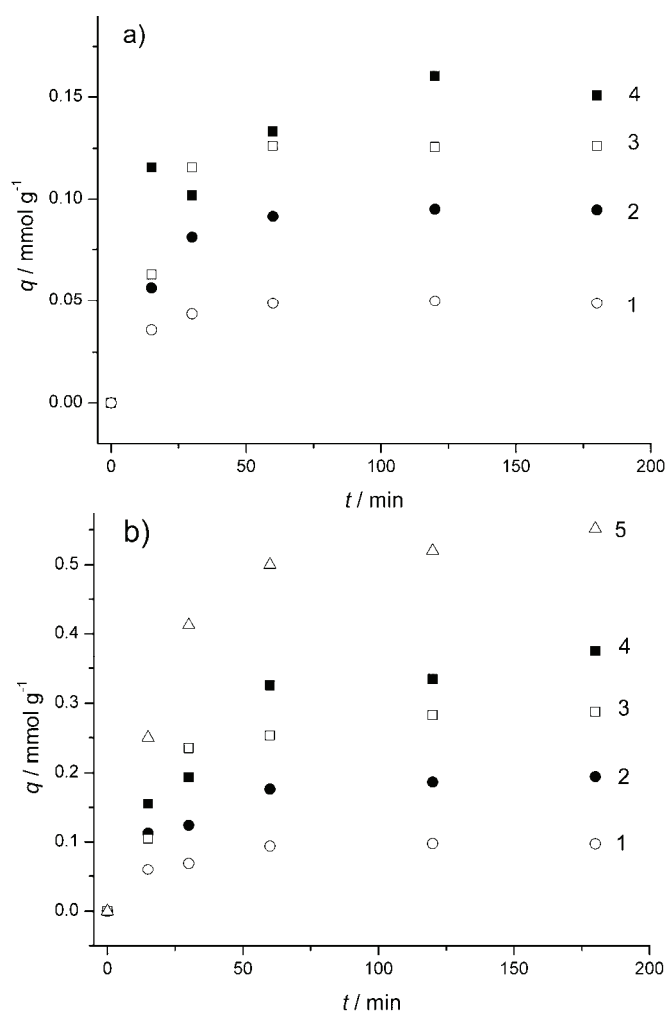

Fig. 3. The effect of contact time on the sorption of a) 2NP and b) 2Cl4NP on CP–S$_A$–DETA at different initial concentrations: 1) 0.5×10^{-4}, 2) 1×10^{-4}, 3) 1.5×10^{-4}, 4) 2×10^{-4} and 5) 3×10^{-4} mol dm^{-3}.

The affinity of CP–S$_A$–DETA toward phenol derivatives was found to increase in the following order 2NP < 4NP < 2Cl4NP. This could be ascribed to

chemical structure of these phenol derivatives and the hydrogen bonds that they could form with the sorbent. Intramolecular hydrogen bonds are present in 2NP making it less soluble in water than 4NP. Due to the intramolecular hydrogen bonds and steric hindrance in 2NP, this derivative is less capable of making hydrogen bonds with the amino groups in the functionalized composite CP–S$_A$– –DETA. Both 2NP and 4NP are hydrophobic while the amino-functionalized composite is hydrophilic. The adsorption capacity of different phenols, in general, is related to their solubility in water[20] and to the hydrophobic character of their substituents. Therefore, it could be expected that 2NP being less soluble in water than 4NP would be more efficiently sorbed on CP–S$_A$–DETA, but due to intramolecular hydrogen bonds and steric hindrance, this is not the case.

TABLE II. Pseudo-first-order-kinetics and pseudo-second-order-kinetics for the sorption of 2NP and 2Cl4NP on CP–SA–DETA at 25 °C

| Parameter	2NP				2Cl4NP				
$c_0 \times 10^4$ / mol dm^{-3}	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0	3.0
q_{exp} / mmol g^{-1}	0.050	0.122	0.126	0.161	0.098	0.195	0.288	0.376	0.551
Pseudo-first-order									
$k_1 \times 10^2$ / min^{-1}	1.02	4.20	2.47	1.28	2.02	1.66	3.15	2.39	2.93
q_e^{calc} / mmol g^{-1}	0.295	0.317	0.223	0.123	0.577	0.541	0.510	0.388	0.266
R^2	0.931	0.946	0.921	0.560	0.856	0.800	0.954	0.933	0.946
Pseudo-second-order									
k_2 /g mmol^{-1} min^{-1}	0.540	0.818	1.366	4.666	0.102	0.079	0.324	0.302	0.855
q_e^{calc} / mmol g^{-1}	0.164	0.134	0.117	0.050	0.601	0.433	0.305	0.212	0.105
R^2	0.995	0.997	0.999	0.999	0.997	0.990	0.999	0.997	0.997
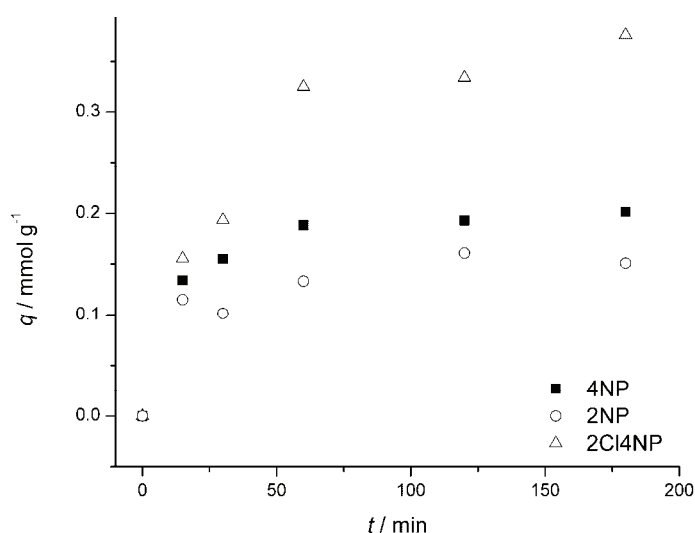
Fig. 4. The effect of contact time on the sorption of different phenol derivatives by CP–S$_A$–DETA ($c_0 = 2 \times 10^{-4}$ mol dm^{-3}, at 25 °C).

2Cl4NP has the lowest solubility in water. The chlorine atom is electron withdrawing and stabilizes the negative charge at the *ortho* position through the inductive withdrawing effect. However, it also has a weak resonance donating effect. The negative inductive effect of chlorine prevails over the positive resonance effect in this case. In addition, the NO_2 group has a negative resonance and a negative inductive effect.

The pK_a values of the phenol derivatives are 7.16, 7.23 and 5.42 for 2NP, 4NP and 2Cl4NP, respectively.[1] Therefore, 2Cl4NP is the strongest acid and it can easier release a proton than 2NP and 4NP. All three derivatives are in their molecular form in the presented sorption experiments ($pK_a < pH_{unadjusted}$).

The amino groups on CP–S_A–DETA are in the protonated form when $pK_a < pH$. The pK_a of diethylenetriamine is 10.45.[47] It could be assumed that diethylenetriamine in CP–S_A–DETA was in the protonated form during the sorption experiments and thus, the sorbent surface was positively charged.[48] Since phenols act as proton acceptor hydrogen bonds, this creation is a favorable process in this system.

Boyd[49] studied the sorption of undissociated phenol and its derivatives on a soil sample at pH 5.7 to evaluate the effect of the presence of other functional groups in the phenol molecule. With decreasing water solubility of the phenol derivatives with the following functional groups: –CH_3, –OCH_3, –NO_2, or –Cl, the sorption increased. Moreover, the sorption of the substituted phenols, with the exception of 2NP, was generally greater than that predicted for hydrophobic sorption, most likely due to hydrogen bond formation. Probably, a similar explanation could be applied to the experimental data obtained in the present study.

The isotherm data were fitted with the Freundlich and Langmuir models, and a better correlation was found with the Langmuir model, with the coefficients of determination for all the studied phenol derivatives > 0.99. Maximal sorption capacities (q_{max}) were calculated using Langmuir model. The obtained values of q_{max} of CP–S_A–DETA toward phenol derivatives increased in the following order $q_{max(2NP)} = 0.342$ mmol $g^{-1} < q_{max(4NP)} = 0.581$ mmol $g^{-1} < q_{max(2Cl4NP)} = 0.704$ mmol g^{-1}. The $q_{max(4NP)}$ was previously reported.[29]

Among phenol and phenol derivatives, the sorption of phenol[2,3] and 4NP[6,23,50–52] were the most investigated. The sorption of 2NP was seldom tested,[23,53] while, to the best of our knowledge, the sorption of 2Cl4NP has not been investigated. The literature data on $q_{max(4NP)}$ varied from 2.26 mmol g^{-1} at 25 °C for activated carbon fibers,[6] down to 0.33 mmol g^{-1} on commercial Amberlite XAD-4 resin.[52] With $q_{max(4NP)} = 0.581$ mmol g^{-1}, CP–S_A–DETA could be regarded as an acceptable sorbent for 4NP. The more expressed affinity of CP–S_A–DETA for the 2Cl4NP evaluates CP–S_A–DETA as a promising sorbent for phenolic wastewater.

CONCLUSION

A macroporous nanocomposite of poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) and acid modified bentonite was prepared by the radical suspension copolymerization of their mixture and then functionalized with diethylenetriamine.

The obtained functionalized nanocomposite CP–S$_A$–DETA, was investigated as wastewater sorbent for the removal of phenol derivatives. Sorption of 4NP was exothermic, having $E_a = 54.8$ kJ mol^{-1} that indicates chemisorption. Kinetics of sorption of all phenol derivatives (2NP, 4NP and 2Cl4NP) was well described by the pseudo-second-order kinetic model. The isotherm data were best fitted with Langmuir model for all derivatives. It was found that the affinity of CP–S$_A$–DETA toward phenol derivatives increases in the following order 2NP < < 4NP < 2Cl4NP. Such behavior could be ascribed to the chemical structure of these phenol derivatives and the hydrogen bonds that they could form with the sorbent.

И З В О Д

СОРПЦИЈА ДЕРИВАТА ФЕНОЛА НА ФУНКЦИОНАЛИЗОВАНОМ МАКРОПОРОЗНОМ НАНОКОМПОЗИТУ ПОЛИ(ГЛИЦИДИЛ-МЕТАКРИЛАТ-*КО*-ЕТИЛЕН-ГЛИКОЛ--ДИМЕТАКРИЛАТ) И КИСЕЛО-МОДИФИКОВАНОГ БЕНТОНИТА

САЊА Р. МАРИНОВИЋ[1], АЛЕКСАНДРА Д. МИЛУТИНОВИЋ-НИКОЛИЋ[1], АЛЕКСАНДРА Б. НАСТАСОВИЋ[2], МАРИЈА Ј. ЖУНИЋ[1], ЗОРИЦА М. ВУКОВИЋ[1], ДУШАН Г. АНТОНОВИЋ[3] и ДУШАН М. ЈОВАНОВИЋ[1]

[1]*Универзитет у Београду – Институт за хемију, технологију и металургију, Центар за катализу и хемијско инжењерство, Његошева 12, Београд,* [2]*Универзитет у Београду – Институт за хемију, технологију и металургију, Центар за хемију, Његошева 12, Београд и* [3]*Универзитет у Београду – Технолошко–металршки факултет, Карнегијева 4, Београд*

Макропорозни нанокомпозит добијен је радикалном суспензионом кополимериза-цијом поли(глицидил-метакрилат-*ко*-етилен-гликол-диметакрилата) и кисело-модифи-кованог бентонита. Како би се омогућила сорпција деривата фенола добијени наноком-позит је функционализован диетилен триамином (DETA), реакцијом отварања прстена епоксидне групе. Овај нови, недовољно испитани материјал, развијене порозне струк-туре, је означен са CP–S$_A$–DETA. У овом раду је испитан утицај температуре на сорпцију 4-нитрофенола (4NP) на CP–S$_A$–DETA. Добијена вредност енергије активације од 54,8 kJ mol^{-1} указује на хемисорпцију као доминантан процес. По одређивању оптималних услова сорпције за 4NP, испитана је сорпција 2-нитрофенола (2NP) и 2-хлор-4-нитро-фенола (2Cl4NP) на CP–S$_A$–DETA. Проучаван је утицај pH, почетне концентрације и времена контакта на сорпцију. 2NP је у малој мери испитиван као сорбат, док, по нашим сазнањима, 2Cl4NP није испитиван. Потврђено је да је CP–S$_A$–DETA добар сорбент за сва три деривата фенола, а поготову за 2Cl4NP. Утврђено је да Лангмирова изотерма најбоље описује сорпцију у испитаним системима, а да сорпциона динамика прати кине-тику псеудо-другог реда за све деривате.

REFERENCES

1. N. Calace, E. Nardi, B. M. Petronio, M. Pietroletti, *Environ. Pollut.* **118** (2002) 315
2. R. I. Yousef, B. El-Eswed, A. H. Al-Muhtaseb, *Chem. Eng. J.* **171** (2011) 1143
3. F. A. Banat, B. Al-Bashir, S. Al-Asheh, O. Hayajneh, *Environ. Pollut.* **107** (2000) 391
4. M. Kilic, E. Apaydin-Varol, A. E. Putun, *J. Hazard. Mater.* **189** (2011) 397
5. Z. Ioannou, J. Simitzis, *J. Hazard. Mater.* **171** (2009) 954
6. Q. S. Liu, T. Zheng, P. Wang, J. P. Jiang, N. Li, *Chem. Eng. J.* **157** (2010) 348
7. O. A. Ekpete, M. Horsfall Jr., T. Tarawou, *Int. J. Biol. Chem. Sci.* **5** (2011) 1143
8. S. Suresh, V. C. Srivastava, I. M. Mishra, *Chem. Ind. Chem. Eng. Q.* **19** (2013) 195
9. J. Chen, W. H. Rulkens, H. Bruning, *Water Sci. Technol.* **35** (1997) 231
10. M. C. Tomei, S. Rossetti, M. C. Annesini, *Chemosphere* **63** (2006) 1801
11. S. A. Boyd, D. R. Shelton, D. Berry, J. M. Tiedje, *Appl. Environ. Microbiol.* **46** (1983) 50
12. G. Gonzalez, G. Herrera, M. T. Garcia, M. Peña, *Bioresource Technol.* **80** (2001) 137
13. S. H. Lin, C. L. Pan, H. G. Leu, *J. Hazard. Mater.* **65** (1999) 289
14. Y. Park, A. H. P. Skelland, L. J. Forney, J. H. Kim, *Water Res.* **40** (2006) 1763
15. J. Luana, A. Plaisier, *J. Membrane Sci.* **229** (2004) 235
16. Y. Yavuz, A. S. Koparal, *J. Hazard. Mater.* **136** (2006) 296
17. S. H. Lin, C. H. Chiou, C. K. Chang, R. S. Juang, *J. Environ. Manage.* **92** (2011) 3098
18. S. H. Lin, R. S. Juang, *J. Environ. Manage.* **90** (2009) 1336
19. J. M. Chern, Y. W. Chien, *Water Res.* **37** (2003) 2347
20. C. Moreno-Castilla, J. Rivera-Utrilla, M. V. Lopez-Ramon, F. Carrasco-Marin, *Carbon* **33** (1995) 845
21. B. H. Hameed, A. A. Rahman, *J. Hazard. Mater.* **160** (2008) 576
22. S. Al-Asheh, F. Banat, L. Abu-Aitah, *Sep. Purif. Technol.* **33** (2003) 1
23. H. Koyuncua, N. Yıldız, U. Salgınc, F. Koroglu, A. Calımlı, *J. Hazard. Mater.* **185** (2011) 1332
24. K. Abburi, *J. Hazard. Mater.* **105** (2003) 143
25. B. Pan, W. Du, W. Zhang, X. Zhang, Q. Zhang, B. Pan, L. Lv, Q. Zhang, J. Chen, *Environ. Sci. Technol.* **41** (2007) 5057
26. A. Li, Q. Zhang, G. Zhang, J. Chen, Z. Fei, F. Liu, *Chemosphere* **47** (2002) 981
27. R. Ardelean, C. M. Davidescu, A. Popa, *Chem. Bull. "Politehnica" Univ. Timisoara, Romania* **55** (2010) 132
28. Z. Sandić, A. Nastasović, N. Jović-Jovičić, A. Milutinović-Nikolić, D. Jovanović, *J. Appl. Polym. Sci.* **121** (2011) 234
29. S. Marinović, A. Milutinović-Nikolić, M. Žunić, Z. Vuković, D. Maksin, A. Nastasović, D. Jovanović, *Russ J. Phys. Chem., A* **85** (2011) 2386
30. V. V. Podlesnyuk, J. Hradil, R. M. Marutovskii, N. A. Klimenko, L. E. Fridman, *React. Funct. Polym.* **33** (1997) 275
31. S. Marinović, Z. Vuković, A. Nastasović, A. Milutinović-Nikolić, D. Jovanović, *Mater. Chem. Phys.* **128** (2011) 291
32. Z. Vuković, A. Milutinović-Nikolić, Lj. Rozić, A. Rosić, Z. Nedić, D. Jovanović, *Clay. Clay Miner.* **54** (2006) 697
33. Z. Vuković, A. Milutinović-Nikolić, J. Krstić, A. Abu-Rabi, T. Novaković, D. Jovanović, *Mater. Sci. Forum* **494** (2005) 339
34. M. Žunić, A. Milutinović-Nikolić, A. Nastasović, Z. Vuković, D. Lončarević, I. Vuković, K. Loos, G. ten Brinke, D. Jovanović, *Polym. Bull.* **70** (2013) 1805
35. Lj. Malović, A. Nastasović, Z. Sandić, J. Marković, D. Đorđević, Z. Vuković, *J. Mater. Sci.* **42** (2007) 3326

36. L. Zhu, B. Chen, S. Tao, C. T. Chiou, *Environ. Sci. Technol.* **37** (2003) 4001
37. P. K. Malik, *Dyes Pigments* **56** (2003) 239
38. W. J. Weber Jr., J. C. Morris, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **89** (1963) 31
39. W. Guan, J. Pan, X. Wang, W. Hu, L. Xu, X. Zou, C. Li, *J. Sep. Sci.* **34** (2011) 1244
40. Q. Zhou, H. P. He, J. X. Zhu, W. Shen, R. L. Frost, P. Yuan, *J. Hazard. Mater.* **154** (2008) 1025
41. S. J Allen, L. J. Whitten, M. Murray, O. Duggan, *J. Chem. Technol. Biot.* **68** (1997) 442
42. M. Dogan, M. Alkan, *Chemosphere* **50** (2003) 517
43. M. Dogan, H. Abak, M. Alkan, *J. Hazard. Mater.* **164** (2009) 172
44. V. Singh, A. K. Sharma, D. N. Tripathi, R. Sanghi, *J. Hazard. Mater.* **161** (2009) 955
45. D. Kavitha, C. Namasivayam, *Bioresource Technol.* **98** (2007) 14
46. V. O. Arief, K. Trilestari, J. Sunarso, N. Indraswati, S. Ismadji, *Clean-Soil Air Water* **36** (2008) 937
47. J. A. Riddick, W. B. Bunger, T. K. Sakano, *Techniques of Chemistry, Vol. II, Organic Solvents,* 4th ed., Wiley, New York, 1985, p. 420
48. D. Maksin, A. Nastasović, A. Milutinović-Nikolić, Lj. Surucić, Z. Sandić, R. Hercigonja, A. Onjia, *J. Hazard. Mater.* **209**–**210** (2012) 99
49. S. A. Boyd, *Soil Sci.* **134** (1982) 337
50. S. Dutta, J. K. Basu, R. N. Ghar, *Sep. Purif. Technol.* **21** (2001) 227
51. F. Ahmada, W. M. A. W. Daud, M. A. Ahmad, R. Radzi, *Chem. Eng. J.* **178** (2011) 461
52. J. Huang, C. Yan, K. Huang, *J. Colloid Interface Sci.* **332** (2009) 60
53. S. J. Allen, B. Koumanova, Z. Kircheva, S. Nenkova, *Ind. Eng. Chem. Res.* **44** (2005) 2281.