

Comparative study on the adsorption kinetics and equilibrium of common water contaminants onto bentonite

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ABSTRACT

The adsorption of phenol (Ph), bisphenol A (BPA), 2,4-dichlorophenoxyacetic acid (2,4-D) and ibuprofen (IBU) from aqueous solutions on two raw bentonites was investigated. The adsorption was strongly pH-dependent—the removal of all the adsorbates decreased significantly with an increase in the initial pH of the solution. The kinetics was fitted with the pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models and the adsorption kinetics was better represented by the pseudo-second-order equation. The adsorption rate increased in the order: Ph < 2,4-D < BPA < IBU on both the adsorbents. The equilibrium adsorption data were modeled with Langmuir, Freundlich, and Langmuir-Freundlich equations and results showed that it was better described by the Langmuir-Freundlich equation. Adsorption of the selected contaminants on both the adsorbents increased in the order Ph < 2,4-D < BPA < IBU, which correlates well with the respective decrease in solubility of the adsorbates. Adsorption of the Ph, BPA, 2,4-D, and IBU on the bentonites is more or less comparable with other low-cost sorbents.

Keywords: Bentonite; Adsorption; Phenol; Bisphenol A; 2,4-D; Ibuprofen

1. Introduction

The global increase in agricultural and industrial activities has led to the production of environmental pollution. This is a serious environmental problem because many organic contaminants are toxic and excessive use of them creates negative impacts on the environment and living organisms. Therefore, more efficient water purification technologies are necessary. Among various methods commonly used for removal of organic contaminants from water, including adsorption, biodegradation, photodegradation, and oxidation, adsorption is a widely used effective technology, due to the relatively low cost, high efficiency, advantages of easy operation as well as no residual risk of highly toxic by-products [1].

Undoubtedly, the most popular adsorbents are activated carbons, mainly due to their unique physico-chemical properties, including high porosity, high surface reactivity, superior mechanical strength, and in consequence, strong adsorption capacity. However, the high cost of their use (the relatively high price of activated carbons and the need for regeneration) has prompted the search for alternative adsorbents [2]. In recent years, a number of low-cost adsorbents have been used for the removal of organic compounds from water what was the subject of discussion in number of review papers [1–5]. According to the classification proposed by De Gisi et al. [3], they can be assigned into five main groups: (1) household and agricultural wastes, (2) industrial by-products, (3) sea materials, (4) sludge as well as (5) soil and ore materials.

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Among such adsorbents, natural clays, including montmorillonite and bentonite, have gained significant interest due to high availability, low price, and relatively high specific surface area. In addition, these materials can be easily modified, which generally improves their adsorption capacity. The adsorptive removal of a number of organic and inorganic pollutants by clay-based materials has been described [6–9]. One of the promising clay-based adsorbents seems to be bentonite. In most of the works, it was used to remove only one impurity or several compounds belonging to the same group of pollutants. In addition, the Authors used various bentonites with different physico-chemical properties. All this makes it difficult to assess the suitability of bentonite as a universal adsorbent. Therefore, the aim of this work is the comparative study for adsorption of common water contaminants from aqueous solutions on two various bentonites.

The adsorption of a number of pollutants was evaluated, namely, phenol (Ph), bisphenol A (BPA), 2,4-dichlorophenoxyacetic acid (2,4-D), and ibuprofen (IBU). These compounds belong to the most important groups of organic contaminants found in the aquatic environment: Phs, herbicides, and pharmaceuticals.

Adsorption of these compounds on various adsorbents has been the subject of many works [10–39]. Numerous papers have described adsorption of Ph on raw and modified bentonites [10–21]. Adsorption capacity varied in a very wide range from 0.842 mg/g on raw bentonite [11] to 175.8 mg/g onto cationic surfactant (hexadecyltrimethylammonium bromide, HTAB) modified organobentonite [17]. Ortiz-Martínez et al. [23] described the adsorption of BPA from aqueous solutions on transition metal modified inorganic-bentonite composites. Li et al. [24] studied the adsorption of BPA onto raw bentonite and bentonite modified with HTAB. The adsorption affinity for BPA was 3.413 mg/g of raw bentonite and 10.449 mg/g of HTAB-bentonite, respectively. Adsorptive removal of herbicide 2,4-D was investigated using bentonites prepared by co-adsorption

of cetyltrimethylammonium (CTMA) ions onto bentonites intercalated by poly(hydroxo aluminum) or poly(hydroxo iron) cations [26], N-cetylpyridinium modified bentonite [27] and bentonite treated with ammonium salts [28]. Jacobo-Azuara et al. [21] described the adsorption of 2,4-D and Ph from aqueous solutions onto raw and HTAB-modified bentonite. After surfactant modification, the surface area of the bentonite was reduced from 50 to 2 m²/g. 2,4-D was adsorbed on organobentonite ($q_m = 47.2$ mg/g), but not on bentonite. The adsorption capacity of Ph on raw and modified bentonite was 13.6 and 191 mg/g, respectively. Salihi and Mahramanlioglu [29] reported the adsorption of IBU and other drugs onto raw bentonite ($S_{\text{BET}} = 23$ m²/g). The adsorption capacity values found for the adsorption of IBU at 18°C, 25°C, and 37°C were 53.76, 16.41, and 7.69 mg/g, respectively. Recently, Ghemit et al. [30] described adsorption of IBU from aqueous solution on organobentonites modified with CTMA bromide.

The present study compared the adsorption kinetics and adsorption capacity of four compounds –Ph, BPA, 2,4-D, and IBU from aqueous solution onto two raw bentonites.

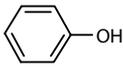
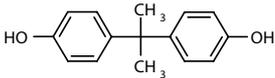
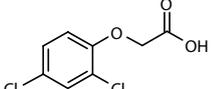
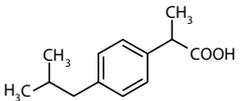
2. Experimental

2.1. Materials and methods

In the experiments the following adsorbates were used: >99% Ph, >99% BPA, 99% 2,4-D, and >99% IBU. The chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA). The molecular structures and physicochemical properties of the selected compounds are given in Table 1. The HPLC-grade acetonitrile and reagent grade acetic acid were obtained from Avantor Performance Materials (Gliwice, Poland).

Two bentonites [Wyoming (B-WY) and Clair T (B-CT)] were chosen as adsorbents. The materials used in the experiments were obtained from Source Clay Repository of the

Table 1
Physicochemical properties of Ph, BPA, 2,4-D, and IBU

Compound	Chemical structure	CAS number	Molecular weight	Solubility in water at 20°C (g/L)	logK _{ow}	pK _a
Ph		108-95-2	94.11	83	1.64	10.0
BPA		80-05-7	228.29	0.2	3.32	9.6
2,4-D		94-75-7	220.04	0.89	2.81	3.0
IBU		15687-27-1	206.29	0.021	3.50	4.9

Clay Mineral Society, and EURO-WIN for B-WY and B-CT, respectively.

Prior to use, the materials were dried in an oven at 110°C to a constant mass and stored in a desiccator until use in adsorption experiments without any further treatment.

The materials were characterized by means of nitrogen adsorption–desorption isotherms at 77.4 K (Micromeritics ASAP 2010, Norcross, USA) as well as water and benzene vapor adsorption isotherms at 298 K using dynamic vapor sorption apparatus of the type DVS Advantage (Surface Measurement Systems Ltd., London, UK).

2.2. Adsorption experiments

The batch adsorption method was used for the removal of Ph, BPA, 2,4-D, and IBU from aqueous solutions. The adsorption experiments were carried out at room temperature and the native initial pH values of adsorbate solutions. A series of 0.01 L solutions containing different initial concentrations of the adsorbates (from 10 to 100 $\mu\text{mol/L}$) were prepared in 0.05 L Erlenmeyer flasks, then a fixed amount of the bentonites (0.1 g) were added into the solutions. The samples were shaken under constant conditions [31], then after the completion of pre-set time intervals (adsorption kinetics) or after reaching equilibrium (adsorption equilibrium), the solutions were centrifuged for 5 min at 2,500 rpm to collect the supernatant. The amount of adsorbate adsorbed at the time t , q_t ($\mu\text{mol/g}$), as well as the adsorption capacity q_e ($\mu\text{mol/g}$) were calculated by the following Eq. (1) and (2):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 is the initial adsorbate concentration ($\mu\text{mol/L}$), C_t is the concentration after the time t ($\mu\text{mol/L}$), C_e is the final (equilibrium) adsorbate concentration in the liquid phase, V is the volume of the solution (L), and m is the mass of the adsorbent (g).

To investigate the effect of pH on the adsorption, experiments were conducted at different pH values from 2 to 11 for initial adsorbates concentrations of 50 $\mu\text{mol/L}$. The initial solution pH was controlled using 0.1 mol/L HCl or 0.1 mol/L NaOH.

All the experiments were performed at room temperature in duplicate and the average values were used for further calculations. The experimental error is around 5% (mean value).

The concentrations of Ph, BPA, 2,4-D, and IBU in the samples were determined by high-performance liquid chromatography (HPLC; Shimadzu LC-20 series liquid chromatograph, Kyoto, Japan). Separations were achieved on the analytical Phenomenex Luna C_{18} column (4.6×150 mm, 3 μm , Torrance, CA, USA) at a mobile phase flow rate of 0.25 mL/min under isocratic conditions. The mobile phase consisted of acetonitrile and water adjusted to pH 3.0 with CH_3COOH (50/50, v/v). The detection wavelengths were

269, 274, 278, and 220 nm for the Ph, BPA, 2,4-D, and IBU, respectively.

3. Results and discussion

3.1. Adsorbents characterization

The adsorption-desorption isotherms of N_2 on the bentonites are presented in Fig. 1a, while the adsorption isotherms of benzene vapors are shown in Fig. 1b. The specific surface areas (S_{BET}), as well as the micropore (V_{mi}) and mesopore (V_{me}) volumes were calculated from both the adsorption isotherms and results are listed in Table 2. The (S_{BET}) was calculated by the BET method, while the V_{mi} and V_{me} volumes were calculated using the t -plot method.

In the case of B-CT bentonite, one can observe about 8 times greater values of S_{BET} or V_{mi} in comparison with these parameters for B-WY bentonite. This observation takes place for N_2 as adsorbate as well as for benzene.

The water vapor adsorption isotherms of the bentonites are presented in Fig. 2. The shape of the isotherms indicates

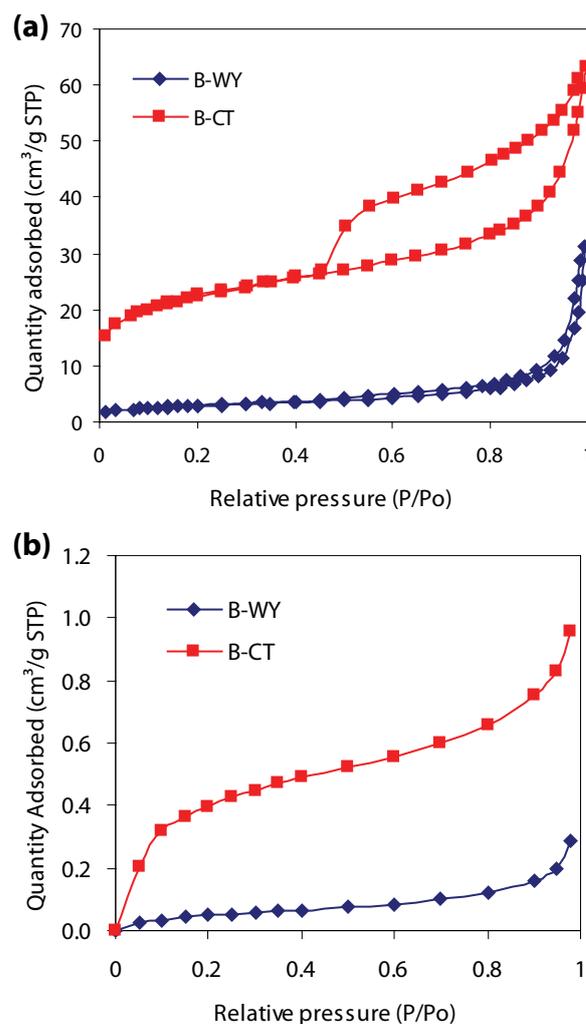


Fig. 1. Adsorption isotherms for bentonites using (a) nitrogen and (b) benzene.

Table 2
Physical properties of the bentonites

Adsorbent	Nitrogen isotherm			Benzene isotherm		
	S_{BET} (m ² /g)	V_{mi} (cm ³ /g)	V_{me} (cm ³ /g)	S_{BET} (m ² /g)	V_{mi} (cm ³ /g)	V_{me} (cm ³ /g)
B-WY	10.2	0.0041	0.0443	12.0	0.0038	0.0179
B-CT	79.3	0.0332	0.0645	89.1	0.0325	0.0738

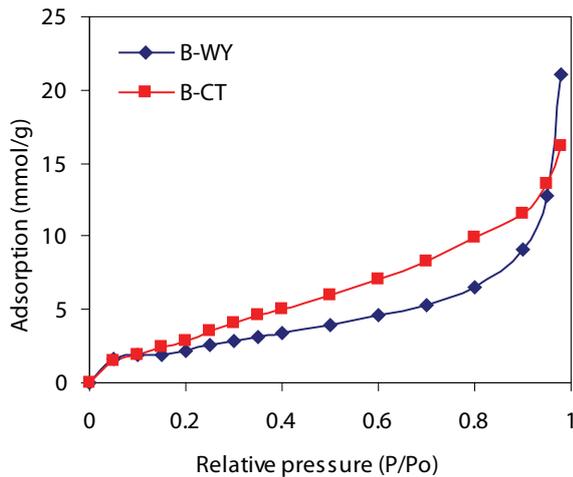


Fig. 2. Isotherms of water adsorption on the B-WY and B-CT bentonites.

comparable and a relatively good wettability of the tested adsorbents. According to the IUPAC classification, the isotherms of both the adsorbents are of Type II.

3.2. Adsorption kinetics

The kinetic studies were conducted for an initial adsorbates concentrations of 50 $\mu\text{mol/L}$ and the mass of the adsorbent 0.1 g (10 g/L). Fig. 3 shows the effect of contact time on the adsorption of the Ph, BPA, 2,4-D, and IBU from aqueous solutions onto the bentonites as a function of q_t . The presented results show that while the adsorption of the adsorbates was quite rapid initially, the rate of adsorption became slower with the time and reached a constant value (equilibrium) after ~60–90 min.

To investigate the adsorption kinetics of the selected compounds, three reaction-based kinetic equations, namely, pseudo-first-order, pseudo-second-order, and Elovich models were analyzed [32].

The pseudo-first-order equation, in the linear form, is expressed by the Eq. (3):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where k_1 is the pseudo-first-order adsorption rate constant (min^{-1}).

The linearized form of the pseudo-second-order model is as follows:

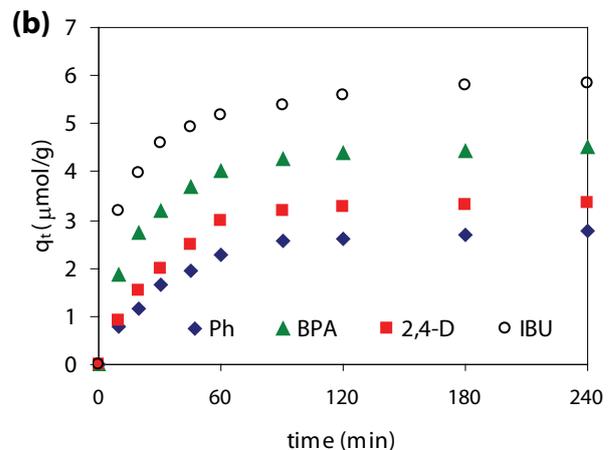
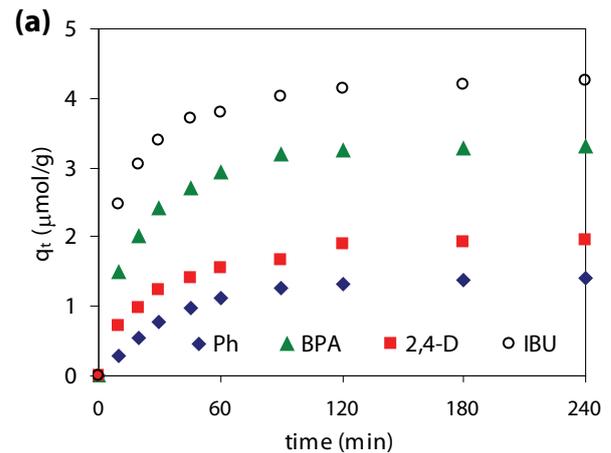


Fig. 3. Adsorption kinetics of Ph, BPA, 2,4-D, and IBU on (a) B-WY and (b) B-CT bentonites.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 is the pseudo-second-order rate constant ($\text{g}/\mu\text{mol min}$).

The linear form of Elovich Eq. (5) is as follows:

$$q_e = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

where β is the desorption constant ($\text{g}/\mu\text{mol}$) and α is the initial adsorption rate ($\mu\text{mol/g min}$).

The validity of the adsorption kinetic model was based on the regression coefficients (R^2). The calculated parameters for all of the kinetic models are listed in Table 3.

The correlation coefficients for the pseudo-second-order kinetic model are close to the unit in all cases. This indicates that the adsorption system belongs to the second-order kinetic model. The best fit of the pseudo-second-order model shows that the rate-limiting step is chemisorption involving forces caused by sharing or exchange of electrons between adsorbent and adsorbate. All of the adsorbates were adsorbed faster on the B-WY than on the B-CT bentonite. The adsorption rate increased in the order: Ph < 2,4-D < BPA < IBU.

In order to investigate the mechanism of the adsorption the Weber and Morris intraparticle diffusion model was used:

$$q_t = k_i t^{0.5} + C_i \quad (6)$$

where k_i is the intra-particle diffusion rate constant ($\text{mg/g min}^{-0.5}$) and C_i is the thickness of the boundary layer.

The Weber-Morris intra-particle diffusion model plots (q_t vs. $t^{0.5}$) are presented in Fig. 4. When the intercept C_i equals zero (the straight line passes through the origin), then the intra-particle diffusion is the only controlling step. The plots of $q_t = f(t^{0.5})$ can form only one straight line or can form two or more straight lines. If only one plot is obtained and

the intercept C_i equals zero then the adsorption is controlled only by intra-particle diffusion, but if has two or more plots and the straight line does not pass through the origin that many processes have occurred. As shown in Fig. 4, the plots have two-stage. The multi-linearity indicates that several steps are involved. The first stages are the boundary layer diffusion and the second stage is the intraparticle diffusion process. Moreover, none of the lines passed through the origin. This indicates that the adsorption processes occur in two kinetic steps, and the intra-particle diffusion is not the rate-determining step.

3.3. Adsorption isotherms

The adsorption isotherms of Ph, BPA, 2,4-D, and IBU from aqueous solutions are presented in Fig. 5. The obtained adsorption data were determined and modeled with the Freundlich, Langmuir, and Langmuir-Freundlich isotherm equations [33,34]. The Eqs. (6)–(8) of the isotherms can be represented as follows:

Table 3
Kinetic model parameters for adsorption of Ph, BPA, 2,4-D, and IBU on the B-WY and B-CT bentonites

Kinetic model	Ph	BPA	2,4-D	IBU
		B-WY		
Pseudo-first-order model				
k_1, min^{-1}	0.0215	0.0278	0.0235	0.0289
R^2	0.968	0.961	0.971	0.932
Pseudo-second-order model				
$k_2, \text{g}/\mu\text{mol min}$	0.0182	0.0225	0.0210	0.0255
R^2	0.996	0.998	0.999	0.999
Elovich model				
$\alpha, \mu\text{mol/g}\cdot\text{min}$	0.747	1.529	1.009	3.181
$\beta, \text{g}/\mu\text{mol}$	2.734	2.424	1.682	1.803
R^2	0.959	0.952	0.927	0.943
	B-CT			
Pseudo-first order model				
k_1, min^{-1}	0.0202	0.0246	0.0231	0.0266
R^2	0.929	0.946	0.963	0.970
Pseudo-second-order model				
$k_2, \text{g}/\mu\text{mol}\cdot\text{min}$	0.0111	0.0153	0.0120	0.0162
R^2	0.997	0.999	0.998	0.999
Elovich model				
$\alpha, \mu\text{mol/g}\cdot\text{min}$	0.323	1.165	0.745	2.466
$\beta, \text{g}/\mu\text{mol}$	1.222	1.194	1.489	1.207
R^2	0.921	0.925	0.948	0.949

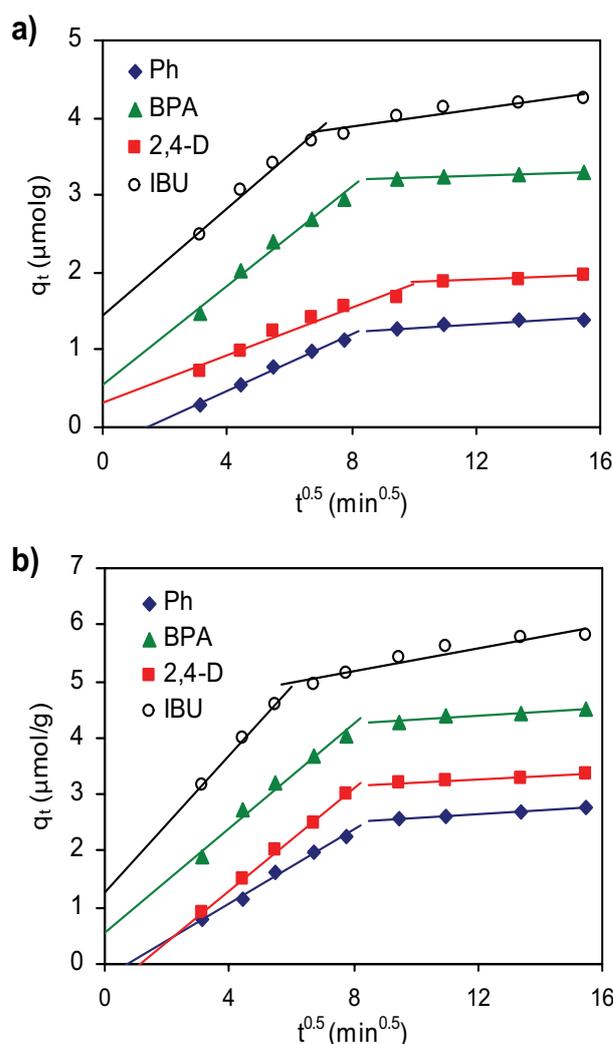


Fig. 4. Intra-particle diffusion model plots for the adsorption of Ph, BPA, 2,4-D, and IBU on (a) B-WY and (b) B-CT bentonites.

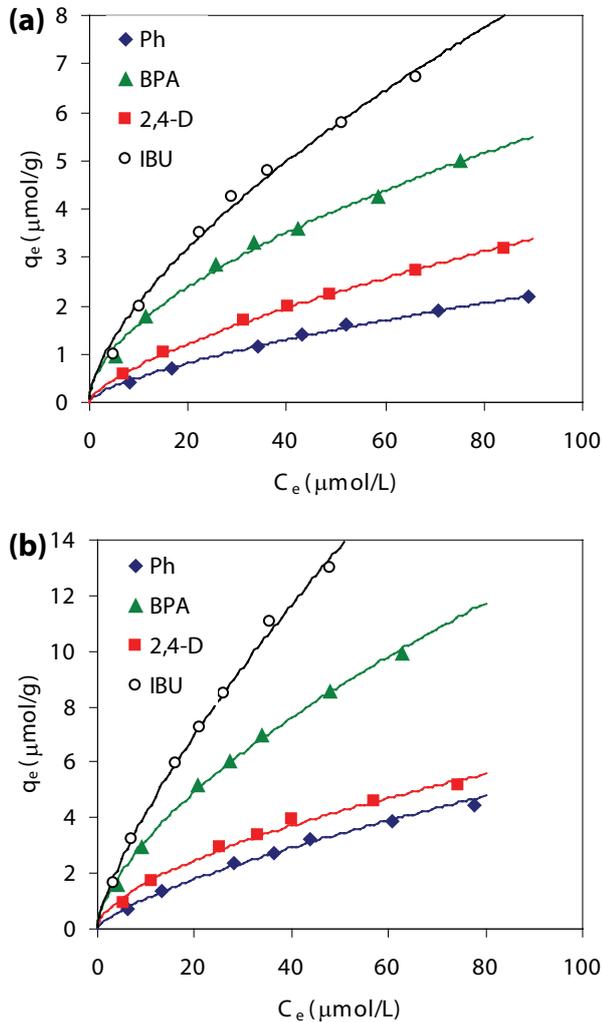


Fig. 5. Adsorption isotherms of Ph, BPA, 2,4-D, and IBU from aqueous solution on (a) B-WY and (b) B-CT bentonites.

Langmuir model

$$q_e = \frac{q_{mL} K_L C_e}{1 + K_L C_e} \quad (7)$$

Freundlich model

$$q_e = K_F C_e^{1/n} \quad (8)$$

Langmuir-Freundlich model

$$q_e = \frac{q_{mLF} (K_{LF} C_e)^m}{1 + (K_{LF} C_e)^m} \quad (9)$$

where q_{mL} ($\mu\text{mol/g}$) is the Langmuir maximum adsorption capacity, K_L ($\text{L}/\mu\text{mol}$) is the Langmuir constant, K_F [$(\mu\text{mol/g}) (\text{L}/\mu\text{mol})^{1/n}$], and n are the Freundlich equation constants, q_{mLF} ($\mu\text{mol/g}$) and K_{LF} ($\text{L}/\mu\text{mol}$) are the Langmuir-Freundlich

constants representing the monolayer adsorption capacity and the energy of adsorption, respectively, m is the L-F empirical constant.

All of the model parameters were evaluated by non-linear regression analysis using the OriginPro 7.5 software. The estimated constants of the isotherm equations and related correlation coefficients are listed in Table 4.

The correlation coefficients of adsorption are quite high for all the models, however, the best fitting results were obtained with the Langmuir-Freundlich isotherm model ($R^2 \geq 0.997$). The Langmuir isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites and assumes uniform adsorption on the surface and no transmigration in the plane of the surface. The Freundlich isotherm is valid for the description of the non-ideal and reversible adsorption and can be applied to multilayer adsorption, on the basis of an assumption concerning the energetic surface heterogeneity. The Langmuir-Freundlich equation is a versatile isotherm expression that can simulate both Langmuir and Freundlich; at high adsorbate concentration, it becomes

Table 4
Isotherm parameters of Ph, BPA, 2,4-D, and IBU adsorption on the B-WY and B-CT bentonites

Isotherm equation	Ph	BPA	2,4-D	IBU
	B-WY			
Langmuir				
q_{mL} $\mu\text{mol/g}$	3.965	7.013	5.397	12.03
K_L $\text{L}/\mu\text{mol}$	0.0013	0.0028	0.0015	0.0019
R^2	0.982	0.980	0.973	0.990
Freundlich				
K_F ($\mu\text{mol/g}$) ($\text{L}/\mu\text{mol}$) $^{1/n}$	0.111	0.412	0.157	0.471
n	1.508	1.802	1.466	1.565
R^2	0.996	0.993	0.998	0.992
Langmuir-Freundlich				
q_{mLF} $\mu\text{mol/g}$	6.326	12.95	11.50	15.07
K_{LF} $\text{L}/\mu\text{mol}$	0.0050	0.016	0.0080	0.0050
m	0.854	0.957	0.868	0.702
R^2	0.999	0.997	0.998	0.997
B-CT				
Langmuir				
q_{mL} $\mu\text{mol/g}$	7.922	15.90	8.117	28.02
K_L $\text{L}/\mu\text{mol}$	0.016	0.024	0.023	0.016
R^2	0.982	0.981	0.979	0.971
Freundlich				
K_F ($\mu\text{mol/g}$) ($\text{L}/\mu\text{mol}$) $^{1/n}$	0.212	0.698	0.429	0.757
n	1.406	1.595	1.709	1.349
R^2	0.995	0.996	0.988	0.996
Langmuir-Freundlich				
q_{mLF} $\mu\text{mol/g}$	9.326	32.01	16.82	45.43
K_{LF} $\text{L}/\mu\text{mol}$	0.017	0.0080	0.0050	0.0070
m	0.921	0.801	0.702	0.902
R^2	0.998	0.998	0.997	0.999

the Langmuir isotherm while at low concentration this model becomes the Freundlich isotherm.

The adsorption efficiency was measured using separation factor (R_L):

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

where K_L is Langmuir constant ($L/\mu\text{mol}$) and C_0 is the initial concentration ($\mu\text{mol/L}$).

The value of R_L indicates the nature of the adsorption process: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The plots of $R_L = f(C_0)$ are presented in Fig. 6. The calculated R_L values varies from 0.246 to 0.885 ($0 < R_L < 1$) indicated the favorable adsorption of all of the adsorbates on both bentonites. This is also confirmed by the Freundlich n parameters >1 (Table 5).

The values of the Langmuir-Freundlich adsorption capacity ($q_{m,LF}$) were 6.326, 12.95, 11.50, and 15.07 $\mu\text{mol/g}$ for adsorption of the Ph, BPA, 2,4-D, and IBU on the B-WY bentonite and 9.326, 32.01, 16.82, and 45.43 $\mu\text{mol/g}$ for adsorption of the Ph, BPA, 2,4-D, and IBU on the B-CT

bentonite, respectively. The Freundlich (K_F), as well as the Langmuir ($q_{m,L}$) constants increase in the same order: Ph $<$ 2,4-D $<$ BPA $<$ IBU. This suggests that the adsorption is correlated with a respective decrease in the solubility of the adsorbates (Table 1). All of the compounds were preferably adsorbed on the B-CT bentonite ($S_{\text{BET}} = 79.28 \text{ m}^2/\text{g}$) than on the B-WY ($S_{\text{BET}} = 10.17 \text{ m}^2/\text{g}$). Nevertheless, the adsorption does not depend only on the porous structure (specific surface area) of the materials used. The S_{BET} of the B-CT is about 8 times higher than the B-WY bentonite. The adsorption capacity of B-CT bentonite, in comparison to B-WY, is only 2–3 times higher. This suggests that the adsorption also affects the chemical properties of the adsorbent surface. Table 5 comparing the results for the adsorbents used in this study with the results of others, it can be concluded that the bentonites have adsorbed 2,4-D as effectively as the bituminous shale [35] or better than the rubber granules [36] or wood charcoal [36]. Adsorption of other test compounds (Ph, BPA, and IBU) on bentonite is also more or less comparable with other low-cost adsorbents.

3.4. Effect of solution pH

The solution pH is an important parameter in the adsorption process from aqueous phase because it determines the charge of both the adsorbent and adsorbate electrostatic interactions. Fig. 7 shows the results of the adsorption of all the four adsorbates on the bentonites according to the solution pH.

The adsorption of the Ph was almost constant at a pH range of 2–8 and decreased with the further increase in the pH (from pH 8 to 11). A very similar relationship was observed for BPA (which has a $\text{p}K_a$ value close to the Ph). Adsorption of IBU decreased continuously with increasing pH, while the removal of 2,4-D decreased significantly with the increase in initial pH of the solution from 2 to about 7, and was almost constant at the basic pH range. The adsorption behavior of the adsorbates on B-WY and B-CT

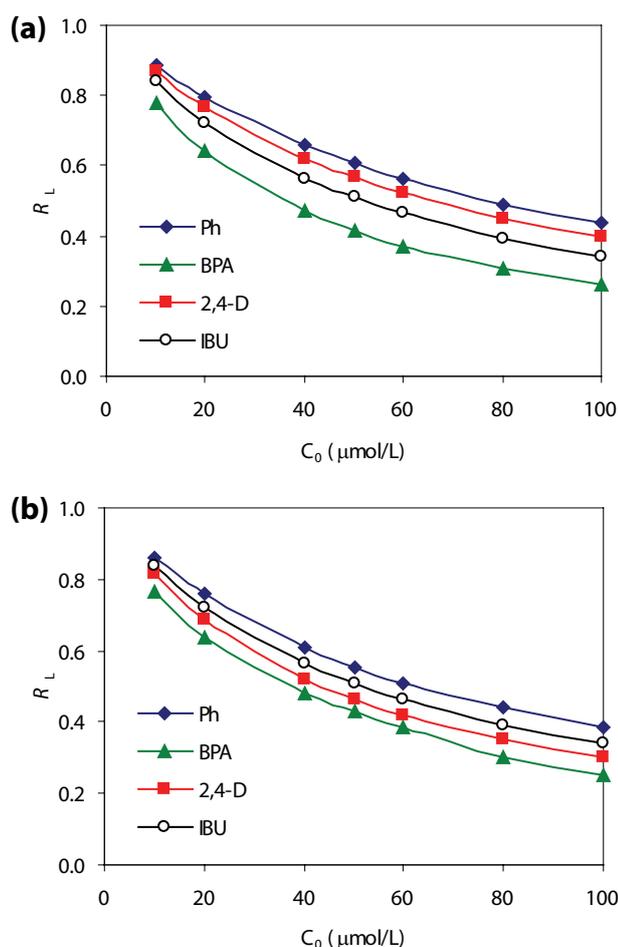


Fig. 6. Effect of the initial concentration of Ph, BPA, 2,4-D, and IBU on the separation factor (R_L) for (a) B-WY and (b) B-CT bentonites.

Table 5

The adsorption capacities of 2,4-D on various low-cost adsorbents

Adsorbent	Adsorption capacity, q_m (mg/g)	References
B-WY bentonite	1.19	This study
B-CT bentonite	1.79	This study
Rubber granules	0.40	[36]
Wood charcoal	0.70	[36]
Bituminous shale	1.19	[35]
Raw Na-bentonite	1.36	[27]
Fly ash	4.03	[37]
NCP-modified bentonite	37.6	[27]
Organobentonite	47.2	[21]
Organo-modified bentonite	50.4	[28]
Carbon black	68.6	[38]
Pristine biomass	88.0	[39]

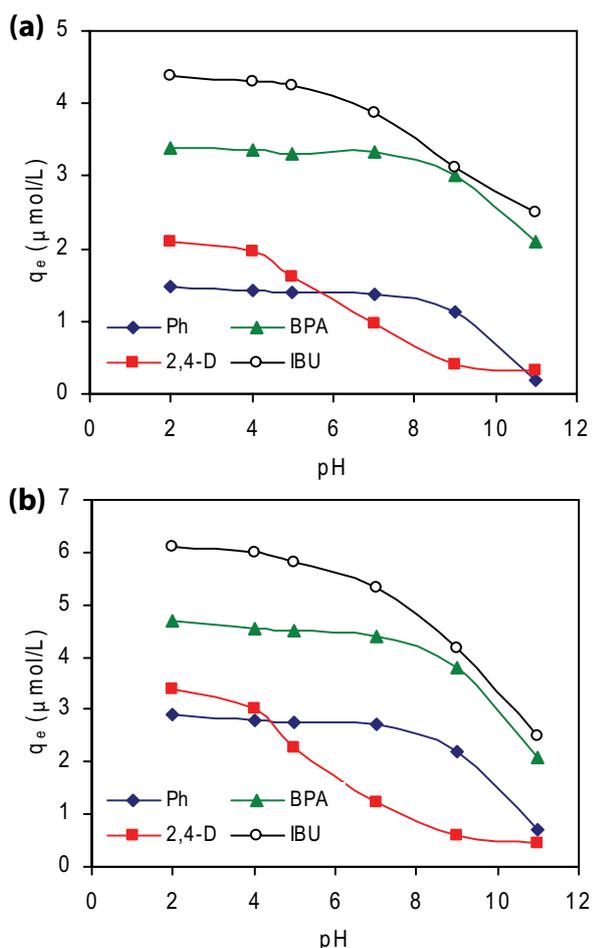


Fig. 7. Effect of initial solution pH on the adsorption of Ph, BPA, 2,4-D, and IBU on (a) B-WY and (b) B-CT bentonites.

bentonites was similar from pH 2 to pH 11 due to the fact that, the points of zero charge (pH_{PZC}) values of both of the materials are very similar. The pH_{PZC} of the bentonites were measured according to the procedure described elsewhere [38] and were found to be 7.25 for B-WY and 6.95 for B-CT. This adsorption behavior can be explained by the net signs of the surface charge of the adsorbent and the adsorbate species at the different pH values. The nature of the adsorbent surface groups changes with pH; at a $\text{pH} < \text{pH}_{\text{PZC}}$ the surface of the adsorbents had a net positive charge, while at a $\text{pH} > \text{pH}_{\text{PZC}}$ the surface had a net negative charge. The pK_a of the Ph, BPA, 2,4-D, and IBU is 10.0, 9.6, 3.0, and 4.9, respectively. It means that at a pH greater than the pK_a the adsorbates existed predominantly in anionic forms as negatively charged ions. The decrease in the adsorption with increasing solution pH, observed in Fig. 7, is attributed to the increased electrostatic repulsion between the negative charge on the adsorbate molecule and the surface of the bentonite that gradually becomes more negatively charged.

4. Conclusions

In this work, the potential of two raw bentonites as low-cost adsorbents for the removal of four compounds:

Ph, BPA, 2,4-D, and IBU from aqueous solution was investigated. The adsorption was studied kinetically using different kinetic models, and the experimental data were best fitted using the pseudo-second-order kinetic model with high correlation coefficients. The adsorption occurs in two kinetic steps and the intra-particle diffusion was not only the rate-determining step. The adsorption rate on both the adsorbents increased in the order: Ph < 2,4-D < BPA < IBU. The adsorption equilibrium data were fitted with the Langmuir, Freundlich, and Langmuir-Freundlich isotherm models. The results showed that the experimental data followed Langmuir-Freundlich isotherm. The adsorption of the adsorbates on both the bentonites increased in the order: Ph < 2,4-D < BPA < IBU.

In summary, it can be said that bentonites are one of the known low-cost adsorbents. These materials characterize not high adsorption efficiency but are comparable to other low-cost adsorbents. On the other hand, they reveal quite good kinetic properties, adsorption equilibrium establishes after about one hour for all types used by us organic water contaminants. Other papers present the results dealing commonly only one type of organic pollutants.

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