Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20930

80 (2017) 297–305
June

Adsorptive removal of hazardous organic water pollutants by humic acid–carbon hybrid materials: kinetics and isotherm study

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Received 7 December 2016; Accepted 14 May 2017

ABSTRACT

The adsorption characteristics of phenol, 2,4,6-trichlorophenol (2,4,6-TCP) and atrazine onto humic acid–carbon hybrid materials were investigated under different experimental conditions (ionic strength, pH, adsorbent dose, agitation time and initial concentration). It was found that ionic strength has insignificant effect on the adsorption process which peaked at acidic pH. The kinetic data were fitted to Elovich equation and intra-particle diffusion models. Kinetics results showed that the adsorption can be represented by two steps: a rapid step dominating the first 5 min followed by a slower uptake to the final steady-state value. On the other hand, equilibrium data were examined by Freundlich and Langmuir equations. Langmuir was the best model fit for the adsorption of 2,4,6-TCP onto the studied materials, phenol adsorption on carbon-coated insolubilized humic acid and atrazine adsorption onto insolubilized humic acid and carbon-coated insolubilized humic acid. The study proved that humic acid–carbon hybrid material has higher adsorption capacity than the pure materials.

Keywords: Phenol; 2,4,6-Trichlorophenol; Atrazine; Porous carbon; Insolubilized humic acid; Carbon-coated insolubilized humic acid; Insolubilized humic acid mounted on porous carbon

1. Introduction

Phenol and its derivatives appear in the environment either by the introduction or degradation of phenolic compounds. Phenol is both a synthetic and naturally produced chemical. Naturally, it is found in some foods, decomposing organic material and in human and animal wastes. Synthetically, it ranks in the top 50 in production volumes for chemicals produced in the United States [1]. Therefore, phenol is one of the most common organic water pollutants. It has high water solubility and toxicity (even at low concentrations) and forms harmful derivative (chlorophenols) during disinfection and oxidation processes [2]. 2,4,6-Trichlorophenol (2,4,6-TCP) is mainly used as a biocide and preservative. It has been detected in the fossil fuel combustion emissions, municipal waste incineration and chlorinated water that contain phenol or certain aromatic acids [3]. It considered a priority environmental pollutant worldwide because of its high toxicity, carcinogenic properties, adverse

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effects on the human nervous system and respiratory problems, structural stabilization and persistence in the environment [4,5]. Therefore, the removal of 2,4,6-TCP from the environment is urgent.

Since the development of atrazine in the late 1950s, it has been used worldwide for the control of annual weed crops [6]. Due to its application in large quantities in various soils, transportation to the water bodies and persistence in the environment, atrazine has repeatedly been detected in fresh water at levels above the permissible limits [7]. Most of the studies regarding the effect of atrazine on the human health did not show a direct relationship of atrazine use with cancer in humans, but in some cases it has been suggested that it increased the risk [6]. On the other hand, atrazine can act as an endocrine disrupting compound affecting the central nervous, endocrine and immune systems [8]. The practical management of the atrazine contaminated environment and achieving high removal efficiency rate remains a valid research challenge [9].

Photocatalytic degradation, membrane filtration, biodegradation, electrochemical oxidation and adsorption have been used for the removal of organic pollutants from water. Of these techniques, adsorption is the most versatile and widely used, since it removes many types of pollutants and the design and operation are convenient [5,10]. Activated carbon is the most common and widely applied adsorbent in water purification due to its high surface area, porous structure and special surface reactivity [11]. Yet, the costs of production and regeneration decrease its economic feasibility as an adsorbent. Therefore, the search for a low cost and abundant adsorbent has led many investigators to search more economic and efficient techniques to use natural materials as adsorbents [1,12–16].

Previously [17] we reported the preparation, characterization and the adsorption properties of humic acid–carbon hybrid materials. The results showed that humic acid–carbon hybrid materials are a promising low-cost adsorbent to be used in the removal of organic micropollutants from aqueous solutions. In the current study, we aim to complete the picture and gain more insight on the adsorption characteristics of the humic acid–carbon hybrid materials. In this context, we report for the first-time exhaustive study on (1) the effects of contact time, adsorbent dose, pH and adsorbates initial concentration on the adsorption of organic micropollutants by the humic acid–carbon hybrid materials; (2) the feasibility of using the humic acid–carbon hybrid materials to remove phenol, 2,4,6-TCP and atrazine from aqueous solution with regard to adsorption kinetics and isotherms and (3) a full comparison between the hybrid materials and the pure materials to prove the merit of the hybrid materials.

2. Materials and methods

2.1. Adsorbents

Four different adsorbent materials, namely porous carbon (PC), insolubilized humic acid (IH), carbon-coated insolubilized humic acid (CIH) and insolubilized humic acid mounted on porous carbon (IHPC), were used in this study. The preparation procedures and characterization of these adsorbents are described in [17]. In brief, these adsorbents are mesoporous, and the overall order of Brunauer-Emmett-Teller (BET) surface area is CIH>PC>IHPC>IH. Also, FTIR analysis proves that IH is the main source of chemical functionalities which were retained by CIH and IHPC, but with lower content.

2.2. Chemicals and aqueous solutions

Phenol GC grade (≥99%), 2,4,6-TCP standard 98% and atrazine PESTANAL® analytical standard were obtained from Sigma-Aldrich (Canada) and used as obtained without further purification. GC grade *n*-hexane was used for the extraction of atrazine. HPLC-grade acetonitrile and HPLC-grade water were used as a mobile phase in HPLC.

Stock solutions of phenol and 2,4,6-TCP were prepared in double-distilled water (DDW) while atrazine stock solution was prepared in GC-grade methanol. All working solutions were prepared by diluting the stock solutions with DDW just before use. All other reagents were of analytical grade and DDW was used to prepare all solutions.

2.3. Adsorption procedure

Batch adsorption experiments were conducted as described elsewhere [17]. In brief, a 50.0 mL of known initial concentration of an adsorbate (phenol, 2,4,6-TCP or atrazine) in a single-component adsorption was placed in 100 mL reagent bottles and accurately weighed amounts of adsorbent were added separately into the bottles. The solution was equilibrated in a mechanical shaker (200 rpm at room temperature), the samples were filtered then the residual concentration was measured. Two portions of the sample were processed by the same procedure, but only mean values are presented, and a procedural blank was analyzed. The uptake capacity of an adsorbent at equilibrium, q_e (mg/g), was calculated by mass balance as follows:

$$q_e = \left(C_i - C_e\right)\frac{V}{m} \tag{1}$$

where C_i and C_e are the initial and the equilibrium concentrations of the solute (mg/L) in solution, respectively. V is the volume of the solution (L) and m is the weight of the adsorbent (g).

2.3.1. Effect of ionic strength

The initial solution pH was kept at its original value (10, 8 and 5 for phenol, 2,4,6-TCP and atrazine, respectively) without change. The initial concentration of adsorbates and adsorbent dose was kept at 15 and 3 g/L, respectively, while different concentrations of NaCl were added to water solutions over the range of 0.005–0.100 M.

2.3.2. Effect of adsorbent dose

The obtained optimum ionic strength was selected for the solution and the initial solution pH was kept at its original value. Adsorbent doses of 0.50, 1.00, 2.00, 2.50, 3.00, 3.50, 4.00 and 4.50 g/L were used.

2.3.3. Effect of pH

The optimum ionic strength and dose were used and different initial solution pHs, namely, 2, 4, 5, 6, 7 and 8 were employed. The pH was adjusted by adding a few drops of 0.1 N NaOH or 0.1 N HCl. The values of pHs were determined using a digital pH meter.

2.3.4. Adsorption isotherms

150 mg of adsorbent was shook with 50 mL of adsorbates of different concentrations in glass bottles and the procedure was continued as mentioned. The adsorbates solution pH was adjusted at 2 and no NaCl was added.

2.3.5. Adsorption kinetics

15 mg/L initial concentration of adsorbates was put in contact with an adsorbent dose of 3 g/L and samples were withdrawn at different pre-assigned time intervals. These samples were filtered and analyzed as above.

2.4. Analytical procedures

Phenol was determined following the APHA standard method 5530 D [18] using a "Jasco V-530 UV/Vis" spectrophotometer. 2,4,6-TCP was determined using a "Varian pro star 210" high-performance liquid chromatography. Isocratic elution used a solvent mixture of 60% acetonitrile (0.1% formic acid) and 40% water (0.1% formic acid) at a flow rate of 1.5 mL/min. The wavelength of detection was 280 nm. Determination of atrazine was carried out following the EPA method 505.2 [19] using an "Agilent 6890N series" gas chromatograph. Detailed analytical procedures are described in [17].

3. Results and discussion

3.1. Effects of ionic strength, adsorbent dose and pH

3.1.1. Effect of ionic strength

Ionic strength has an important effect on the adsorption process when the main adsorption mechanism is electrostatic interaction [20]. The effect of ionic strength is often linked to distinguishing the electrostatic interaction types between adsorbents and adsorbates [21]. When the interactions are attractive, an increase in ionic strength will decrease the adsorption capacity. Contrariwise, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption [22]. Table 1 illustrates the effect of the increase of ionic strength on the removal of the different adsorbates by IH, PC, IHPC and CIH. It is obvious that ionic strength has no remarkable effect on the removal of the adsorbates. The absence of ionic strength effect in this experiment indicates that (1) the net charge was not changed during the adsorption process and (2) the electrostatic attraction is not the sole mechanism for the adsorption process. This happens in adsorption driven by water insolubility, London forces, hydrogen bonding, charge transfer complexing and/or covalent bond formation. There is no specific indication from the experiment which of these possibilities is applicable. Similar results have been reported for the adsorption of phenols and atrazine from aqueous solutions by other adsorbents [6,23].

3.1.2. Effect of adsorbent dose

The changes in removal percentages of adsorbates as a function of adsorbent dose are shown in Fig. 1. In general, the adsorbates removal increases with the increasing adsorbent

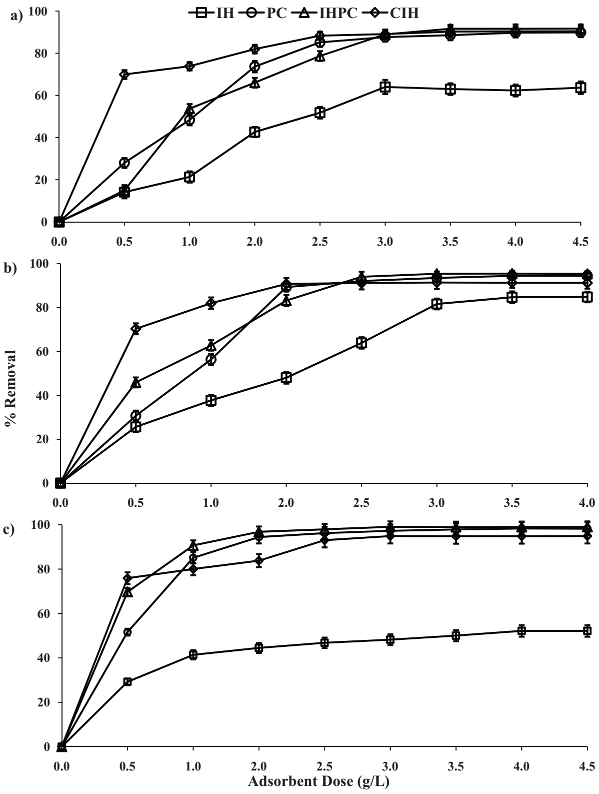

Fig. 1. Effect of adsorbent dose on the removal of (a) phenol, (b) 2,4,6-trichlorophenol and c) atrazine by different adsorbents.

Table 1
The effect of ionic strength on the percentage removal of adsorbates by different adsorbents

Ionic strength (M)	Phenol				2,4,6-Trichlorophenol				Atrazine			
	IH	PC	IHPC	CIH	IH	PC	IHPC	CIH	IH	PC	IHPC	CIH
<0.001	47.06	81.35	72.30	87.01	60.59	86.20	85.67	86.40	40.47	94.41	96.80	78.00
0.005	47.38	82.85	74.78	88.04	63.86	92.33	90.93	88.93	41.80	94.77	96.72	79.90
0.010	47.71	85.15	76.50	89.06	63.75	92.33	94.00	90.75	43.00	94.73	96.74	81.62
0.050	51.80	85.08	78.69	89.05	63.78	92.33	93.90	90.65	44.49	94.94	96.22	83.81
0.100	51.80	85.08	78.60	89.08	63.25	92.33	93.88	90.70	44.40	94.35	95.68	83.72

dose up to certain levels and then levels off. This observation is in agreement with the precedents [15,24,25].

It is readily understood that the increasing adsorbent dose results in (increasing the number of) available adsorption sites, and consequently, increasing the removal efficiency. For IH, the flatten in adsorption extent at high dose may be due to the formation of aggregates which decrease the total surface area and increase the diffusional path length [1]. For other adsorbents, the level off in adsorption extent at high adsorbent dose is due to approaching 100% removal.

Fig. 1(a) indicates that 64% phenol removal was achieved when IH dose was 3.00 g/L. While, PC, IHPC and CIH achieve about 89% removal of phenol using 4.00, 3.00 and 2.50 g/L, respectively. For TCP (Fig. 1(b)), 84% removal was achieved by 3.5 g/L IH. CIH with a dose of 2.00 g/L achieves 90% removal of TCP while 2.50 g/L of IHPC and PC achieves 94% and 92% TCP removal, respectively. In case of atrazine (Fig. 1(c)) only 52% removal was achieved using 4.00 g/L of IH. CIH, PC and IHPC behave similarly as in the case of TCP; CIH with a dose of 2.50 g/L achieves 93% removal of atrazine while 3.00 g/L of IHPC and PC achieves 99% and 97% TCP removal, respectively.

In general, Fig. 1 shows that the highest removal percentages were observed for atrazine followed by 2,4,6-TCP then phenol. This order agrees with the order of solubility hydrophobicity of adsorbates suggesting that the water solubility plays an important role in the adsorption process. In the same time, a higher optimum dose was observed for atrazine followed by phenol then 2,4,6-TCP. Also, the hybrid materials (IHPC and CIH) achieved higher removal percentages at lower optimum doses compared with the pure materials (IH and PC). This could be attributed to the features of the hybrid material which is a combination of high surface area acquired from PC and high binding ability due to the functional groups acquired from IH.

3.1.3. Effect of pH

Generally, two prevalent variables determine the effect of pH. First, pH variation facilitates or reduces the electrostatic interaction through changing the electric charges of adsorbent surfaces. Second, it affects the degree of adsorbate dissociation [26–28].

The surface of the four adsorbents contains a number of functional groups, the adsorbents containing IH has the larger number of these functional groups [17]. Lowering the pH enhances the hydrophobic character of the adsorbents, through neutralizing the negative charges at the adsorbents surface (e.g., –COOH functionality), which results in more favourable adsorbate interaction, possibly through hydrogen bonding and/or donor–acceptor interactions between the aromatic ring of adsorbates and the surface groups on the adsorbents.

On the other hand, phenol (pKa of 9.9 [29]) exists in its undissociated form at all these reported pHs. 2,4,6-TCP (pKa of 6.23 [30]) exists mostly in its undissociated form at pH 2 and 6, whereas at all other reported pH it exists in an anionic form. Atrazine (pKa of 1.7 [31]) is significantly protonated at pH 2, whereas at all other reported pH it is neutral.

Fig. 2 displays the effect of pH on the removal of the different adsorbates by the investigated adsorbents. In general, the optimum pH was 2 indicating a favourable role for surface protonation. The optimum pH for the removal of phenol by PC and 2,4,6-TCP by IHPC are exceptions (pH 8 and 6, respectively). Also, the 2,4,6-TCP removal capabilities of PC and the atrazine removal capabilities of PC and IHPC were only slightly affected by pH. This observation indicates that adsorption of the undissociated form of the adsorbates is more favourable than the anionic form. Consequently, the adsorption might be driven by hydrogen bonding, donor–acceptor interactions and/or water insolubility (poor aqueous solvation). Similar trends have been reported for the adsorption of adsorbates from aqueous solutions by other adsorbents [5,6,15,28,32–35].

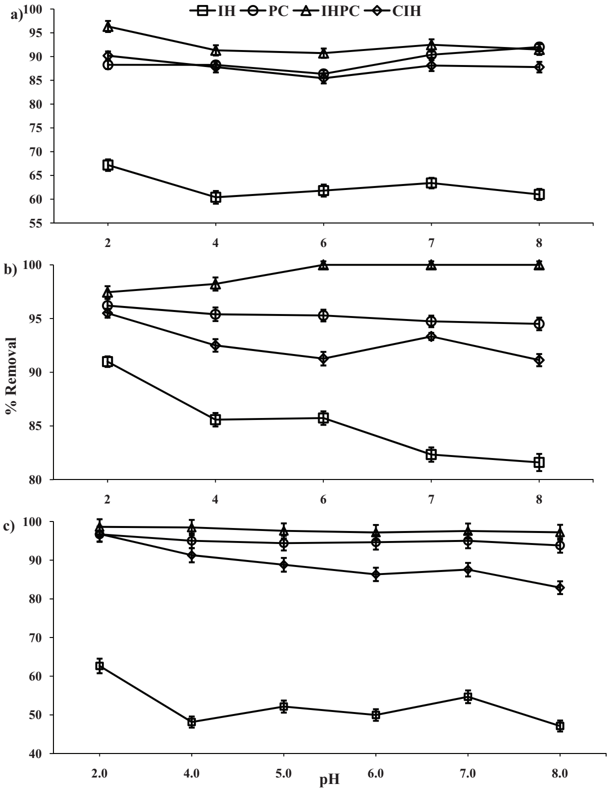

Fig. 2. Removal of (a) phenol, (b) 2,4,6-trichlorophenol and c) atrazine by different adsorbents as a function of pH.

3.2. Adsorption isotherm

The adsorption isotherms of different adsorbates onto all the investigated adsorbents are displayed in Fig. 3. The adsorption isotherms of phenol and 2,4,6-TCP (Figs. 3(a) and (b)) present an L-shape according to Giles [36] classification. On the other hand, atrazine adsorption isotherm (Fig. 3(c)) presents an L-shape in case of IH while other adsorbents present H-shape. The L-shape is common in the case of phenolic compounds [37–44] and atrazine [34] adsorption from water. It suggests the completion of monolayer on the adsorbent surface [15] and absence of strong competition between the adsorbate and the solvent to occupy the adsorption sites [39,42,44]. On the other hand, the H-shape results from very strong adsorption at very low concentrations giving rise to an apparent intercept on the ordinate [39]. It indicates the high affinity of the adsorbents towards atrazine with weaker adsorption emerging at higher coverage, and that there is no strong competition from the solvent for sorption sites [15,36,45].

3.2.1. Adsorption isotherm modelling

Optimizing the design of a practical adsorption system requires information about the strength of adsorbate binding and the capacity of the adsorbent to carry the adsorbate. These parameters will be derived from the model that best fits the case and provides this information. For this reason, the adsorption data was treated using; Freundlich and Langmuir. The Langmuir model [46] assumes effectively homogenous adsorption surface, where the Freundlich isotherm [47] is a suitable tool for data management for a highly heterogeneous surface. The Langmuir model provides two guiding parameters for comparison of adsorbents; K_L as an indicator of adsorption strength and the maximum adsorption capacity (Q_o) as an indicator of adsorption capacity.

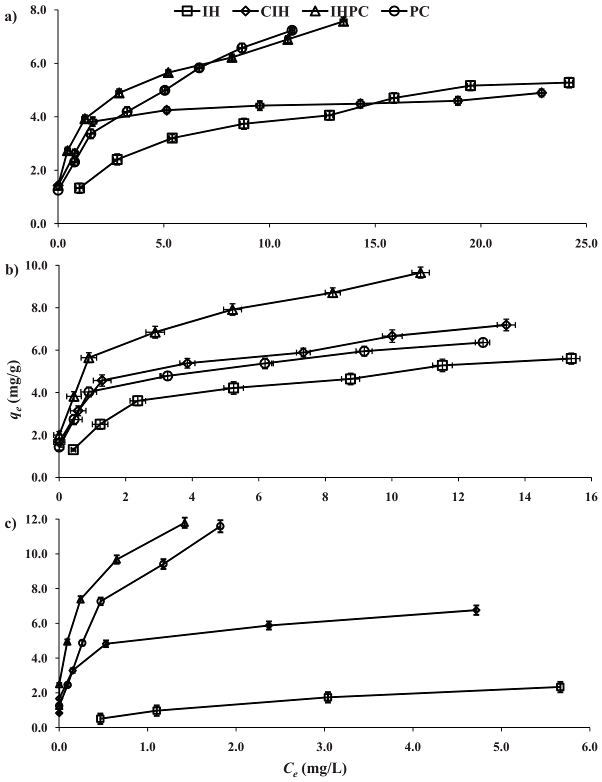

Fig. 3. Adsorption isotherm of (a) phenol, (b) 2,4,6-trichlorophenol and (c) atrazine on different adsorbents.

The parameters for each of these models were derived by plotting the linear forms (Table 2) of each model equation. The fitted parameter values are recorded in Table 3. Although both Freundlich and Langmuir models gave good fit to the experimental data for the studied systems, the best model describing the adsorption data will be judged by the R^2; the highest the R^2 value, the most suitable equation to describe the adsorption data.

Table 3 shows that the Freundlich isotherm is the best fitting phenol adsorption data on PC, IH and IHPC the experimental data. Fitting to Freundlich suggests that some heterogeneity in the surface or pores of these adsorbents may play a role in phenol adsorption.

On the other hand, the Langmuir model is the best fitting model for phenol adsorption onto CIH and 2,4,6-TCP adsorption onto the studied adsorbents. Suggesting that monolayer coverage of these adsorbates at the surface of the adsorbents is significant. The values of K_L and Q_o indicate that the hybridization between humic acid and carbon increases the adsorption strength and theoretical monolayer saturation capacity manifesting the advantage of the hybrid material over the pure material. Also, Table 3 indicates that Langmuir model is best in fitting the adsorption data for IH and CIH.

Table 2
Linear forms of the isotherm models adopted in this work and their parameters

Isotherm	Linear form
Freundlich	$\log q_e = \log K_f + \frac{1}{n}\log C_e$
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e$

q_e, The uptake capacity at equilibrium (mg/g); C_e, the equilibrium concentrations (mg/L) in solution; K_f, Freundlich constant (mg/g (mg/L)^n)); 1/n, constant (dimensionless); K_L, Langmuir isotherm constants (L/g); $\frac{a_L}{K_L}$ is the theoretical monolayer saturation capacity ((Q_o (mg/g)).

Table 3
Freundlich and Langmuir models driven parameters

Model	Parameter	Phenol				2,4,6-Trichlorophenol				Atrazine			
		IH	PC	IHPC	CIH	IH	PC	IHPC	CIH	IH	PC	IHPC	CIH
Freundlich	K_f	1.44	2.63	3.54	3.11	2.13	3.63	5.17	3.87	0.87	9.10	10.90	5.03
	N	2.35	2.40	3.51	6.74	2.62	4.43	3.83	4.23	1.94	1.95	3.20	4.99
	R^2	0.98	0.99	0.99	0.84	0.95	0.94	0.96	0.96	0.96	0.97	0.99	0.96
Langmuir	K_L	1.27	4.43	7.14	8.61	3.23	10.42	14.18	9.38	1.29	43.29	156.25	56.82
	Q_o	6.20	7.75	7.63	4.83	6.10	6.42	9.74	7.23	3.37	12.72	11.99	6.75
	R^2	0.98	0.94	0.98	0.99	0.99	0.99	0.99	0.99	0.99	0.95	0.98	0.99

Note: Q_o is the theoretical monolayer saturation capacity.

3.2.2. Adsorption kinetics and mechanistic implications

Fig. 4 illustrates the adsorption of different adsorbates onto the studied adsorbents as a function of time. It was observed that the humic acid–carbon hybrid materials (CIH and IHPC) have higher q_e than the starting materials (IH and PC). In case of 2,4,6-TCP, the q_e of IHPC was the highest. For atrazine, the q_e of CIH and IHPC is within error the same for both, but IHPC needs shorter time.

Also, for all the set of experiments, the adsorption can be represented by two steps: a rapid adsorption step dominating the first 5 min that is followed by a slower uptake to the final steady-state value. This behaviour might be due to the large concentration gradient, availability of surface sites and absence of the steric hindrance exerted by adsorbed molecules in the initial stage of the whole adsorption process. Also, the slow step corresponds to sites that may be located on the internal network of micropores of adsorbents that become accessible with time. A similar trend has been reported by several authors for adsorbates adsorption from aqueous media by other adsorbents [6,13,16,32,48]. In case of (1) phenol adsorption on PC and IHPC, (2) 2,4,6-TCP adsorption on PC and (3) atrazine adsorption on IH, PC and IHPC, changes of q after 5 min are so small as to render further attempts to extract kinetic parameters meaningless.

The data do not allow resolution of the faster step, but it was interesting to test Elovich's equation [49] and the Weber–Morris intra-particle diffusion model [50] to yield suggestions about the coverage of adsorption sites, the diffusion mechanism and to verify the interpretation of the data as biphasic. The parameters for Elovich and intra-particle diffusion models were derived by plotting the linear forms (given in Table 4) of each model equation (Figs. 4 and 5). The fitted parameter values are listed in Table 5.

On one hand, generally, R^2 values of Elovich model indicated that the model represents the adsorption kinetics satisfactorily. Moreover, in spite of the poor R^2 values in some cases, the calculated q_e values using the Elovich equation agreed quite well with the experimental q_e values (Table 5). Therefore, the hypothesis of the exponential covering of adsorption sites that implies multilayer adsorption is applicable.

On the other hand, the overall rate of adsorption can be described as follows: (1) surface diffusion, the adsorbate is transported from the bulk solution to the outer surface of

Table 4
Linear forms of the kinetic models adopted in this work and their parameters

Model	Linear form
Elovich	$q_t = \dfrac{1}{\beta \ln(\alpha\beta)} + \dfrac{1}{\beta}\ln t$
Intra-particle diffusion	$q_t = k_p\, t^{1/2} + C$

q_e, The uptake capacity at equilibrium (mg/g); q_t, the uptake capacity at time t (mg/g); k_1, the pseudo-first-order rate constant (g/mg min); k_2, the pseudo-second-order rate constant (g/mg min); α and β are Elovich constants; k_p, the intra-particle diffusion rate constant (mg/g hr$^{1/2}$); C is constant (mg/g).

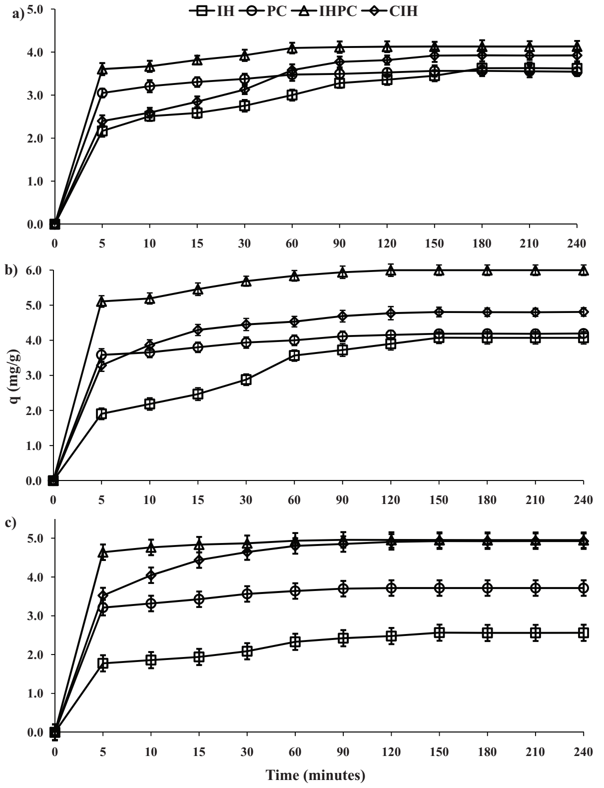

Fig. 4. Adsorption kinetics profiles for the uptake of (a) phenol, (b) 2,4,6-trichlorophenol and (c) atrazine by the different adsorbents.

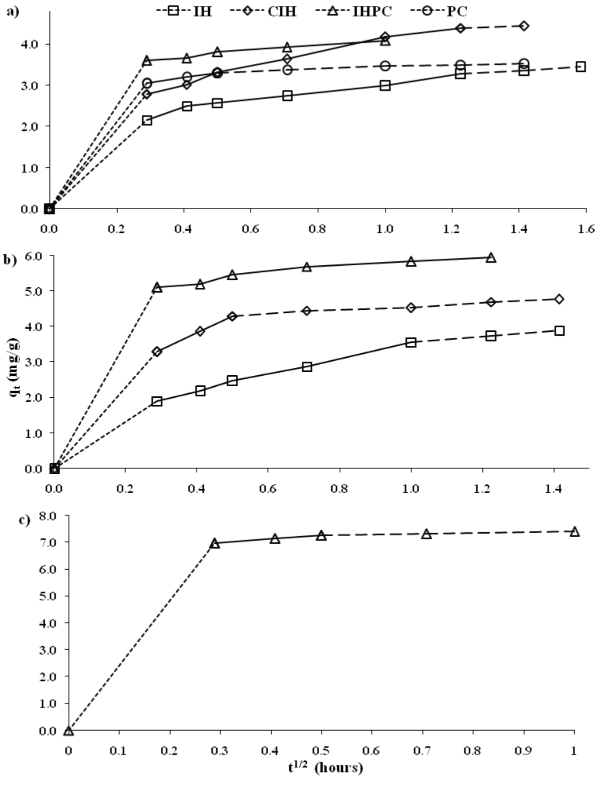

Fig. 5. Intra-particle diffusion kinetics of (a) phenol, (b) 2,4,6-trichlorophenol and (c) atrazine by different adsorbents.

Table 5
Kinetic models driven parameters

Model	Parameter	Phenol				2,4,6-Trichlorophenol				Atrazine			
		IH	PC	IHPC	CIH	IH	PC	IHPC	CIH	IH	PC	IHPC	CIH
Elovich	$q_{e,\exp}$	3.63	3.56	4.11	4.57	4.08	4.19	6.00	4.81	2.57	7.43	7.44	4.91
	$q_{e,\mathrm{cal}}$	3.49	3.59	4.16	4.62	4.05	4.20	6.05	4.96	2.52	3.54	7.50	5.13
	α	28.8	7.55E+07	1.96E+06	14.1	2.00	1.05E+07	9.85E+05	420.90	67.7	8.85E+06	2.55E+16	396.9
	β	2.7	7.0	4.9	1.8	1.50	5.50	3.30	2.40	4.2	2.9	5.9	2.3
	R^2	0.984	0.961	0.975	0.989	0.99	0.98	0.97	0.88	0.981	0.986	0.939	0.899
Intra-particle diffusion	k_{p1}	7.50	9.68	12.49	10.57	6.60	12.41	17.70	11.39	6.15	22.25	24.10	12.20
	k_{p2}	1.05	1.74	0.69	1.21	2.31	0.50	0.90	4.77	0.78	1.70	1.40	4.33
	C_2	1.99	2.36	3.42	2.70	1.26	3.50	4.92	1.91	1.55	5.95	6.56	2.27
	$(R_2)^2$	0.959	0.984	0.971	0.997	1.00	0.94	0.92	1.00	0.999	0.985	0.993	1.000
	k_{p3}	0.48	0.26	–	0.24	0.80	–	–	0.51	0.36	0.52	0.30	0.56
	C_3	2.69	4.08	–	3.20	2.76	–	–	4.06	1.97	6.76	7.10	4.20
	$(R_3)^2$	0.994	–	–	0.944	0.99	–	–	0.98	0.990	1.00	0.996	0.932

$q_{e,\exp}$ and $q_{e,\mathrm{cal}}$ are the experimental and calculated amount of adsorbates uptake capacity at equilibrium, respectively; k_1 and k_2 are the pseudo-first and second-order rate constants, respectively; α and β are Elovich constants; k_p is the intra-particle diffusion rate constant (mg/g hr$^{1/2}$) and C (mg/g) is constant.

adsorbent; (2) intra-particle diffusion, the adsorbate move into the interior of adsorbent particles and (3) adsorption on the interior sites of the adsorbent, this step may be very rapid so it is conventionally assumed that it does not affect the overall kinetics [51]. Therefore, the overall rate of adsorption process will be controlled by either surface diffusion or intra-particle diffusion.

The multisectorial character of Fig. 5 suggests that the adsorption occurs in two and in some cases three phases. The first sharper region represents film diffusion. The second region represents intra-particle diffusion. The slope of this region characterizes the adsorption rate where intra-particle diffusion is rate-limiting. The intercept on the other hand signifies the extent of the boundary layer effect; larger intercepts suggest a greater role as the rate-limiting step. The third region represents the final equilibrium state between numerous accessible adsorption sites and less accessible but more favourable adsorption sites. This trend is in agreement with precedents [4,13,14,33].

These observations could be consistent with three processes controlling the adsorption rate but only one is the rate-limiting step. This model implies the two-phase interpretation of the kinetics considered qualitatively above, (Fig. 5), with the adsorption rate initially fast and then slowing. In this model, k_{p1} is the higher early phase rate constant and k_{p2} is the resolvable slower step (Table 3). Unfortunately, with six fitting parameters and no more than eight data points, degrees of freedom are exhausted and the small k_{p3} is almost certainly buried in noise and has no physical significance.

4. Conclusions

The adsorption process for phenol, 2,4,6-TCP and atrazine onto humic acid–carbon hybrid materials has been investigated with respect to both equilibrium and kinetics. The influence of ionic strength, adsorbent dose, pH, contact time and initial adsorbate concentration on such process has been analyzed. Based on the results, it may be concluded that the adsorption process is more favoured at acidic pH with negligible effect of ionic strength suggesting that the neutral molecule and perhaps the conjugate acid are adsorbed. In most cases, the equilibrium data were best described by the Langmuir isotherm model indicating an approximate "phenomenological" monolayer coverage of adsorbates on adsorbents surface. Adsorption kinetics were initially rapid, but there is evidences for a slower second component, which may be associated with intra-particle diffusion.

The key result shows that (1) hybridization of humic acid and carbon favours adsorption, consequently, the hybrid materials have higher adsorption capacity than the pure materials and (2) insolubilized humic mounted on porous carbon is the most effective adsorbent of the novel hybrids. These characteristics recommend these new materials for application. Further investigation to exploit widely available natural humic extracts to achieve practical adsorbents of technical and economic interest is required.

Acknowledgments

The authors gratefully acknowledge the financial support of the Egyptian cultural affairs and missions sector through a scientific channel program between the National Research Centre, Egypt, and University of Calgary, Canada. Some assistance for experiments in Calgary came from the Natural Sciences and Engineering Research Council of Canada.

Conflict of interest

The authors declare no conflict of interest. The sponsors had no role in study design, data collection analysis or interpretation, writing of the manuscript or the decision to publish.

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