Removal of phenoxy herbicides from aqueous solutions using lignite as a low-cost adsorbent

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ABSTRACT

This work aims to evaluate the potential of raw lignite as a low-cost adsorbent material for the removal of phenoxy herbicides including phenoxyacetic acid (PAA), 4-chlorophenoxyacetic acid (4-CPA), 2,4-dichlorophenoxyacetic acid (2,4-D), and 4-chloro-2-methylphenoxyacetic acid (MCPA) from aqueous solutions. Batch adsorption experiments at different operating parameters such as pH and ionic strength were carried out, and the results revealed that adsorption of the herbicides was strongly pH- and ionic strength dependent. The adsorption kinetics was fitted with the pseudo-first-order and pseudo-second-order models, while adsorption equilibrium data were fitted using Langmuir, Freundlich, and Langmuir–Freundlich isotherm equations. The obtained data obeyed the pseudo-second-order kinetic and Freundlich isotherm type. Adsorption efficiency of the herbicides increased in the order PAA < 4-CPA < 2,4-D < MCPA and the monolayer adsorption capacities were 20.53, 27.10, 35.21, and 37.04 µmol/g, respectively. The results showed that the raw lignite may be used as an effective low-cost adsorbent without any treatment or any other modification for the removal of phenoxy herbicides from the aqueous solutions.

Keywords: Adsorption; 2,4-Dichlorophenoxyacetic acid; 4-Chloro-2-methylphenoxyacetic acid; Phenoxy herbicides; Low-cost adsorbent; Lignite

1. Introduction

Sorption is a cheap, universal, and easy-to-implement method of removing organic and inorganic substances from the aquatic environment. The most effective and most commonly used sorbent is activated carbon. However, the growing demand and the costs of producing activated carbons mean that extensive research is still being conducted on the use of other raw materials, in particular of natural origin, as effective and cheap sorbents. Among the whole range of raw materials, more and more attention is paid to the possibility of using lignite and mineral resources accompanying lignite deposits, both as precursors of activated carbons and as natural sorbents [1,2].

Worldwide, 85% of the lignite produced is used in power plants and combined heat and power plants located in the vicinity of the mines. The remaining 15% is coal for industry and households, including the raw material for production sorbents, soil-forming preparations, and soil supplements for fertilizing arable soils. Lignite can also be mixed with mineral fertilizers. Ash from lignite combustion can also be used as a fertilizer [3].

The use of lignite as sorbents (and catalysts) results from both their developed porous structure and the chemical structure of the surface [4]. The studies of the porous structure of lignite described in the works [5,6], carried out based on CO_2 sorption isotherms, indicate the microporous structure of these coals, and the specific surface area ranges

from 116 to 395 m^2/g depending on the location of the deposit (Australia, Indonesia, USA, India). The determined higher values of the specific surface area result from the smaller dimensions of the CO_2 molecule (3.3 Å) compared to the N_2 molecule (3.65 Å) and easier migration into the micropores. The main components of brown coals are high-molecular aromatic structures and oxygen-containing functional groups [7]. The model of brown coal with the total composition of $C_{270}H_{240}O_{90}N_3S_3M_{10}$ developed by Hütittinger and Michenfelder [8] shows the presence of functional groups such as carboxyl groups, phenolic hydroxyl groups, and groups with the structure of quinones and aromatic rings as well as long hydrocarbon chains and metal cations. It is the presence of oxygen functional groups that is responsible for the ion exchange capacity of brown coals and the possibility of their use as heavy metal sorbents [9]. An important advantage of brown coals resulting from their chemical composition and construction is the possibility of using these materials in the soil and water environment, both to restore humic substances in the topsoil and bind pollutants, as well as fill sorption barriers or as additives to natural sorption barriers and as sleeve fillings for isolating pollution foci. However, this application requires thorough research in the field of evaluation of sorption capacity to selected groups of pollutants, understanding the mechanisms and kinetics of binding individual groups of contaminants on the surface of these sorbents, which justifies research in this area.

The potential of lignite as an effective sorbent for various contaminants in pollution prevention has led to extensive studies of its adsorptive properties. As a consequence, there are more and more studies in the literature on the use of brown coal also as a sorbent for organic pollutants. It has been shown by Polat et al. [10] that sorption of phenol on brown coal is the result of π–π interactions between the aromatic ring of phenol and the surface of brown coal, as well as the formation of hydrogen bonds between oxygen groups and the hydroxyl group of phenol, it has also been shown that multilayer sorption occurs. The high usefulness of brown coal for the treatment of wastewater containing organic pollutants has been demonstrated [11] with a significant reduction in the value of the TOC index indicating the removal of organic matter. Lignite has been used as a sorbent for enzymes formed during the decomposition of wood [12]. Brown coal from deposits in Turkey has been successfully used as sorbents for a non-ionic emulsifier (polyoxyethylene sorbitan monooleate) [13]. The suitability of brown coal for the removal of cationic dyes from wastewater has been reported by Qi et al. [14]. The usefulness of lignite (including minerals accompanying brown coal seams) in combination with compost as a material filling sorption barriers for the removal of trichloroethylene from groundwater has been demonstrated by Grajales-Mesa et al. [15]. In this paper, attention was paid to the hydraulic parameters of brown coal and mixtures with compost (filtration coefficients). As in the previous work, this also showed that combining materials with sorption capacity, and at the same time classified as low-cost sorbents, including brown coals, allows for the modification and optimization of sorption capacity, which significantly extends the possibilities of their use as sorbents [16]. The lignite from Bełchatów deposit (Poland) has been employed

as an adsorbent for the removal of phenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol from aqueous solutions [17]. Recently, the adsorption of bisphenol A from an aqueous solution on raw lignite and its fly ash has also been reported by the study of Kuśmierek et al. [18].

All the above-mentioned studies showed that lignite is an effective adsorbent for the removal of various pollutants from aqueous solutions and that its use as an adsorbent material has the advantages of low cost and abundance in nature. Despite the good sorption capacity shown above, in particular concerning organic substances, lignite has not been considered as sorbents for the removal of pesticides, which are one of the main pollutants of the soil and water environment in agricultural areas. This threat results from high persistence, toxicity, and biological activity to living organisms [19], with their widespread use. Pesticides derived from phenoxyacetic acid, commonly used as herbicides, constitute a special group. For this reason, this study aimed to demonstrate the usefulness of brown coal from the Bełchatów Brown Coal Mine (Poland) as a sorbent for the removal of phenoxyacetic acid (PAA), 4-chlorophenoxyacetic acid (4-CPA), 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(4-chloro-2-methylphenoxy)acetic acid (MCPA) from aqueous solutions. An additional justification for the advisability of researching the use of lignite as a sorbent is its availability, low cost (in comparison to commercial sorbents), and the possibility of direct distribution in a given area, without the need for prior treatment. The research took into account the influence of the variability of environmental conditions by examining the influence of pH and ionic strength on the binding efficiency of the analyzed herbicides on brown coal. To our best knowledge, lignite has not been used for the removal of phenoxy herbicides yet.

2. Materials and methods

The sample of brown coal was received from the Brown Coal Mine "Bełchatów" (Poland). The raw lignite was crushed, sieved to a particle size less than 250 μm, dried in an oven at 120°C to a constant weight, and used in this study without further modification.

The lignite sample was characterized using nitrogen low-temperature adsorption–desorption measurement (ASAP 2010, Micromeritics, Norcross, USA), scanning electron microscope (SEM, LEO 1430VP, Electron Microscopy Ltd., Cambridge, England, integrated with energy-dispersive X-ray analysis system Quantax 200, Bruker AXS Microanalysis, Berlin, Germany), Fourier-transform infrared spectra (Perkin-Elmer Spectrum 2000 Series FT-IR spectrometer, Waltham, MA, USA), thermal analysis (TG-DTA/DSC apparatus STA 449 Jupiter F1, Netzsch, Germany) as well as water and benzene vapor adsorption isotherms (dynamic vapor sorption apparatus, DVS Advantage, Surface Measurement Systems Ltd., London, UK), and the results are reported in our previous papers [17,18].

The herbicide standards: phenoxyacetic acid (>98%) and 4-chlorophenoxyacetic acid (98%) were purchased from Acros Organics (Geel, Belgium) while 2,4-dichlorophenoxyacetic acid (97%) and 4-chloro-2-methylphenoxyacetic acid (>98%) were received from Sigma-Aldrich (St. Louis, USA). The most important physicochemical properties of these

pesticides are listed in Table 1. The other chemicals were obtained from Avantor Performance Materials (Gliwice, Poland) and are of analytical grade.

Batch adsorption experiments were performed at room temperature by adding 0.4 g of lignite to 20 mL herbicides solutions of known concentration. Samples, in Erlenmeyer flasks, were agitated (100 rpm), then the mixtures were filtered and analyzed. The kinetic studies as well as the effects of adsorbent dose, solution pH, and ionic strength were conducted for an initial herbicides concentration of 500 μmol/L. The effect of adsorbent dose on the percentage removal of herbicides was studied by contacting 20 mL of PAA, 4-CPA, 2,4-D, and MCPA solutions with different amounts of adsorbent: 0.1, 0.2, 0.3, and 0.4 g (5, 10, 15, and 20 g/L). The pH dependence of herbicides adsorption was investigated using a series of experiments with the initial pH of the solutions ranging from 2 to 11. The pH of the tested solutions was adjusted using 0.1 mol/L NaOH and 0.1 mol/L HCl. To study the effect of ionic strength on adsorption, the experiments were carried out under NaCl concentrations ranging from 0 to 0.5 mol/L. Equilibrium adsorption experiments were carried out by varying the initial adsorbates concentrations in the range of 200–1,000 μmol/L.

All of the adsorption experiments were carried out in duplicate, and the average values were used for further calculations. The maximum relative standard deviation observed was less than 8%.

After adsorption, the residual herbicides in filtrates were measured by high-performance liquid chromatography with UV detection (Shimadzu LC-20, Kyoto, Japan) according to the procedure described elsewhere [20]. The calibration curves for the phenoxy acids were linear in the tested ranges from 10 to 750 μmol/L with correlation coefficients ≥ 0.998. The equations for the regression line were: $y = 0.162x + 3.395$ for PAA, $y = 0.176x + 5.159$ for 4-CPA, $y = 0.228x + 4.318$ for 2,4-D, and $y = 0.207x + 0.529$ for MCPA, respectively.

The amounts of pesticides adsorbed on the lignite surface at any time (q_t) and equilibrium (q_e) were calculated by Eqs. (1) and (2):

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

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

where C_0, C_e, and C_t are the initial, equilibrium and concentration of herbicide at any time t (μmol/L), respectively, while m and V are the mass of the adsorbent (g) and the volume of the solution (L).

The adsorption kinetics was investigated by the pseudo-first-order Eq. (3) and the pseudo-second-order Eq. (4) models [21,22]:

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

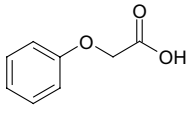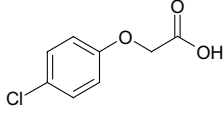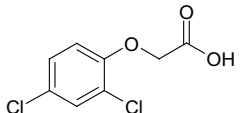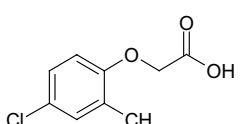$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

where k_1 and k_2 are the pseudo-first-order (1/min) and the pseudo-second-order rate constants (g/μmol·min), respectively.

To explain the adsorption mechanism and the rate-controlling steps in the adsorptive removal of the herbicides by the lignite the Weber–Morris model (intraparticle diffusion) and the Boyd model (film diffusion) were applied [21,22].

The Weber–Morris model equation is expressed as:

$$q_t = k_i t^{0.5} + C_i \tag{5}$$

Table 1
Physico-chemical properties of the herbicides

Adsorbate	CAS No.	Molecular formula	Molecular weight (g/mol)	Solubility in water (g/L)	pK$_a$
PAA	122-59-8		152.15	10	3.70
4-CPA	122-88-3		186.59	0.96	3.10
2,4-D	94-75-7		221.04	0.89	2.98
MCPA	94-74-6		200.62	0.82	3.14

where k_i is the intraparticle diffusion rate constant (μmol/g min$^{-0.5}$), and C_i is the thickness of the boundary layer.

Boyd's kinetic model was applied using Eq. (6):

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_1^\infty \left(\frac{1}{n^2}\right) \exp\left(-n^2 B_t\right) \qquad (6)$$

which can be rearranged into the following modified forms:

$$B_t = \pi \left(1 - \sqrt{1 - \frac{\pi}{3}\frac{q_t}{q_e}}\right)^2 \qquad (7)$$

for $q_t/q_e < 0.85$

$$B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \qquad (8)$$

for $q_t/q_e > 0.85$

where B_t is a mathematical function of q_t/q_e.

Adsorption equilibrium data were fitted using Langmuir, Freundlich, and Langmuir–Freundlich isotherm equations [23].

The Langmuir isotherm assumes a homogeneous and monolayer adsorption mechanism. The model is given by the following equation:

$$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e} \qquad (9)$$

where: q_{mL} and b_L are the maximum adsorption capacity (μmol/g) and the Langmuir constant (L/μmol).

The Freundlich model is applicable for multilayer adsorption and it exhibits the heterogeneous behavior of the adsorbent surface. The adsorption isotherm equation of this model is expressed as follows:

$$q_e = K_F C_e^{1/n} \qquad (10)$$

where: K_F ((μmol/g)(L/μmol)$^{1/n}$) and n are the Freundlich constants.

The Langmuir–Freundlich model is a mix of the Langmuir and Freundlich isotherms:

$$q_e = \frac{q_{mLF} \left(b_{LF} C_e\right)^m}{\left(1 + b_{LF} C_e\right)^m} \qquad (11)$$

where: q_{mLF} (μmol/g) is the L-F constants representing the monolayer adsorption capacity, b_{LF} (L/μmol) is the L-F constants representing the energy of adsorption, and m is the L-F empirical constant.

The correlation coefficients (R^2) and the chi-square tests (χ^2) were employed as a criterion for the fitting quality.

3. Results and discussion

3.1. Effect of adsorbent dose

Fig. 1 shows the effect of adsorbent dose on the removal of the herbicides from aqueous solutions by lignite. As can be seen, with an increase in the adsorbent doses from 5 to 20 g/L the removal efficiency increased from 5.8% to 18.5% for PAA, from 8.1% to 26.1% for 4-CPA, from 9.8% to 31.2% for 2,4-D, and from 12.1% to 35.8% for MCPA, respectively. This phenomenon, an increase in adsorption with increasing adsorbent dose, can be explained by an increase in the availability of adsorbent surface area and a greater number of adsorption sites available to adsorbate molecules. Increasing the number of adsorption sites increases the possibility of collision between adsorbent and adsorbate and thus increases the efficiency of the process of removing contaminants from water [24]. A dose of 20 g/L (0.4 g) of the lignite was considered for further experiments.

3.2. Adsorption kinetics

The adsorption behavior of the phenoxy herbicides as a function of contact time was investigated and the results are presented in Fig. 2. The adsorption was fast and the process reached equilibrium after about 30 min. Lignite shows better kinetic properties than activated carbons, for which the time required to reach equilibrium is about 60–120 min [20,25,26].

Table 2 shows the adsorption kinetic parameters calculated from the pseudo-first-order and the pseudo-second-order kinetic models.

Both the k_1 and k_2 values increased in the following order: MCPA < 2,4-D < 4-CPA < PAA. The highest values of R^2 (0.996–0.999) and the lowest values of χ^2 (0.156–0.275) were obtained using the pseudo-second-order equation. Moreover, the calculated equilibrium adsorption capacities ($q_{e2(cal)}$) recorded for the pseudo-second-order agreed well with the experimental equilibrium adsorption capacities ($q_{e(exp)}$). This suggests that the adsorption of the herbicides
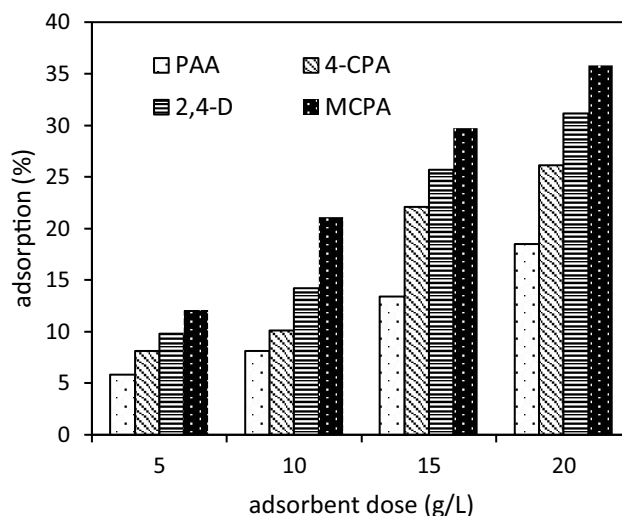

Fig. 1. Effect of adsorbent dose on adsorptive removal of PAA, 4-CPA, 2,4-D, and MCPA from aqueous solutions.
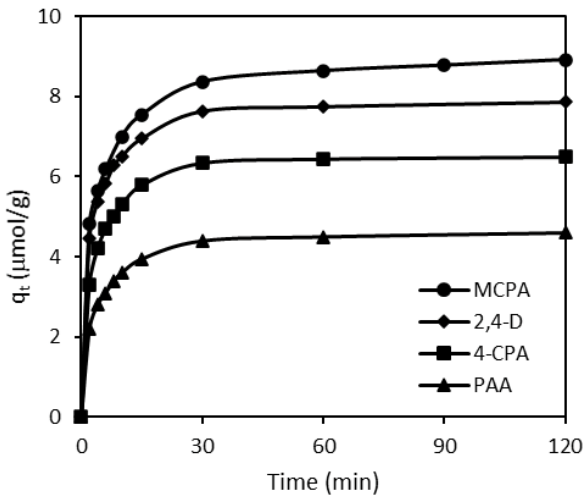
Fig. 2. Adsorption kinetics of PAA, 4-CPA, 2,4-D, and MCPA onto lignite from aqueous solutions.

Table 2
Parameters for adsorption kinetics of PAA, 4-CPA, 2,4-D, and MCPA onto lignite from aqueous solutions

Parameter	PAA	4-CPA	2,4-D	MCPA
$q_{e(exp)}$ (µmol/g)	4.603	6.501	7.868	8.917
Pseudo-first-order				
k_1 (1/min)	0.0473	0.045	0.041	0.0394
$q_{e1(cal)}$ (µmol/g)	2.264	3.122	3.227	3.713
R^2	0.931	0.957	0.916	0.908
χ^2	1.651	1.797	3.227	2.958
Pseudo-second-order				
k_2 (g/µmol min)	0.0580	0.0507	0.04675	0.0412
$q_{e2(cal)}$ (µmol/g)	4.699	6.649	8.001	9.058
R^2	0.999	0.998	0.996	0.999
χ^2	0.275	0.156	0.215	0.198

on lignite follows the pseudo-second-order kinetics which shows the adsorption phenomena with the complete extent of contact time, with chemisorption as the rate-determining step. Since the kinetics indicate chemisorption, that is, by chemical bonding it is a relatively stable bond, suggesting that there is no danger of easy re-release of adsorbates into the environment under given conditions.

The process of adsorption from solution involves several consecutive steps: (i) diffusion in the boundary film (film diffusion or external diffusion), (ii) diffusion in the internal structure (intraparticle diffusion), (iii) adsorption – localization of adsorbate molecules on the active sites of the adsorbent surface [21]. This last step of adsorption occurs fastest, so it does not limit the adsorption kinetics. The kinetics is determined by the slowest processes. Thus, film diffusion, intraparticle diffusion, or possibly both together will be the limiting factors for the adsorption rate. The Weber–Morris and Boyd models allow the identification of the adsorption mechanism [21,22].

The Weber–Morris plot is given in Fig 3a. If adsorption occurs by intraparticle diffusion only, then the relation $q_t = f(t^{0.5})$ would be straight-line in the whole range, moreover, the curve would pass through the origin of the graph. The lack of linearity (broken line in the graph) indicates that several processes are involved in the adsorption process and not only intraparticle diffusion. As shown in Fig. 3a, none of the curves passed through the origin of the coordinate system which suggests that intraparticle diffusion is not the only limiting step in the adsorption process of the herbicides from water. In addition, the dependence of q_t on $t^{0.5}$ throughout the considered time range was not linear indicating that the adsorption rate depends not only on intraparticle diffusion.

Based on B_t vs. time, the plot of the Boyd model was obtained and is presented in Fig. 3b. This model assumes that if the plot of B_t against t is non-linear (or linear) and does not pass through the origin (intercept ≠ 0), then the main determinant of adsorption will be film diffusion or external mass transport. On the other hand, if Boyd's plot is a straight line and passes through the origin (intercept = 0), then adsorption is controlled by the intraparticle diffusion mechanism.
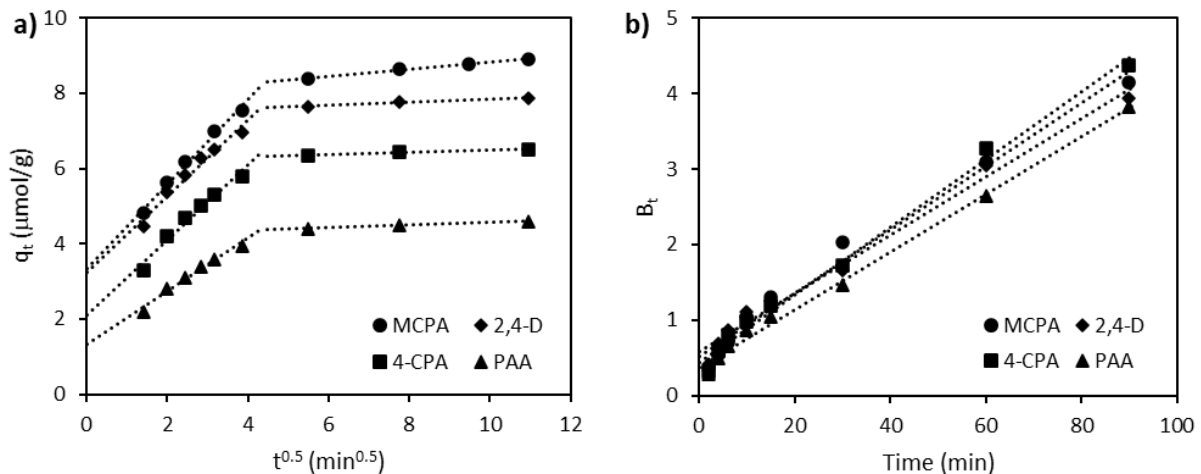

Fig. 3. The Weber–Morris model (a), and the plot of Boyd model (b) for the adsorption of PAA, 4-CPA, 2,4-D, and MCPA onto lignite from aqueous solutions.

From the plot of B_t vs. t presented in Fig. 3b, it was observed that all the curves are linear ($R^2 \geq 0.984$) but do not pass through the origin, confirming that adsorption of all the herbicides on the lignite is a film diffusion mechanism.

3.3. Adsorption equilibrium

The percentage removal of the PAA, 4-CPA, 2,4-D, and MCPA from aqueous solutions by lignite for their different initial concentrations at equilibrium is shown in Fig. 4a, while the adsorption isotherms ($q_e = f(C_e)$) are presented in Fig. 4b.

To explain and better understand the adsorption process of the above adsorbates on brown coal the equilibrium data were analyzed using Langmuir, Freundlich, and Langmuir–Freundlich isotherm models. The various model parameters are illustrated in Table 3. The results showed that all three models described adsorption fairly well. However, the Freundlich model exhibited slightly better correlation coefficients (≥ 0.990) and lower χ^2 values (≤ 0.069) than the Langmuir and Langmuir–Freundlich models. The good correlation with the Freundlich isotherm model suggests multi-layer adsorption with interactions between the herbicides molecules and heterogeneous adsorbent surface.

The adsorption efficiency of the herbicides increased in the order: PAA < 4-CPA < 2,4-D < MCPA. The 2,4-D was adsorbed better than 4-CPA and PAA and the adsorption of these herbicides was positively correlated with hydrophobicity, a molecular weight of the adsorbate molecules, and inversely correlated with their solubility in water (Table 1). The adsorption efficiency of the adsorbates increased with the increasing –Cl substituents in the molecule. Chlorine atoms substituted in the aromatic ring reduce its electron density, which increases the hydrophobicity of the molecule and reduces its solubility in water. The increasing degree of chlorine atoms on the molecule enhances the interaction between the herbicide molecule and the hydrophobic surface of the adsorbent, which increases the

adsorption efficiency. A similar trend (PAA < 4-CPA < 2,4-D) was observed for the adsorption of these herbicides on peat [27] and various activated carbons [20,25]. Kavanagh et al. [28] studied the adsorption of the phenoxyacetic acid herbicides (PAA, 2,4-D, MCPA, and 2,4,5-T) on goethite. They found that sorption of the herbicides on goethite increased in the order of PAA < 2,4-D < MCPA < 2,4,5-T. The 2,4-D was adsorbed better than PAA but weaker than MCPA, as is the case in this paper. Similar observations (greater adsorption of MCPA than 2,4-D) have previously

Table 3
Adsorption isotherm parameters for PAA, 4-CPA, 2,4-D, and MCPA adsorption onto lignite from aqueous solutions (non-linear)

| Parameter	PAA	4-CPA	2,4-D	MCPA
Langmuir				
q_{mL} (μmol/g)	20.53	27.10	35.21	37.04
b_L (L/μmol)	0.00077	0.00084	0.00082	0.00095
R^2	0.942	0.931	0.929	0.959
χ^2	0.078	0.085	0.123	0.104
Freundlich				
K_F ((μmol/g)(L/μmol)$^{1/n}$)	0.047	0.057	0.073	0.088
$1/n$	0.769	0.794	0.795	0.788
R^2	0.993	0.991	0.994	0.990
χ^2	0.034	0.069	0.048	0.061
Langmuir–Freundlich				
q_{mLF} (μmol/g)	19.869	24.90	28.14	30.38
b_{LF} (L/μmol)	0.0021	0.002	0.0012	0.0004
m	1.321	1.196	1.083	0.900
R^2	0.971	0.965	0.980	0.988
χ^2	0.058	0.085	0.088	0.097
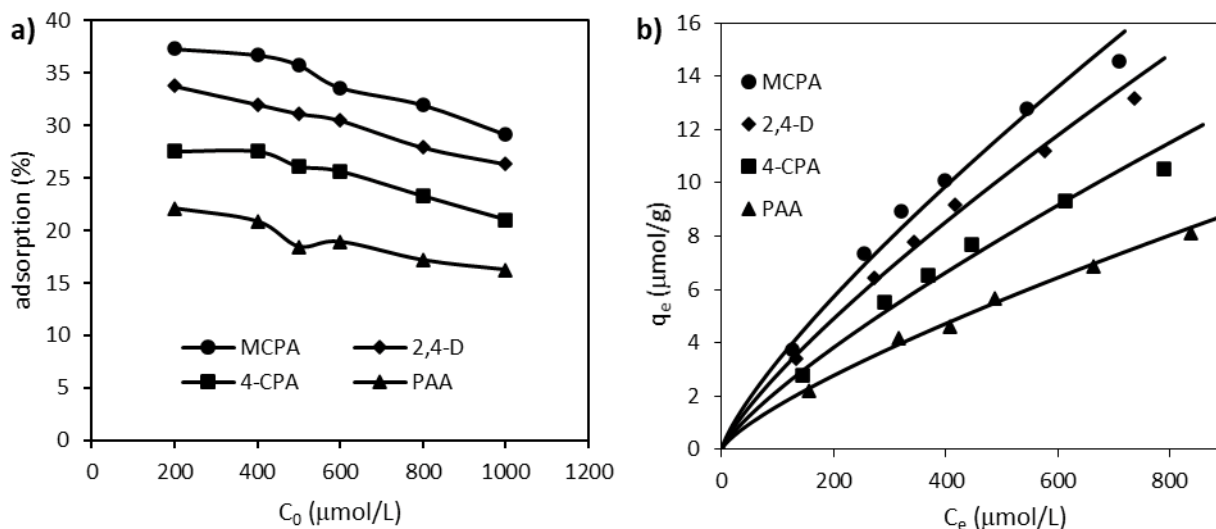
Fig. 4. Adsorptive removal of the herbicides from aqueous solutions by lignite for their different initial concentrations at equilibrium – (a), and adsorption isotherms of PAA, 4-CPA, 2,4-D, and MCPA onto lignite from aqueous solutions – (b).

been described by authors studying the adsorption of these two herbicides on commercial activated carbons [25,29,30] as well as activated carbons prepared from rice straw [31], and lignocellulosic materials [26]. Abdel daiem et al. [29] attribute less 2,4-D adsorption than MCPA to the presence of two chlorine groups on the aromatic ring of the 2,4-D molecule. This indicates that these chlorine substituents act as electron-withdrawing groups, weakening the dispersive interactions between π electrons of the aromatic ring of 2,4-D and π electrons of the graphene planes of the carbon adsorbents. On the other hand, a contrary phenomenon, better adsorption of 2,4-D than MCPA, was reported for montmorillonite modified by N,N'-didodecyl-N,N'-tetramethylethanediammonium (DEDMA) cations [32], switchgrass biochar [33], or MgAl-layered double hydroxides [34]. This suggests that better adsorption of 2,4-D or MCPA is determined by the individual properties of the adsorbent used in the experimental studies.

3.4. Effect of pH

The effect of pH was observed by studying the adsorption of the herbicides over the pH range from 2 to 11 and the results are presented in Fig. 5.

Results showed that the adsorption is affected greatly by the pH of the solution. The pH of 2 was viable for maximum adsorption of the herbicides, after which the adsorption decreased significantly. This could be explained using the pH_{pzc} concept. The point of zero charge of the lignite, defined as the pH value wherein the liquid phase charge of the adsorbent is equal to zero, was found to be 6.2 [17]. So, in an acidic solution (pH < 6.2) the surface of the lignite was positively charged, while at a pH greater than 6.2, the surface had a net negative charge. The pK_a values for the individual herbicides range from 2.98 to 3.70 (Table 1), which means that at low pH (below pK_a) the herbicide molecules are protonated, while at a pH greater than the pK_a value, they exist predominantly in anionic forms.
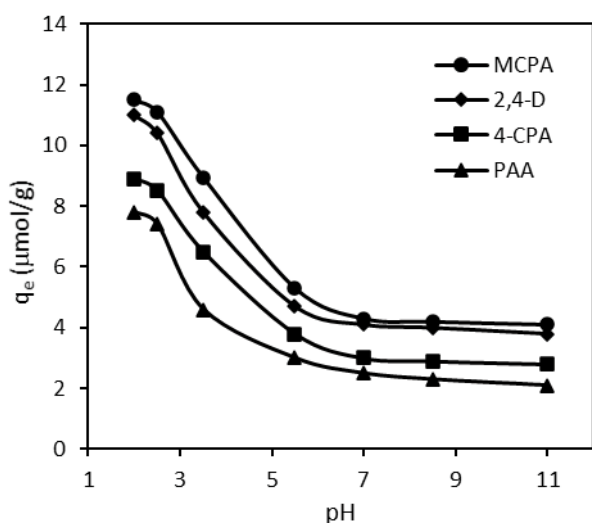
The non-dissociated forms of the herbicides were preferred by the positively charged lignite surface. As the pH increased, the degree of dissociation of the phenoxyacetic acids increased, thereby making them more negatively charged. As a consequence, the electrostatic repulsion between negatively charges adsorbent surface (pH > 6.2) and dissociated herbicide molecules increases, and resultantly, the adsorption capacity was reduced. Similar adsorption behavior of the phenoxy herbicides with a variation in the solution pH was reported on the activated carbons [26,30]. From the fact that sorption in an acidic environment is higher, it follows that in the conditions of acidification of the environment with which we deal with a large area of agricultural land, the use of lignite as an effective sorbent in these conditions seems to be justified.

3.5. Effect of ionic strength

The effect of ionic strength on adsorption is presented in Fig. 6. The data indicate that the presence of salt in the solution improved the adsorption capacity of the lignite, and the amounts of herbicides adsorbed increased with increasing NaCl concentrations. As the NaCl concentration in the solution increased from 0 (distilled water) to 0.5 mol/L, the adsorption capacity increased from 4.60 to 7.01 μmol/g for PAA, from 6.52 to 8.62 μmol/g for 4-CPA, from 7.81 to 9.53 μmol/g for 2,4-D, and from 8.95 to 10.74 μmol/g for MCPA, respectively. The increase in the adsorption of herbicides along with the increase in NaCl concentration in the solution can be attributed to the salting-out effect, which reduces their solubility, thus increasing their adsorption on the adsorbent [29]. The practical significance of the above results can be seen in the context of the presence of various ions under real conditions.

4. Conclusions

Batch adsorption experiments were carried out for the adsorption of the phenoxyacetic acid (PAA),

Fig. 5. Effect of initial solution pH on the adsorption of PAA, 4-CPA, 2,4-D, and MCPA on lignite.
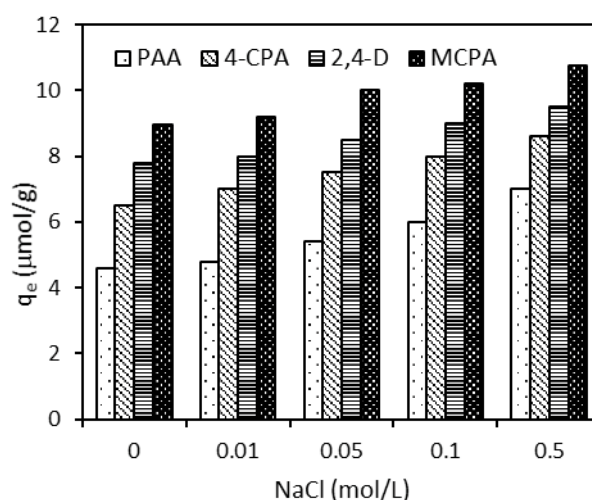

Fig. 6. Effect of ionic strength on the adsorption of PAA, 4-CPA, 2,4-D, and MCPA on lignite.

4-chlorophenoxyacetic acid (4-CPA), 2,4-dichlorophenoxyacetic acid (2,4-D), and 4-chloro-2-methylphenoxyacetic acid (MCPA) from an aqueous solution using raw lignite as the adsorbent. The pseudo-first-order, pseudo-second-order as well as the Langmuir, Freundlich, and Langmuir–Freundlich models were used to describe the experimental data. Results showed that the adsorption kinetics and adsorption equilibrium followed the pseudo-second-order kinetic model and the Freundlich isotherm model, respectively. Adsorption efficiency of the herbicides increased in the order PAA < 4-CPA < 2,4-D < MCPA and the monolayer adsorption capacities were 20.53, 27.10, 35.21, and 37.04 μmol/g, respectively. The effects of solution pH and ionic strength were also studied. The adsorption was strongly pH- and ionic strength dependent. The adsorption efficiency of all the herbicides decreased significantly with an increase in the initial pH of the solution and increased with the increase in NaCl concentration in the solution. The obtained results showed that the raw lignite may be used as an effective low-cost adsorbent without any pretreatment for the removal of phenoxy herbicides from the aqueous solutions in real conditions.

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