Environment Protection Engineering

Vol. 43 2017 No. 4

DOI: 10.37190/epe170412

KRZYSZTOF KUŚMIEREK[1], ANDRZEJ ŚWIĄTKOWSKI[1], LIDIA DĄBEK[2]

REMOVAL OF 2,4,6-TRICHLOROPHENOL FROM AQUEOUS SOLUTIONS USING AGRICULTURAL WASTE AS LOW-COST ADSORBENTS

Agricultural waste products including sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells were used as low-cost adsorbents for the removal of 2,4,6-trichlorophenol (TCP) from aqueous solutions. The effects of adsorbent dosage, pH and ionic strength on the adsorption of TCP were investigated. The results showed that the adsorption of TCP was pH dependent and increased upon increasing the ionic strength of the solution. The adsorption kinetics was found to follow a pseudo-second order kinetics. The equilibrium adsorption data were fitted to the Langmuir, Freundlich and Sips isotherms and the best results were achieved with the Freundlich model. The desorption of TCP using deionized water, water/methanol mixture or 5% sodium hydroxide was also studied. The results suggest that the tested materials may be used as an effective adsorbents without any treatment or any other modification for removal of TCP from the aqueous medium.

1. INTRODUCTION

Excessive release of organic contaminants into the environment due to industrialization, intensive agriculture and urbanization gives rise to worldwide concern. The pollution of water resources is responsible for several damages to the environment and adversely affecting the health of the people. For this reason, the removal of organic impurities from water is a very important and urgent problem. Numerous technologies have been proposed for the removal of organic contaminants from water. Among them, physical adsorption is generally considered to be the best, effective and most frequently

[1]Institute of Chemistry, Military University of Technology, ul. Kaliskiego 2, 00-908 Warsaw, Poland, e-mail address: krzysztof.kusmierek@wat.edu.pl

[2]Faculty of Environmental, Geomatic and Energy Engineering, Kielce University of Technology, ul. Studencka 2, 25-314 Kielce, Poland.

used method [1]. The adsorption process has an advantage over the other methods due to its low cost, flexibility and simplicity of design, ease of use and sludge free clean operation. The most popular and widely used adsorbent for water purification is activated carbon. However, its use is associated with several disadvantages. A relatively high initial cost and the need for a costly regeneration system make the activated carbon an expensive material. Thus, more cost-effective practical adsorbents are needed. In recent years a number of non-conventional low-cost sorbents including house hold wastes (e.g., spent tea leaves, fruit waste, scrap tyres), agricultural products (e.g., rice husk, sawdust), industrial wastes (e.g., sugar industry waste, fly ash, red mud, sludges) and natural materials (e.g., chitosan, clay, peat) have been proposed by several authors [1]. These materials are cheap, easily available and disposable without regeneration. Agricultural (biological) products and byproducts as sorbents have many advantages over traditional materials because after use, they can be utilized as fuel for power generation or as ferment substrates. The use of agricultural solid wastes for the treatment of contaminated water could be helpful also in solving the solid waste disposal problem to farmers and agri-food industry.

The main objective of this research was to study the potential of agricultural waste such as sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells as low-cost adsorbents for the removal of 2,4,6-trichlorophenol (TCP) from water. The effects of various parameters like mass of the adsorbent, pH and ionic strength on the adsorption of TCP were studied using batch experiments. The adsorption kinetics and isotherms parameters were also evaluated. We chose 2,4,6-trichlorophenol as the target contaminant because even at low level it is poisonous to aquatic life, plants and people and is commonly found in drinking water.

Sunflower and pumpkin are one of the most important oil plants. The industrial processing of sunflower seeds leave as by-product hulls, which constitute biological waste material that can be used for the sorption. Also walnut and peanut shells are waste products for which no important industrial use have been developed. Sunflower, pumpkin, walnut and peanut waste products for the removal of various pollutants from water have been investigated by number of authors. Sunflower seed hulls were applied for the removal of heavy metal ions [2], dyes [3, 4] and some pesticides including atrazine, alachlor, endosulfan sulfate, trifluralin, chlorfenvinphos, chlorpyrifos and simazine [5, 6]. The redundant pumpkin husks were used for the removal of Reactive Red 120 [7] from water. Hameed and El-Khaiary [8] successfully used pumpkin seed hulls for the removal of methylene blue from aqueous solutions. Peanut shells were already effectively used as an adsorbent for dye [9] and heavy metals [10]. Walnut shells were used as sorbents for the removal of monochlorophenols [11], sulfamethoxazole [12], malachite green [13] and heavy metal ions [2]. However, to the best of our knowledge, the removal of 2,4,6-TCP from aqueous solutions by these materials has not been reported in literature.

2. MATERIALS AND METHODS

Reagents. 2,4,6-trichlorophenol (TCP) was received from Sigma-Aldrich (St. Louis, USA). Acetic acid, hydrochloric acid, sodium sulfate, sodium hydroxide, sodium chloride, methanol and the HPLC-grade acetonitrile for high-performance liquid chromatography were obtained from the Avantor Performance Materials (Gliwice, Poland).

Adsorbents. Sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells were obtained from a local market. In order to remove dust and soluble pollutants from the residues, the samples were washed with distilled water three times and then were dried in an oven at 110 °C for 24 h. The dried shells were broken into small pieces, milled and sieved through a 0.5 mm size before use in adsorption experiments without any further treatment. The SEM analysis of the tested materials was performed with scanning electron microscope QUANTA 250 FEG (FEI). For chemical (elemental) microanalysis of adsorbent surfaces, the energy-dispersive X-ray spectroscopy (EDS) was used. The points of zero charge (pH_{PZC}) of the sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells were determined by the pH drift method. To determine the pH_{PZC} a series of mixture solutions (0.5 g adsorbent and 50 cm^3 of 0.01 mol/dm^3 NaCl) in an Erlenmeyer flasks were prepared at various initial pH (ranging from 2.0 to 11.0) adjusted with 0.1 mol/dm^3 HCl and/or NaOH. Then, the flasks were shaken for 24 h, and the final pH of the solution was measured. The final pH was plotted against the initial pH and the intersection point of the obtained curve was taken as the point of zero charge, pH_{PZC}.

Adsorption experiments. The adsorption studies were conducted at room temperature by mixing a given amount of adsorbents (0.1–0.5 g) in Erlenmeyer flasks containing 20 cm^3 of aqueous solutions of TCP at various concentrations (from 0.1 to 0.5 $mmol/dm^3$). The flasks were agitated at constant rate of 200 rpm. The kinetic studies were conducted for an initial TCP concentration of 0.25 $mmol/dm^3$ and the mass of the adsorbent of 0.5 g (25 g/dm^3). The samples were withdrawn at appropriate time intervals and analyzed. The amount of TCP adsorbed at the time t, q_t (mmol/g), was calculated:

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

where C_0 and C_t are the initial TCP concentration and concentration at time t ($mmol/dm^3$), V is the volume of the solution (dm^3) and m is the mass of the adsorbent (g). Adsorption isotherm experiments were conducted by adding 25 g/dm^3 of adsorbents to TCP of different concentrations (0.1–0.5 $mmol/dm^3$). The mixtures were agitated at 200 rpm for 4 h, filtered and analyzed. The adsorption capacity q_e (mmol/g) was calculated following Eq. (2).

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

where C_e is the final (equilibrium) concentration of TCP in the liquid phase (mmol/dm^3). The effect of salt presence (ionic strength) on TCP removal was investigated similarly as described above with the difference that the chlorophenol was adsorbed from the 0.05 mmol/dm^3 solutions of Na_2SO_4. The pH studies were conducted to determine the optimum pH at which maximum TCP removal could be achieved. The initial TCP concentration was 0.25 mmol/dm^3 and the initial pH of the solutions (from 2.5 to 11.0) was adjusted by 0.1 mol/dm^3 HCl or NaOH. All experiments were carried out in duplicate and the average values were used in calculations. The maximum deviation was found to be below 5%.

Desorption experiments. 20 cm^3 of the TCP solution (0.25 mmol/dm^3) was agitated with 0.5 g (adsorbent dose 25 g/dm^3) of the sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells for 4 h. After then, the mixtures were filtered and the concentration of the TCP was measured. The adsorbent was separated from the solution and dried in an oven at 110 °C for 24 h. Desorption experiments were conducted on 0.5 g of used adsorbent which was agitated at 200 rpm for 4 h with 20 cm^3 of distilled water, water/methanol (50/50) mixture or 5% sodium hydroxide. Subsequently, the mixtures were filtered and analyzed. These procedures were repeated three times, resulting in three desorption steps.

Analytical method. The concentration of TCP was determined by high-performance liquid chromatography with UV detection (Shimadzu LC-20, Kyoto, Japan). The measurements were carried out under isocratic conditions on a Phenomenex Luna C-18, 4.6×150 mm, 3 μm column (Torrance, USA) thermostated at 40 °C. The chromatographic conditions were as follows: mobile phase consisted of acetonitrile/water adjusted to pH 3.0 with acetic acid (55/45); flow rate of 0.25 cm^3/min; an analytical wavelength of 281 nm. The calibration plot of peak area vs. TCP concentration showed a linear working range from 0.001 to 0.5 mmol/dm^3 with the correlation coefficient of 0.9992.

3. RESULTS AND DISCUSSION

3.1. ADSORBENTS CHARACTERIZATION

The scanning electron micrographs of all adsorbents are shown in Fig. 1. These images show that the surface of the materials has agglomerate shape with uneven, porous, and heterogeneous structure. The elemental analysis data (Table 1) showed that all adsorbents have more or less similar compositions. The point of zero charge (pH_{PZC})

of selected plant residues was 4.4, 6.2, 7.1 and 7.5 for walnut shells, peanut shells, pumpkin seed shells and sunflower seed hulls, respectively.

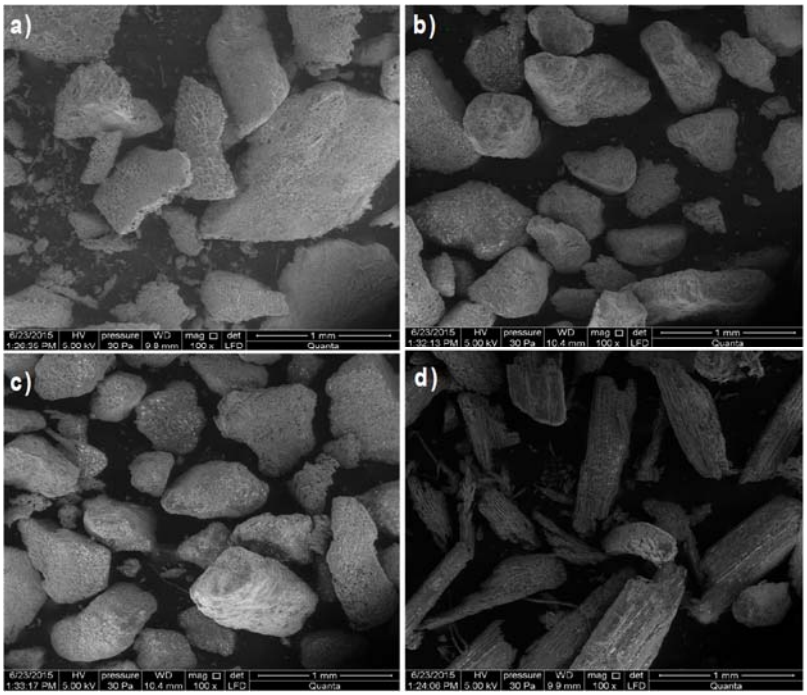

Fig. 1. SEM images of the studied agricultural wastes:
a) peanut shells; b) walnut shells; c) pumpkin seed shells; d) sunflower seed hulls

Table 1

Elemental composition of all sorbents from SEM-EDS [wt. %]

Element	Peanut	Walnut	Pumpkin	Sunflower
C	58.85	59.69	63.50	59.46
O	37.02	37.33	28.42	36.89
N	3.36	2.74	4.70	2.63
Mg	0.11	–	0.15	0.15
Al	0.12	0.11	0.28	0.13
Si	0.06	–	0.03	–
P	–	–	0.23	0.03
S	0.04	–	0.25	0.05
K	0.14	0.06	1.74	0.41
Ca	0.21	0.07	0.41	0.17
Cu	0.09	–	0.29	0.08

3.2. EFFECT OF ADSORBENT DOSE

The effect of dose of adsorbent on the amount of TCP adsorbed was studied using different adsorbent concentrations ranging from 5 to 25 g/dm^3. The increase in adsorbent dosage from 5 to 25 g/dm^3 resulted in an increase in adsorption from 10 to 65% on peanut shells, from 7 to 56% on walnut shells, from 12 to 68% on pumpkin seed shells and from 9 to 61% on sunflower seed hulls (Fig. 2). The removal efficiency of TCP increased with increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose of the adsorbent. All our subsequent experiments were performed at an adsorbent dosage of 25 g/dm^3.

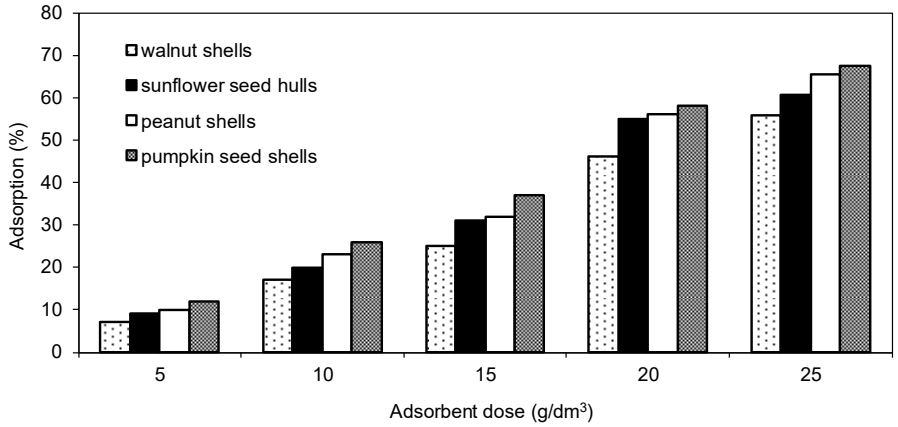

Fig. 2. Effect of adsorbent dose on adsorptive removal of TCP; TCP concentration 0.25 mmol/dm^3, pH 6.0, 25 °C

3.3. ADSORPTION KINETICS

The adsorption kinetic curves of the TCP are shown in Fig. 3a. The adsorption equilibria were achieved after about 45 min for all adsorbents. For the description of the experimental data equations, the pseudo-first and pseudo-second order were considered. The pseudo-first order kinetic model is expressed in linear form as:

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

where: k_1 is the rate constant of pseudo-first order adsorption (1/min) calculated from the plots of $\log(q_e - q_t)$ vs. t. The pseudo-second order equation has the linear form:

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

where k_2 is the rate constant of pseudo-second order adsorption (g/(mmol·min)) calculated from the plots of t/q_t vs. t. The kinetic constants of both models as well as correlation coefficients are presented in Table 2.

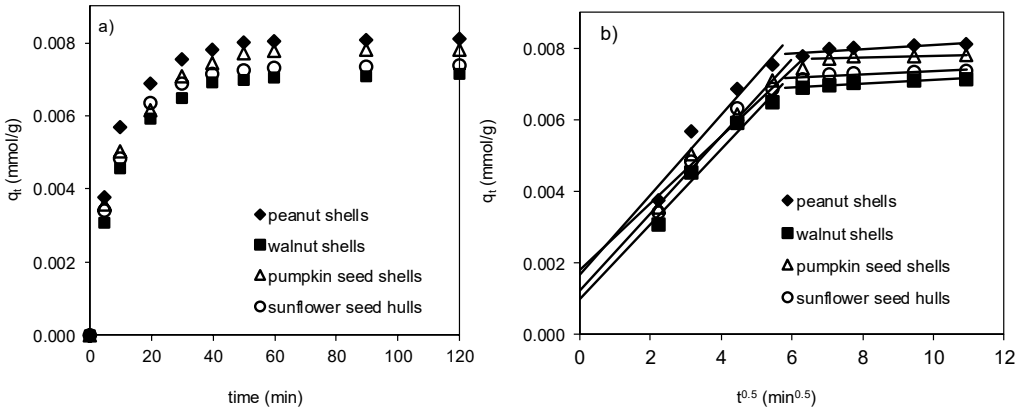

Fig. 3. Adsorption kinetics of TCP (a), and intraparticle diffusion plot (b) for TCP adsorption onto plant residues; TCP concentration 0.25 mmol/dm^3, pH 6.0, adsorbent dose 25 g/dm^3, 25 °C

Table 2

Pseudo-first and pseudo-second order constants for adsorption of TCP on the plant residues

Sorbent	$q_{e\,(exp)}$ [mmol/g]	Pseudo-first order kinetics			Pseudo-second order kinetics		
		k_1 [1/min]	R^2	$q_{e\,(calc)}$ [mmol/g]	k_2 [g/(mmol·min)]	R^2	$q_{e\,(calc)}$ [mmol/g]
Peanut	0.0078	0.0136	0.9871	0.0102	21.72	0.9988	0.0081
Walnut	0.0068	0.0119	0.9848	0.0076	24.15	0.9989	0.0070
Pumpkin	0.0080	0.0189	0.8916	0.0109	26.16	0.9992	0.0084
Sunflower	0.0074	0.0101	0.9662	0.0055	27.42	0.9990	0.0077

According to Table 2, the pseudo-second order kinetic model achieved a higher correlation coefficients ($R^2 > 0.99$) and better agreement between the q_e experimental and calculated values. As a result, the pseudo-second order kinetic model was more representative than the pseudo-first order kinetic model for simulating the kinetic data. The fastest adsorption kinetics was attributed to the sunflower seed hulls with the rate constant k_2 of 27.42 g/(mmol·min), while the slowest to the peanut shells (21.72 g/(mmol·min)). Based on the k_2 values, the adsorption of TCP followed the decreasing sequence: sunflower seed hulls > pumpkin seed shells > walnut shells > peanut shells.

In order to investigate the mechanism of the adsorption, the intraparticle diffusion model was also used:

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

where: k_i is the intraparticle diffusion rate constant (mmol/(g·min$^{-0.5}$)) determined experimentally from the plot of q_t vs. $t^{0.5}$ (Fig. 3b) and C_i is the thickness of the boundary layer.

If the plot of q_t vs. $t^{0.5}$ is linear, diffusion is involved in the entire adsorption process. When the intercept C_i equals zero (the straight line passes through the origin), then the intraparticle diffusion is the only controlling step. However, if C_i does not pass through the origin, it indicates that there are other processes involved in the mechanism of adsorption. As is shown in Fig. 3b, the plots are multilinear. The multilinearity indicates that several steps are involved. In the first sharper region, the sudden increase in slope (within a short time period) means that the TCP molecules are transported to the external surface of the adsorbents through film diffusion. After that, TCP molecules are entered into the adsorbents by intraparticle diffusion through pore, which is represented in second straight line. The slopes of the first part of the plot are about twenty times greater than for the second straight lines, however the slopes are comparable for all adsorbents. Moreover, none of the lines passed through the origin. This suggested that intraparticle diffusion is not the rate limiting step.

3.4. ADSORPTION EQUILIBRIUM

The equilibrium adsorption is very important in the design of an adsorption system, because equilibrium studies of adsorption are used to determine the capacity of the adsorbent. The equilibrium relationships between TCP and the adsorbents are shown in Fig. 4.

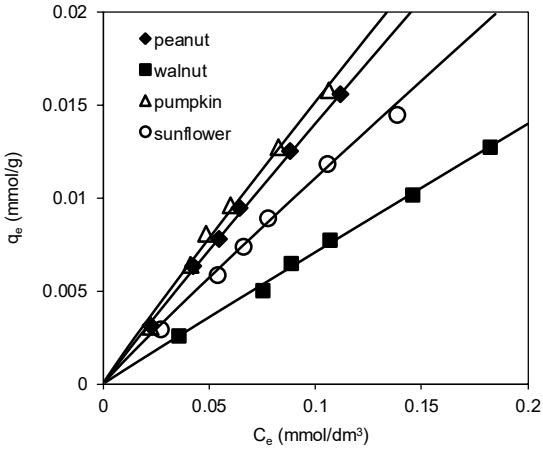

Fig. 4. Adsorption isotherms of TCP onto plant residues from aqueous solutions; TCP concentration range 0.1–0.5 mmol/dm^3, pH 6.0,adsorbent dose 25 g/dm^3, 25 °C

The isotherms are almost linear and the adsorption isotherms are of C1-curve type according to the Giles classification [14]. The C curves (linear curves) are given by

solutes which penetrate into the solid more readily than does the solvent. A similar isotherm shape was observed for sorption of monochlorophenols on nut shells [11] as well as TCP on peat [15], fruit cuticles [16] and potato tuber peryderm [17].

Several isotherm models are often used to interpret the equilibrium data [17]. In the present research, the Langmuir, Freundlich and Sips models were utilized to explain the experimental data.

The Langmuir isotherm is based on the assumptions that the adsorption is monolayer and takes place at specific homogeneous sites on the adsorbent surface, where no further adsorption can occur when a site is occupied with adsorbate. This model is expressed as follows:

$$q_e = \frac{q_{mL} K_L C_e}{1 + K_L C_e} \tag{6}$$

where: q_{mL} is the maximum adsorption capacity (mmol/g) and K_L is the Langmuir constant related to the free energy of adsorption (dm^3/mmol).

The Freundlich isotherm model proposes a multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich equation has the form:

$$q_e = K_F C_e^{1/n} \tag{7}$$

where: K_F is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent ((mmol/g)(dm^3/mmol)$^{1/n}$) and n is the Freundlich constant indicative of the intensity of the adsorption.

The Sips model is the combination of Langmuir and Freundlich models:

$$q_e = \frac{q_{mS} K_S C_e^m}{1 + K_S C_e^m} \tag{8}$$

where: q_{mS} is the Sips maximum adsorption capacity (mmol/g), K_S is the Sips equilibrium constant (dm^3/mmol) and m is the Sips model constant.

All models parameters were evaluated by non-linear regression using OriginPro 7.5 software and are presented in Table 3. Higher values of R^2 indicate the high ability of the model to describe the equilibrium data. It can therefore be concluded that the Freundlich model fitted better the experimental data compared to the other models. The lowest R^2 values (<0.99) were observed for the Langmiur model. According to the K_F values, adsorption of TCP followed the decreasing sequence: pumpkin seed shells (0.1359), peanut shells (0.1274), sunflower seed hulls (0.0994), walnut shells (0.0676 (mmol/g)(dm^3/mmol)$^{1/n}$). Also the Langmuir (q_{mL}) and Sips (q_{mS}) constants decreased in the same order. This

suggests that the pumpkin seed shells are the best adsorbent for the removal of TCP from water. The lowest adsorption capacity towards the TCP had walnut shells. For all cases, the values of the Freundlich constant *n* were greater than one, indicating a favorable adsorption of TCP by all adsorbents.

Table 3

Isotherm model parameters for adsorption of TCP on plant residues

Isotherm model	Parameter	Adsorbent			
		Peanut	Walnut	Pumpkin	Sunflower
Langmuir	q_{mL}, mmol/g	0.1747	0.1377	0.2102	0.1529
	K_L, dm^3/mmol	0.9436	0.7313	0.7150	0.7694
	R^2	0.9850	0.9872	0.9789	0.9854
Freundlich	K_F, (mmol/g)(dm^3/mmol)$^{1/n}$	0.1274	0.0676	0.1359	0.0994
	n	1.0438	1.0199	1.0487	1.0529
	R^2	0.9987	0.9968	0.9939	0.9942
Sips	q_{mS}, mmol/g	0.0467	0.0308	0.0556	0.0349
	K_S, dm^3/mmol	3.0988	4.1619	8.5712	5.9691
	m	1.1274	1.2403	1.3792	1.3376
	R^2	0.9909	0.9919	0.9929	0.9929
Freundlich (in Na_2SO_4)	K_F, (mmol/g)(dm^3/mmol)$^{1/n}$	0.2325	0.0819	0.2235	0.1144
	n	1.0028	1.0599	1.0577	1.1587
	R^2	0.9908	0.9962	0.9994	0.9954

Table 4

TCP sorption capacities of various sorbents

Sorbent	Specific surface area [m^2/g]	Adsorption capacity [mg/g]	Reference
Pumpkin seed shells	–	41.50	this study
Peanut shells	–	34.49	
Sunflower seed hulls	–	30.19	
Walnut shells	–	27.18	
Chitosan	11.8	0.14	[19]
Activated clay	13.2	123.46	[20]
Coconut shells activated carbon	935	122.34	[21]
Acacia leucocephala bark	0.27	256.40	[22]
P. chrysosporium biomass	–	422.54	[23]
Granular activated carbon	929	434.78	[24]
L2S CECA activated carbon	945	573.39	[25]

The comparison of TCP adsorption uptakes for our waste materials and various sorbents described in the literature is difficult. The authors use different units (e.g., mg, mmol) and various mathematical models describing the experimental data. Moreover,

the experiments were carried out at different initial concentration ranges, wastewater composition, pH, and temperatures. Therefore, in the present study, the adsorption properties of the tested materials have been compared with literature data obtained under similar experimental conditions. The K_F values obtained in these studies were in the range from 0.0676 to 0.1359 (mmol/g)(dm^3/mmol)$^{1/n}$ and were comparable with those obtained for peat (0.14) [15], but much lower than the K_F value obtained for the zeolite (1.99) [18]. In Table 4, the maximum sorption capacities of some sorbents used for removal of TCP have been presented.

3.5. EFFECT OF SALT PRESENCE

Water and foremost wastewater effluents are usually high in salinity and contain a certain amount of salt, which may interfere with the adsorption of TCP, thus the effect of salt is an important parameter in adsorption studies. The effect of ionic strength of the solution on the adsorption of TCP onto agricultural wastes was examined under equilibrium conditions. The Freundlich isotherm parameters (K_F and n) characterizing the adsorption of TCP from 0.05 mol/dm^3 sodium sulfate solutions are presented in Table 3. The experimental data indicate that the presence of salt in the solution improves the adsorption capacity of the plant residues. The removal of the TCP increased with the increase in the ionic strength of the solution. This effect was particularly evident for the pumpkin seed shells and the peanut shells for which the K_F values increased twofold (from 0.1359 to 0.2235 and from 0.1274 to 0.2325 (mmol/g)(dm^3/mmol)$^{1/n}$, respectively). It is known that the presence of salts in the solution can modify the electrostatic and hydrophobic-hydrophilic interactions between the adsorbent and adsorbate. When the electrostatic interaction between the adsorbent surface and the adsorbate is attractive, and the surface concentration is sufficiently low, an increase in the ionic strength will decrease the adsorption. On the other hand, when the electrostatic interaction is repulsive, or the surface concentration is sufficiently high, the adsorption will increase with the increased ionic strength which probably occurs during the adsorption of the TCP on the agricultural wastes.

3.6. EFFECT OF pH

pH of an adsorbent solution influences the uptake of adsorbate since pH affects the surface charges of the adsorbent, the degree of ionization of the adsorbent during adsorption and the dissociation or ionization of the adsorbate. The experiments were carried out by changing the initial pH of the solutions from 2.5 to 11.0. The q_e for the initial TCP concentration of 0.25 mmol/dm^3 was plotted versus pH as presented in Fig. 5. As can be seen, the adsorption capacity towards TCP remained stable at pH 2.5–6.0 for walnut shells and at pH 2.5–7.0 for the three other adsorbents and decreased sharply in the alkaline environment. The adsorbate uptake was the highest where pH was below

pK_a of 2,4,6-TCP (6.1 [26]) and below pH_{PZC} of the adsorbent. At pH < pH_{PZC}, the surface of adsorbents was positively charged, while at pH > pH_{PZC}, the surface had a net negative charge. In acidic solution, TCP was undissociated while in basic one, the TCP dissociated, forming phenolate anions.

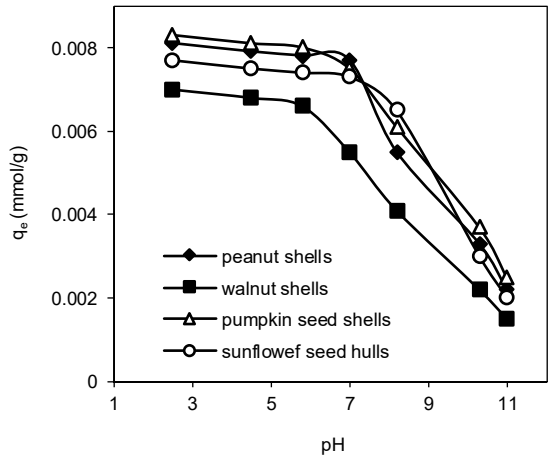

Fig. 5. Effect of pH on the adsorption of TCP onto the plant residues; TCP concentration 0.25 mmol/dm^3, adsorbent dose 25 g/dm^3, 25 °C

The results showed that the undissociated form of TCP was preferred by the positively charged surface of the adsorbents. An increase of pH above 7.0 increased the fraction of negatively charged TCP species and the number of negative charges on the adsorbent surface. As a consequence, electrostatic repulsion between the same charges lowers the adsorption capacity. A similar trend was reported for sorption of TCP on some other materials including activated carbon [21], fly ash [27] and *Acacia leucocephala* bark [22].

3.7. DESORPTION STUDIES

Desorption depends on the strong binding bonds such as covalent and ionic bindings and weak binding forces (e.g., dipole-dipole interaction and Van der Waals forces interactions) formed between the adsorbate molecules and the adsorbent surface. Therefore, the desorption studies can be helpful in explaining the mechanism of adsorption. The TCP adsorbed onto all the plant residues was desorbed in three consecutive cycles using deionized water, water/methanol (50/50) mixture or 5% sodium hydroxide. The results are listed in Table 5.

It has been shown that in distilled water (neutral solution) desorb those TCP molecules that are only weakly attached to the adsorbent. In the first step, the better results were obtained when the alkaline medium was applied, although the total desorption (after three cycles) using water/methanol and 5% NaOH solution was comparable. The

addition of an organic solvent enhanced the elution strength of the solution and improved the TCP solubility which favored desorption. As reported previously, the removal of TCP decrease at the pH increase, and therefore its desorption is also pH dependent. An alkaline solution decreased the interactions due to enhancement of electrostatic repulsion between the adsorbate and the adsorbent which facilitated the desorption of TCP.

Table 5

Adsorption/desorption of TCP on the tested materials

Adsorbent	Adsorption [%]	Solution	Desorption [%]			
			I step	II step	III step	Total
Peanut	70.8	H_2O	27.4	12.0	1.8	41.2
	71.6	H_2O/MeOH	62.8	14.4	0.9	78.1
	72.0	5% NaOH	72.7	4.8	0.7	78.2
Walnut	56.1	H_2O	30.7	15.4	1.2	47.3
	54.4	H_2O/MeOH	71.4	12.5	1.3	85.0
	55.4	5% NaOH	80.2	4.5	0.4	85.1
Pumpkin	72.3	H_2O	24.0	11.1	2.0	37.1
	73.2	H_2O/MeOH	63.3	12.1	1.1	76.5
	72.8	5% NaOH	70.9	5.3	0.5	76.7
Sunflower	64.5	H_2O	33.2	12.8	1.2	47.2
	66.1	H_2O/MeOH	69.2	11.0	1.3	81.5
	65.8	5% NaOH	74.9	6.1	0.4	81.4

The total desorption efficiency of sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells was found to be 81, 77, 85 and 78%, respectively. This suggests that the weak binding forces such as Van der Waals attraction or dipole-dipole interactions are dominant for the adsorption of TCP molecules by tested agricultural wastes. Desorption efficiency decreased in the order: walnut shells > sunflower seed hulls > peanut shells > pumpkin seed shells, and was inversely proportional to the adsorption.

4. CONCLUSIONS

The aim of this work was to determine the potential of application of sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells as adsorbents for removing 2,4,6-trichlorophenol from aqueous solution. The effect of adsorbent dosage, pH and salt presence were investigated. The results showed that the increase in the adsorbent dosage from 5 to 25 g/dm^3 significantly increased the TCP adsorption efficiency from solutions containing chlorophenol in amount of 0.1–0.5 mmol/dm^3. The adsorption was

strongly pH dependent, the adsorption capacity for TCP remained stable at acidic environment and decreased sharply at pH > 7. The presence of salt in the solution improves the adsorption capacity of the adsorbents. The removal of the TCP increased with the increase in the ionic strength of solution. The adsorption process was fast, and it reached equilibrium after about 45 min. The adsorption kinetics was found to follow a pseudo--second order mechanism. The Freundlich, Langmuir as well as the Sips adsorption isotherms were used for mathematical description of the adsorption equilibrium and it was found that experimental data fitted very well to the Freundlich model. Adsorption efficiency of the TCP followed the decreasing sequence: pumpkin seed shells > peanut shells > sunflower seed hulls > walnut shells. The desorption efficiency of biosorbents was approximately 80% which suggests that the weak binding forces such as Van der Waals attraction or dipole-dipole interactions are dominant for the adsorption of TCP molecules by tested agricultural wastes. Consideration of all these results indicate that the sunflower seed hulls, pumpkin seed shells, walnut shells and peanut shells are a potential low-cost materials for the removal of water contaminants. Applying these plant residues as adsorbents could also help to solve the waste disposal problem.

ACKNOWLEDGEMENT

This research has been supported by the Military University of Technology (RMN 08-971).

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