Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22178

117 (2018) 142–148
June

Adsorptive removal of pentachlorophenol from water using agricultural and industrial wastes

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Received 10 December 2017; Accepted 4 March 2018

ABSTRACT

The removal of pentachlorophenol (PCP) from aqueous solution using low-cost biosorbents including sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds was investigated. The effect of experimental parameters such as contact time, initial biosorbent dose, solution pH and ionic strength was evaluated. The adsorption kinetics was investigated according to the pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models. The pseudo-second order model best described the adsorption process. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Sips isotherm models using non-linear regression method. The best results were achieved with the Freundlich model. The values of the Freundlich adsorption parameter (K_F) were 0.127, 0.168, 0.214 and 0.296 (mg/g)(L/mg)$^{1/n}$ for the sunflower seed hulls, milk thistle seeds, hazelnut shells and pine sawdust, respectively. The results showed that the agricultural and industrial wastes may be used as effective adsorbents without any treatment or any other modification for removal of PCP from the aqueous medium.

Keywords: Pentachlorophenol; Adsorption; Low-cost adsorbent

1. Introduction

The population growth as well as increase in industrial and agricultural activities has led to the production of environmental contaminants which are dangerous to the ecosystem and human health. Organic pollutants are present throughout the environment, contaminating *inter alia air*, soil and water including groundwater, surface water and drinking water.

In the last years, many different conventional methods such as biological, chemical and physical processes have been tried for the removal of organic contaminants from aquatic media. Unfortunately, most of them have their advantages and limitations in application. Amongst the numerous purification methods, the adsorption is the most popular and effective technique for water decontamination mainly because of its simplicity, relative flexibility, low cost, ease of operation as well as the no or low generation of harmful substances [1,2]. Currently, activated carbons are the most commonly used adsorbents of proven adsorption efficiency for organic compounds. However, their use in wastewater treatment is restricted due to their high cost and necessity of regeneration. Therefore, the cost-effective alternative technologies are needed and in recent years, extensive research has been undertaken to develop cheaper and effective adsorbents [1–3]. A large variety of non-conventional low-cost adsorbents have been tested for their ability to remove various types of organic contaminants from aqueous media [2–7]. According to the classification proposed by Ali et al. [4] such adsorbents can be classified into: household wastes,

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Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

agricultural products, industrial waste, sea materials, soil and ore materials, as well as metal oxides and hydroxides. These materials have usually low specific surface areas and low adsorption capacities and are thus required in large amounts. Therefore, there is a need to find new, cheap, easily available and highly effective adsorbents.

The objective of this work is to examine the effectiveness of agricultural and industrial wastes such as sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds in removal of pentachlorophenol (PCP) from aqueous solutions. The PCP was chosen as the target water pollutant, because it is poisonous to aquatic life and humans at low level [8] and is found in tap water [9]. In recent years, many adsorbents have been used for PCP removal including activated carbons [10–12] and low-cost adsorbents: peat–bentonite mixtures [13], spent mushroom compost [14], pine bark [15], almond shells [16], natural soil minerals [17] and eggshell [18].

The adsorbents used in this work have already been used to remove various contaminants from water. Sunflower seed hulls were used for the removal of metal ions [19,20], dyes [21–23], trichlorophenol [24] and pesticides [25]. Hazelnut shells were applied for water removal of metal ions [26,27], dyes [28,29] and monochlorophenols [30]. Pine sawdust was used as an adsorbent without treatment for removal of heavy metal ions [31], some dyes [32,33] and chloroorganic compounds [34,35]. Recently, Djelloul and Hasseine [36,37] reported the adsorption of methylene blue from aqueous solution by milk thistle seeds.

However, to our best knowledge, adsorption of PCP from solutions using sunflower seed hulls, hazelnut shells, pine sawdust or milk thistle seeds does not appear to have been studied thus far. Both adsorption kinetic and equilibrium experiments were carried out. Factors affecting adsorption, such as adsorbent dose, pH and presence of inorganic salts were also investigated.

2. Experimental

2.1. Materials

The PCP was obtained from Sigma-Aldrich (St. Louis, MO, USA). The acetonitrile (HPLC grade) and reagent grade sodium hydroxide, sodium chloride, hydrochloric acid and acetic acid were purchased from Chempur (Piekary Slaskie, Poland).

As adsorbents, the sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds were chosen. The raw materials used were collected from a local food, pharmaceutical and furniture manufacturing industry. The materials were washed, dried at room temperature, ground and sieved through a set of laboratory sieves and sieve fraction < 0.5 mm was used in the adsorption experiments. After collection and sieving, the adsorbents were dried in an oven at 120°C to constant mass and stored in a desiccator.

2.2. Adsorption experiments

The batch adsorption experiments were carried out by shaking a series of Erlenmeyer flasks containing different amounts of the adsorbents in 10 mL of different initial solutions of PCP. The samples were agitated at 25°C at constant speed (200 rpm). All of the experiments were carried out in duplicate, and the average values were used for further calculations.

The adsorption isotherms were determined over the concentration range 2–10 mg/L of PCP solutions in a series of Erlenmeyer flasks containing 10 mL solution of each concentration and 0.4 g of the adsorbent. After shaking, the mixtures were filtered (filter discs, 80 g/m^2) and the concentrations of PCP were determined using a high-performance liquid chromatography with UV detection according to the procedure described elsewhere [18]. The amount of PCP adsorbed per unit mass of the adsorbent (q_e, mg/g) was determined using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and the equilibrium concentration of PCP (mg/L) in solution, V is the volume of the solution (L) and m is the mass of the adsorbent (g).

The kinetic studies were conducted for an initial PCP concentration of 5 mg/L. The samples were shaken and taken out at 5, 10, 20, 30, 45, 60, 90 and 120 min. The adsorbent solution mixtures were then filtered and analyzed for the PCP concentration (C_t). The amount of PCP adsorbed onto adsorbent (q_t, mg/g) was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_t is the concentration of PCP at the time t (mg/L).

The effect of solution pH on PCP adsorption was investigated by performing the experiments at various pH levels (from 2.5 to 11.0) adjusted by 0.1 mol/L HCl or 0.1 mol/L NaOH solution. The initial concentration of PCP was fixed at 5 mg/L. The effect of salt presence (ionic strength) on PCP adsorption was investigated similarly with the difference that the adsorbate was adsorbed from the 0.01, 0.05 and 0.1 mol/L solutions of NaCl. The desorption study was conducted by mixing the collected spent adsorbent (0.4 g) with 50% methanol solution. The samples were agitated at 200 rpm for 24 h at room temperature.

3. Results and discussion

3.1. Effect of adsorbent dose

The effect of the adsorbent dose on the PCP adsorption was studied at the adsorbents mass range of 0.1–0.4 g (10–40 g/L), and the adsorbate concentration of 5 mg/L. The percentage removal of PCP as a function of the adsorbent mass is presented in Fig. 1. As can be seen, the adsorption of PCP increased with an increase in the adsorbent dose. The increase in adsorbent mass from 0.1 to 0.4 g resulted in an increase of PCP adsorption from 30% to 84% on sunflower seed hulls, from 41% to 90% on hazelnut shells, from 48% to 96% on pine sawdust and from 34% to 89% on milk thistle seeds. This is due to the fact that increasing the dosage of the adsorbents and keeping the PCP concentration constant

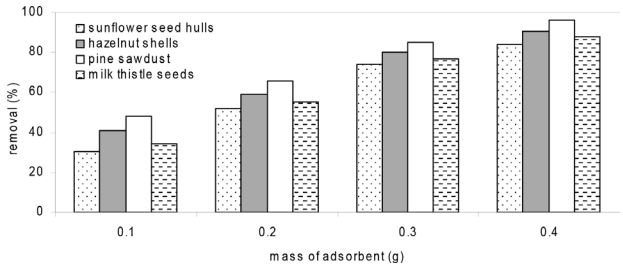

Fig. 1. Effect of adsorbent dose on adsorptive removal of PCP.

makes a large number of sites available for a fixed amount of adsorbate. A dose of 40 g/L (0.4 g) of the adsorbents was considered for further experiments.

3.2. Effect of solution chemistry

The effect of solution pH in the range of 2.5 to 11.0 on the adsorption equilibrium capacity (q_e) of PCP is presented in Fig. 2. The adsorption process depends on the physicochemical properties of the adsorbent and adsorbate as well as on the solution chemistry. Factors from solution chemistry that are most important in the adsorption process are the solution pH and ionic strength. The pH of the solution is a critical parameter as it strongly affects the electrostatic interactions between adsorbent and adsorbate (the adsorbent surface charge, ionization degree and speciation of adsorbate). The presence of salts in the solution (ionic strength) can also modify the strength of the adsorbent–adsorbate electrostatic interactions [38].

As can be seen in Fig. 2, the adsorption of the PCP was almost constant at acidic pH range and decreased with the further increasing in the pH from 7 to 11 for the hazelnut shells, pine sawdust and milk thistle seeds, and from 8 to 11 for the sunflower seed hulls. The value of q_e decreased with an increase in the pH from 2.5 to 11.0 from 0.108 to 0.075 mg/g for sunflower seed hulls, from 0.119 to 0.045 mg/g for hazelnut shells, from 0.130 to 0.051 mg/g for pine sawdust and from 0.112 to 0.061 mg/g for milk thistle seeds, respectively. Less sunflower seed hulls sensitivity to pH changes is probably due to their higher value of the point of zero charge (pH_{PZC}). The pH_{PZC} was determined by the pH drift method and was found to be 4.5, 5.0, 5.7 and 7.6 for the pine sawdust, hazelnut shells, milk thistle seeds and sunflower seed hulls, respectively. The surface charge of the adsorbents is negative when the solution pH is greater than pH_{PZC} and this is positive when $pH < pH_{PZC}$. The PCP dissociation constant (pK_a) is 4.75. Thus, PCP will be mainly in protonated form at $pH < pK_a$ and in deprotonated (ionic) form at $pH > pK_a$. As the pH increased, the degree of dissociation of PCP increased, then the anion species of PCP is predominant in the aqueous solution. The results presented in Fig. 2 showed that the non-dissociated form of PCP is preferred by the positively charged surface of the adsorbents. The strong decrease in adsorption at highly basic conditions suggests a weaker interaction of the negatively charged adsorbent surface with the deprotonated PCP molecules.

The effect of the solution ionic strength on the adsorption of PCP on the low-cost adsorbents is presented in Fig. 3. The results indicate that the presence of salt in the solution

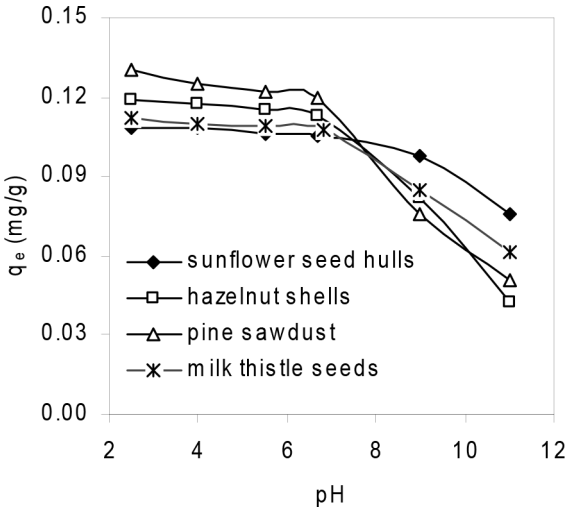

Fig. 2. Effect of initial solution pH on PCP equilibrium adsorption on the waste materials.

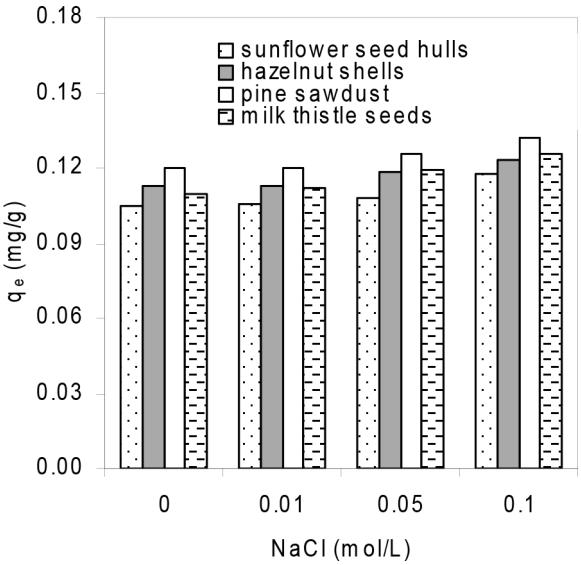

Fig. 3. Effect of ionic strength on the PCP adsorption on the sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds.

slightly improves the adsorption capacity of the adsorbents due to the repulsive interaction between the adsorbent surface and the adsorbate [39]. In comparison with the adsorption from distilled water, the adsorption of the PCP from 0.1 mol/L NaCl solution on all of the adsorbents increased by approximately 10%.

3.3. Adsorption kinetics

Fig. 4 shows the adsorption kinetics of the PCP on sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds. It was observed that the adsorption equilibrium was achieved approximately after 60 min.

Adsorption kinetics of PCP onto agricultural and industrial wastes was analyzed with pseudo-first

order [40] and pseudo-second order [41] kinetic models. The pseudo-first order kinetic model can be written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

Its linear form is given below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

where k_1 is the pseudo-first order rate constant (1/min).

The pseudo-second order equation has the form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

The linear form of the Eq. (5) is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \tag{6}$$

where k_2 is the pseudo-second order rate constant (g/mg·min).

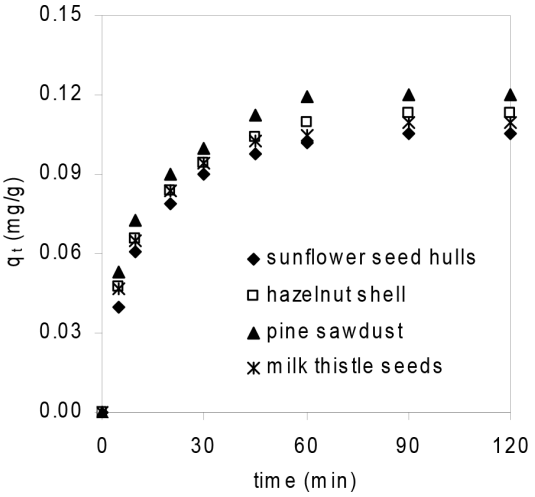

Fig. 4. Adsorption kinetics of PCP on the waste materials.

In the pseudo-first order model, values of q_e and k_1 were obtained from the intercept and slope of the linear graph of $\log(q_e - q_t)$ vs. t. The rate constants of the pseudo-second order adsorption (k_2) were calculated from the straight line plots of t/q_t vs. t. Table 1 presents the kinetic parameters for the adsorption of PCP on the waste adsorbents. The values of R^2 for the pseudo-second order model are higher than those of pseudo-first order model, and the calculated q_e values ($q_{e,CAL}$) are closer to the experimental q_e values ($q_{e,EXP}$). In view of these, it may be concluded that the pseudo-second order kinetic model is more suitable for interpreting the kinetic data in the adsorption system. The k_2 values of the PCP increased in the order: hazelnut shells < sunflower seed hulls ≤ pine sawdust < milk thistle seeds. However, these differences are small.

In order to investigate the mechanism of the PCP adsorption, the intra-particle diffusion model [42] was used:

$$q_t = k_i t^{0.5} + C_i \tag{7}$$

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

Fig. 5 shows the plot of q_t vs. $t^{0.5}$ for the PCP on all of the waste materials. When the regression is linear and intercept is equal to zero, then the intra-particle diffusion is the dominant mechanism of the adsorption. When the regression is linear and intercept is not equal to zero, then the intra-particle diffusion participates in adsorption mechanism but not as the limiting step. The multi-linearity indicates that the adsorption progress consist of several steps. As can be seen in Fig. 5, none of the lines passed through the origin and the plots were not linear over the whole time range. This indicates that more than one process affected the adsorption of the PCP on all four of the biosorbents and that the intra-particle diffusion was not the only rate-controlling step.

3.4. Adsorption and desorption

The adsorption isotherms of the PCP on the sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds are shown in Fig. 6. The equilibrium data were processed according to the Freundlich, Langmuir and Sips isotherms [43].

The Freundlich isotherm is expressed as:

$$q_e = K_F C_e^{1/n} \tag{8}$$

Table 1
Pseudo-first and pseudo-second order rate constants for adsorption of PCP on the waste materials

Kinetic model	Parameter	Adsorbent			
		Sunflower seed hulls	Hazelnut shells	Pine sawdust	Milk thistle seeds
Pseudo-first order	$q_{e,EXP}$ (mg/g)	0.105	0.113	0.120	0.110
	k_1 (1/min)	0.083	0.067	0.084	0.072
	$q_{e,CAL}$ (mg/g)	0.148	0.140	0.145	0.123
	R^2	0.967	0.968	0.972	0.970
Pseudo-second order	k_2 (g/mg·min)	1.044	0.996	1.046	1.121
	$q_{e,CAL}$ (mg/g)	0.114	0.122	0.129	0.118
	R^2	0.999	0.999	0.999	0.999

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

The Langmuir equation is given as follows:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{9}$$

where q_m is a monolayer adsorption capacity (mg/g) and b is the equilibrium adsorption constant (L/mg).

The Sips equation is generally expressed as follows:

$$q_e = \frac{q_{mS} K_S C_e^{\,m}}{1 + K_S C_e^{\,m}} \tag{10}$$

where q_{mS} is the Sips maximum adsorption capacity (mg/g), K_S is the Sips equilibrium constant (L/mg) 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 2. The experimental data were best fitted to the Freundlich isotherm model, since the correlation coefficients calculated for the Freundlich equation were higher than that for the Langmuir and Sips models. This suggests that the adsorption of the PCP on all four waste materials follows the Freundlich model and that the adsorption of PCP may involve multi-layer adsorption. Moreover, the values of the Freundlich constant n were greater than one, indicating a favorable adsorption of PCP by all adsorbents. The values of the Freundlich constant indicative of the relative adsorption capacity (K_F) were 0.127 for the sunflower seed hulls, 0.168 for the milk thistle seeds, 0.214 for the hazelnut shells and 0.296 (mg/g)(L/mg)$^{1/n}$ for the pine sawdust. Also the Langmuir (q_m) as well as the Sips (q_{mS}) adsorption parameters increase in the same order: sunflower seed hulls < milk thistle seeds < hazelnut shells < pine sawdust.

A comparison between the adsorption capacities of the tested materials and other low-cost adsorbents under similar

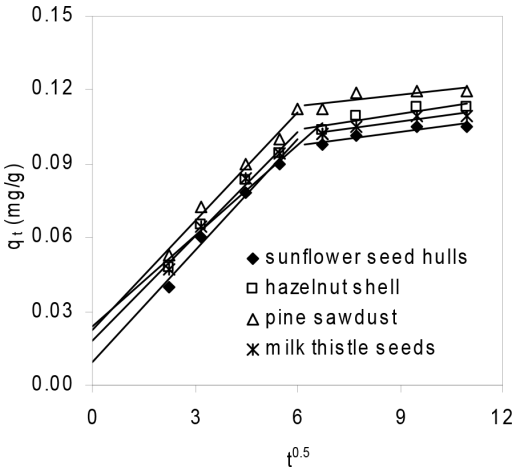

Fig. 5. Intra-particle diffusion plot for PCP adsorption by the sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds.

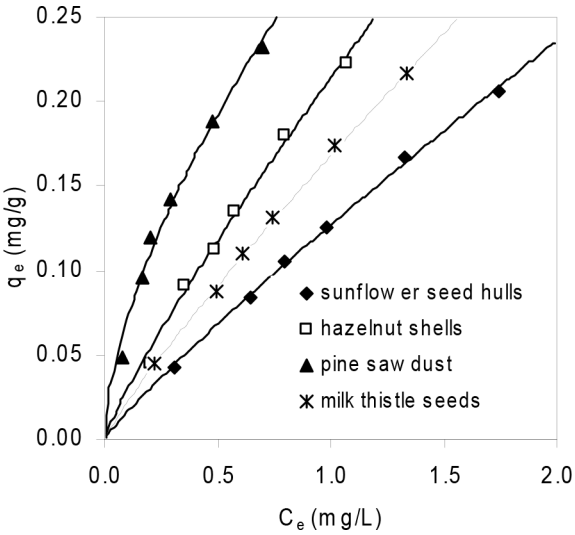

Fig. 6. Adsorption isotherms of PCP from aqueous solutions on the sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds.

Table 2
Freundlich, Langmuir and Sips isotherm model parameters and correlation coefficients for adsorption of PCP on the waste materials

Isotherm model	Parameter	Adsorbent			
		Sunflower seed hulls	Hazelnut shells	Pine sawdust	Milk thistle seeds
Freundlich	K_F (mg/g)(L/mg)$^{1/n}$	0.127	0.214	0.296	0.168
	n	1.117	1.161	1.610	1.130
	R^2	0.998	0.998	0.997	0.998
Langmuir	q_m (mg/g)	0.472	0.658	0.795	0.512
	b (L/mg)	0.113	0.269	0.463	0.159
	R^2	0.909	0.912	0.966	0.923
Sips	q_{mS} (mg/g)	0.352	0.520	0.614	0.409
	K_S (L/mg)	0.177	0.690	0.485	0.137
	m	1.057	1.201	0.891	0.983
	R^2	0.988	0.971	0.981	0.969

Table 3
Comparison of PCP adsorption capacities (K_F) of various low-cost adsorbents

Adsorbent	Freundlich adsorption capacity K_F ((mg/g)(L/mg)$^{1/n}$)	Reference
Pine sawdust	0.296	This study
Hazelnut shells	0.214	This study
Milk thistle seeds	0.168	This study
Sunflower seed hulls	0.127	This study
Pine bark	0.210	[15]
Pencil graphite	0.096	[44]
Almond shell	0.075	[16]
Spent mushroom compost	0.056	[14]
Peat–bentonite mixtures	0.042	[13]
Eggshell	0.028	[18]

conditions is listed in Table 3. As can be seen, the adsorption of the PCP is comparable or greater than on the other low-cost adsorbents. This shows that the agricultural and industrial wastes such as sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds may be used as an effective adsorbents without any treatment or any other modification for removal of PCP from the aqueous medium.

The desorption efficiency of sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds was found to be 85%, 77%, 75% and 81%, respectively. The desorption efficiency decreased in the order: sunflower seed hulls > milk thistle seeds > hazelnut shells > pine sawdust, and was inversely proportional to the adsorption. High desorption efficiency suggests that considerable part of PCP adsorbed was due reversible sorption and that the physisorption has significant effect on PCP removal.

4. Conclusions

The present study showed that sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds are effective in removing of PCP from water. The adsorption was strongly pH dependent, the adsorption capacity for PCP remained stable at acidic environment and decreased sharply in alkaline environment. The presence of inorganic salt in the solution improved the adsorption capacity of the adsorbents. The adsorption kinetics of the PCP on the waste adsorbents follows the pseudo-second order model. The experimental data were well correlated by the Freundlich adsorption isotherm. Adsorption efficiency of the PCP followed the increasing sequence: sunflower seed hulls < milk thistle seeds < hazelnut shells < pine sawdust. The adsorption capacity of the waste materials is comparable or greater than the other low-cost adsorbents. The sunflower seed hulls, hazelnut shells, pine sawdust and milk thistle seeds are available in large quantities, and can, therefore, be used as effective adsorbents for the removal of PCP from aqueous solution. Moreover, after use, they can be utilized as ferment substrates or as fuel for power generation.

References

[1] A. Dąbrowski, P. Podkościelny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, Chemosphere, 58 (2005) 1049–1070.
[2] M.L. Soto, A. Moure, H. Dominguez, J.C. Parajo, Recovery, concentration and purification of phenolic compounds by adsorption: a review, J. Food Eng., 105 (2011) 1–27.
[3] S.H. Lin, R.S. Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review, J. Environ. Manage., 90 (2009) 1336–1349.
[4] I. Ali, M. Hasim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, J. Environ. Manage., 113 (2012) 170–183.
[5] V.S. Tran, H.H. Ngo, W. Guo, J. Zhang, S. Liang, C. Ton-That, X. Zhang, Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water, Bioresour. Technol., 182 (2015) 353–363.
[6] S. De Gisi, G. Lofrano, M. Grassi, M. Notarnicola, Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review, Sustain. Mater. Technol., 9 (2016) 10–40.
[7] M. Sulyman, J. Namiesnik, A. Gierak, Low-cost adsorbents derived from agricultural by-products/wastes for enhancing contaminant uptakes from wastewater: a review, Pol. J. Environ. Stud., 26 (2017) 479–510.
[8] A.T. Proudfoot, Pentachlorophenol poisoning, Toxicol. Rev., 22 (2003) 3–11.
[9] J. Michałowicz, J. Stufka-Olczyk, A. Milczarek, A. Michniewicz, Analysis of annual fluctuations in the content of phenol, chlorophenols and their derivatives in chlorinated drinking waters, Environ. Sci. Pollut. Res., 18 (2011) 1174–1183.
[10] R. Leyva-Ramos, L.A. Bernal-Jacome, J. Mendoza-Barron, M.M.G. Hernandez-Orta, Kinetic modeling of pentachlorophenol adsorption onto granular activated carbon, J. Taiwan Inst. Chem. Eng., 40 (2009) 622–629.
[11] N.T. Abdel-Ghani, G.A. El-Chaghaby, E.M. Zahran, Pentachlorophenol (PCP) adsorption from aqueous solution by activated carbons prepared from corn wastes, Int. J. Environ. Sci. Technol., 12 (2015) 211–222.
[12] N. Douara, B. Bestani, N. Benderdouche, L. Duclaux, Sawdust-based activated carbon ability in the removal of phenol-based organics from aqueous media, Desal. Wat. Treat., 57 (2016) 5529–5545.
[13] T. Viraraghavan, K. Slough, Sorption of pentachlorophenol on peat-bentonite mixtures, Chemosphere, 39 (1999) 1487–1496.
[14] W.M. Law, W.N. Lau, K.L. Lo, L.M. Wai, S.W. Chiu, Removal of biocide pentachlorophenol in water system by the spent mushroom compost of Pleurotus pulmonarius, Chemosphere, 52 (2003) 1531–1537.
[15] I. Bras, L. Lemos, A. Alves, M.F.R. Pereira, Sorption of pentachlorophenol on pine bark, Chemosphere, 60 (2005) 1095–1102.
[16] B.N. Estevinho, N. Ratola, A. Alves, L. Santos, Pentachlorophenol removal from aqueous matrices by sorption with almond shell residues, J. Hazard. Mater., B137 (2006) 1175–1181.
[17] Y. He, F. Zeng, Z. Lian, J. Xu, P.C. Brookes, Natural soil mineral nanoparticles are novel sorbents for pentachlorophenol and phenanthrene removal. Environ. Pollut., 205 (2015) 43–51.
[18] K. Kuśmierek, P. Idźkiewicz, A. Świątkowski, L. Dąbek, Adsorptive removal of pentachlorophenol from aqueous solutions using powdered eggshell, Arch. Environ. Prot., 43 (2017) 10–16.
[19] M. Feizi, M. Jalali, Removal of heavy metals from aqueous solutions using sunflower, potato, canola and walnut shell residues, J. Taiwan Inst. Chem. Eng., 54 (2015) 125–136.
[20] A. Witek-Krowiak, Analysis of temperature-dependent biosorption of Cu^{2+} ions on sunflower hulls: kinetics, equilibrium and mechanism of the process, Chem. Eng. J., 192 (2012) 13–20.

[21] B.H. Hameed, Equilibrium and kinetic studies of methyl violet sorption by agricultural waste, J. Hazard. Mater., 154 (2008) 204–212.
[22] J.F. Osma, V. Saravia, J.L. Toca-Herrera, S. Rodriguez Couto, Sunflower seed shells: a novel and effective low-cost adsorbent for the removal of the diazo dye Reactive Black 5 from aqueous solutions, J. Hazard. Mater., 147 (2007) 900–905.
[23] S.W. Ong, P.S. Keng, S.L. Lee, M.H. Leong, Y.T. Hung, Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annuus*), Int. J. Phys. Sci., 5 (2010) 1270–1276.
[24] K. Kuśmierek, A. Świątkowski, L. Dąbek, Removal of 2,4,6-trichlorophenol from aqueous solutions using agricultural waste as low-cost adsorbents, Environ. Prot. Eng., 43 (2017) 149–163.
[25] R. Rojas, J. Morillo, J. Usero, E. Vanderlinden, H. El Bakouri, Adsorption study of low-cost and locally available organic substances and a soil to remove pesticides from aqueous solutions, J. Hydrol., 520 (2015) 461–472.
[26] T. Altun, E. Pehlivan, Removal of copper(II) ions from aqueous solutions by walnut-, hazelnut- and almond-shells, Clean, 35 (2007) 601–606.
[27] T. Altun, E. Pehlivan, Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell, J. Hazard. Mater., 155 (2008) 378–384.
[28] F. Ferrero, Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, J. Hazard. Mater., 142 (2007) 144–152.
[29] M. Dogan, H. Abak, M. Alkan, Biosorption of methylene blue from aqueous solutions by hazelnut shells: equilibrium, parameters and isotherms, Water Air Soil Pollut., 192 (2008) 141–153.
[30] K. Kuśmierek, A. Świątkowski, Removal of chlorophenols from aqueous solutions by sorption onto walnut, pistachio and hazelnut shells, Pol. J. Chem. Technol., 17 (2015) 23–31.
[31] M.H. Baki, F. Shemirani, R. Khani, Potential of sawdust as a green and economical sorbent for simultaneous preconcentration of trace amounts of cadmium, cobalt, and lead from water, biological, food, and herbal samples, J. Food Sci., 78 (2013) T797–T804.
[32] M. Özacar, I.A. Sengil, A kinetic study of metal complex dye sorption onto pine sawdust, Process Biochem., 40 (2005) 565–572.
[33] A. Witek-Krowiak, Biosorption of malachite green from aqueous solutions by pine sawdust: equilibrium, kinetics and the effect of process parameters, Desal. Wat. Treat., 51 (2013) 3284–3294.
[34] M. Tobiszewski, Sorption of Chlorinated Solvents on Pine and Oak Sawdust, 5th International Conference on Environmental Science and Technology IPCBEE, Vol. 69, 2014, pp. 45–48.
[35] K. Kuśmierek, K. Olkowicz, A. Świątkowski, Efficacy assessment of 2,4,6-trichlorophenol adsorption on sawdust from model water solutions, Ochr. Srod., 37 (2015) 19–24 (in Polish).
[36] C. Djelloul, A. Hasseine, Ultrasound-assisted removal of methylene blue from aqueous solution by milk thistle seed, Desal. Wat. Treat., 51 (2013) 5805–5812.
[37] C. Djelloul, A. Hasseine, O. Hamdaoui, Adsorption of cationic dye from aqueous solution by milk thistle seeds: isotherm, kinetic and thermodynamic studies, Desal. Wat. Treat., 78 (2017) 313–320.
[38] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon, 42 (2004) 83–94.
[39] K. Kuśmierek, A. Świątkowski, The influence of an electrolyte on the adsorption of 4-chlorophenol onto activated carbon and multi-walled carbon nanotubes, Desal. Wat. Treat., 56 (2015) 2807–2816.
[40] S. Lagergren, Theorie der sogenannten adsorption geloester stoffe, K. Sven. Vetensk.akad. Handl., 24 (1898) 1–39.
[41] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.
[42] W. Weber Jr., J. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div., 18 (1963) 31–42.
[43] O. Hamdaoui, E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters, J. Hazard. Mater., 147 (2007) 381–394.
[44] K. Skrzypczyńska, K. Kuśmierek, A. Świątkowski, L. Dąbek, The influence of pencil graphite hardness on voltammetric detection of pentachlorophenol, Int. J. Electrochem. Sci., 13 (2018) 88–100.