

Adsorptive removal of pentachlorophenol from aqueous solutions using powdered eggshell

Krzysztof Kuśmierk¹, Paulina Idźkiewicz¹, Andrzej Świątkowski¹, Lidia Dąbek^{2*}

¹Military University of Technology, Poland
Institute of Chemistry

²University of Technology, Kielce, Poland
Faculty of Environmental Engineering, Geomatics and Power Engineering

*Corresponding author's e-mail: lidiadabek@wp.pl

Keywords: adsorption, pentachlorophenol, eggshell, low-cost adsorbent.

Abstract: The usefulness of untreated powdered eggshell as low-cost adsorbent for the removal of pentachlorophenol (PCP) from aqueous solutions was investigated. The most important parameters affecting the adsorption process, including the pH and ionic strength, were examined. The adsorption characteristics of PCP onto eggshell were evaluated in terms of kinetic and equilibrium parameters. The kinetic data were studied in terms of the pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models. The equilibrium data were analyzed using the Langmuir, Freundlich, Sips and Redlich-Peterson isotherm models. The pseudo-second order model best described the adsorption kinetics. Using the Langmuir equation, the monolayer adsorption capacity of eggshell for PCP was found to be 0.127 mg/g. The results showed that PCP can be effectively removed from aqueous solution employing eggshell as a cheap adsorbent.

Introduction

Chlorinated phenols are widely used in many industrial processes, as synthesis intermediates or as substrates in the manufacturing of pesticides, insecticides, herbicides, wood preservatives, pharmaceuticals, disinfectants or dyes. They are also formed as by-products in the chlorination of drinking water and in the bleaching of pulp with chlorine (Czaplicka 2004). These compounds are highly toxic, persistent and have nasty smell that deteriorates the organoleptic properties of drinking water. Because chlorophenols were found in the water of the Vistula River and drinking water intended for large Polish cities (Michałowicz 2005, Dmitruk et al. 2006, Michałowicz et al. 2011), these compounds are regarded as priority pollutants for which effective removal processes are needed.

Several removal or degradation methods for chlorophenols have been studied extensively. Among them, physical adsorption is generally considered to be the best, effective and most frequently used method. Adsorption is one of the effective methods for the removal of organic pollutants from waste effluent due to its ease of use, high efficiency and sludge-free clean operation. The most popular and widely used adsorbent for removing organic contaminants from water is activated carbon. However, its use is associated with several disadvantages. The 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 alternative adsorbents including natural and biological materials as well

as waste materials from industry and agriculture have been proposed (Ali et al. 2012). These materials are cheap, easily available and disposable without regeneration.

Present investigation addresses the application of unmodified chicken eggshells as a low-cost adsorbent for the removal of chlorophenol from aqueous solutions. Chicken eggshells are a significant solid waste, which is generated on a large scale from household, food industries, bakeries or restaurants. The recent studies show that eggshells can be employed as an effective adsorbent for the removal of metal ions (Flores-Cano et al. 2013, Koumanova et al. 2002, Oke et al. 2008), lignosulfonate (Zulfikar et al. 2012), humic acid (Zulfikar et al. 2013) and dyes including Brilliant Red (Koumanova et al. 2002), Methylene Blue (Tsai et al. 2006), Malachite Green (Chowdhury and Saha 2012), Crystal Violet (Chowdhury et al. 2013) and Congo Red (Zulfikar and Setiyanto 2013). Daraei et al. (2013) investigated the efficiency of eggshell for the removal of phenol from water. The adsorption was dependent upon pH, phenol concentration, initial amount of eggshell and contact time. The adsorption of phenol by eggshell was found to follow the pseudo-first order kinetics and the Freundlich equilibrium models. Koumanova et al. (2002) described the study of adsorption of three chlorophenols including 4-chlorophenol, 2,4-dichlorophenol and 3,5-dichlorophenol on eggshell membranes. They found that the adsorption of dichlorophenols on eggshell membrane was higher than that of 4-chlorophenol. The Langmuir and Redlich-Peterson isotherms better described the adsorption of chlorophenols than the Freundlich isotherm.

In this study, pentachlorophenol (PCP) was selected as the target water contaminant. We chose PCP as the model compound because it is poisonous to aquatic life, plants and humans at low level (Proudfoot 2003) and is found in water (Dmitruk et al. 2006, Michałowicz et al. 2011). As adsorbents for the PCP removal, the peat-bentonite mixtures (Viraraghavan, and Slough 1999), spent mushroom compost (Law et al. 2003), pine bark (Bras et al. 2005), almond shells (Estevinho et al. 2006), fungal biomass (Mathialagan and Viraraghavan 2009), fly ash (Estevinho et al. 2007), carbon nanotubes (Abdel Salam and Burk 2010) as well as activated carbons (Leyva-Ramos et al. 2009, Abdel-Ghani et al. 2015) have been previously used. However, to our best knowledge, the adsorption of pentachlorophenol in the aqueous solutions using unmodified chicken eggshell has not been studied.

In this paper, the removal of pentachlorophenol from aqueous solutions using untreated powdered eggshell was examined. The effects of adsorbent dosage, initial pH and ionic strength on the adsorption of PCP were investigated. The studies were carried out under kinetic and equilibrium conditions. The desorption of PCP was also evaluated.

Materials and methods

Reagents

Pentachlorophenol (PCP) was purchased from Sigma-Aldrich (St. Louis, USA). Sodium hydroxide, sodium sulfate, sodium chloride, hydrochloric acid, acetic acid, methanol and HPLC-grade acetonitrile were obtained from Avantor Performance Materials (Gliwice, Poland). Stock solution of PCP (14 mg/dm³) was made by dissolving its required amount in distilled water.

Adsorbent

Chicken eggshell, collected from a local market, was washed with distilled water, air-dried, ground into powder and sieved to an average particle diameter of 0.5 mm. The eggshell powder thus formed was dried in an oven at 130°C to a constant weight, kept in a desiccator and used as adsorbent without any further pretreatment. The morphology of powdered eggshell was verified by scanning electron microscopy. The SEM analysis was performed with scanning electron microscope QUANTA 250 FEG (FEI). The p*H*_{pzc} (point of zero charge) of the eggshell was determined by the pH drift method.

Adsorption studies

Batch experiments were carried out to examine the adsorption properties of unmodified eggshell. All of the adsorption experiments were conducted at a room temperature of 25°C in Erlenmeyer flasks contacting different initial solutions of PCP (0.01 dm³) with a given amount of eggshell.

The effect of initial dosage was checked in a set of Erlenmeyer's flasks containing 0.01 dm³ of 7 mg/dm³ PCP mixed with different weights of eggshell (from 0.1 to 2.0 g) and shaken at a constant agitation speed of 200 rpm using a laboratory shaker for 4 h until equilibrium was reached.

The kinetic studies were conducted for two initial PCP concentrations of 5 and 10 mg/dm³ and mass of the adsorbent of 1 g. The flasks were agitated at 200 rpm and a 0.02 cm³ sample solution was withdrawn from the mixture at fixed time intervals and filtered. The filtrates were then analyzed for

residual PCP concentration using a high-performance liquid chromatography (HPLC). The amount of adsorption at time *t*, *q_t* (mg/g), was calculated by the following equation:

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

where *C*₀ and *C*_{*t*} are the initial PCP concentration and its concentration at time *t* (mg/dm³), *V* is the volume of the solution (dm³) and *m* is the mass of the eggshell (g).

The equilibrium studies were conducted by contacting 0.01 dm³ of PCP solutions of concentration 2, 4, 6, 7, 8, 10, 12 and 14 mg/dm³ with 1 g of the eggshell. After 4 h, the mixtures were filtered and analyzed. The equilibrium amount of the PCP adsorbed per unit mass of eggshell, *q_e* (mg/g), was calculated by the equation:

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

where *C_e* is the equilibrium concentration of PCP (mg/dm³) in solution.

In order to investigate the effect of pH a mass of 1 g of eggshell was added to a number of Erlenmeyer's flasks containing 0.01 dm³ of 7 mg/dm³ PCP solution. The pH of the solutions was adjusted over the pH range 4–10 using 0.1 mol/dm³ HCl or 0.1 mol/dm³ NaOH (prior to the addition of the adsorbent). The solution pH was measured using a pH meter. The effect of the ionic strength on the adsorption of the PCP was investigated according to the same procedure with a difference that it was adsorbed from the solutions containing various amounts of sodium sulfate. All the experiments were carried out in duplicate, and average values were used for further calculations. The maximum deviation was found to be below 5%.

Desorption studies

Desorption of the PCP was investigated according to a similar procedure as the equilibrium studies. The solutions of PCP with different initial concentrations (2, 4, 6, 7, 8, 10, 12 and 14 mg/dm³) were added to an Erlenmeyer flasks containing 1 g of eggshell and agitated at 200 rpm for 4 hours. After completion of the adsorption study, the mixtures were filtered and the concentration of the PCP was measured while the eggshells were separated from the solution and dried in an oven at 110°C for 6 h. Next, the same amount of eggshell was placed in an Erlenmeyer flask containing 0.01 dm³ of methanol. The flasks were then kept in a shaker at 200 rpm for 4 h. After this period of time, the mixtures were filtered again and analyzed.

Analytical method

The concentration of PCP was measured by reversed phase high-performance liquid chromatography with UV detection (Shimadzu LC-20, Kyoto, Japan). The chromatographic measurements were carried out on a Luna C₁₈, 4.6×150 mm, 3 μm column (Phenomenex, Torrance, CA, USA). The mobile phase was a mixture of acetonitrile and water adjusted to pH 3.0 using acetic acid (70/30, v/v). The flow rate of the mobile phase was set at 0.25 cm³/min in the isocratic mode, and an

analytical wavelength was 295 nm. The calibration plot of peak height vs. PCP concentration showed a linear working range from 0.1 to 14 mg/dm³ ($y = 2.167x + 0.408$) with a correlation coefficient of 0.996.

Results and Discussion

Eggshell properties

The scanning electron micrographs of eggshell are presented in Figure 1. The images confirm the porous nature of eggshell. Other methods conventionally used for the characterization of adsorbents (e.g. Fourier transform infrared spectroscopy, X-Ray diffraction) were not used. The characterization of eggshells was previously reported by many authors and, consequently, their physicochemical properties are well researched and documented (Carvalho et al. 2011, Guru and Dash 2014, Tsai et al. 2006, Zulfikar et al. 2013). The chemical composition of the eggshell was reported as 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and approximately 4% of organic matter (Carvalho et al. 2011). The whole eggshell is composed of calcium carbonate (eggshell) and eggshell membrane (ESM). The results from the elemental analyzer (Tsai et al. 2006) revealed that the eggshell contains carbon C (13.1 wt.%), hydrogen H (0.4 wt.%), nitrogen N (0.5 wt.%) and oxygen O (29.5 wt.%) while the eggshell membrane is composed of C (47.5 wt.%), H (6.8 wt.%), N (15.3 wt.%), O (12.0 wt.%) and sulfur S (3.0 wt.%). The pore properties between eggshell and eggshell membrane are very similar. The Brunauer-Emmett-Teller (BET) surface area of the eggshell and eggshell membrane were found to be 1.023 ± 0.339 and 1.294 ± 0.424 m²/g, respectively (Tsai et al. 2006).

Effect of adsorbent dose

The effect of the adsorbent dose was studied at a room temperature (25°C) by varying the eggshell amounts of 0.1, 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 g. The percentage removal of PCP increased on average from 24 to about 77% as the adsorbent dosage increased from 0.1 g up to 2.0 g due to the greater availability of the surface area at higher concentration of the adsorbent. A dose of 1.0 g of eggshell was considered for further experiments.

Adsorption kinetics

Fig. 2a presents the adsorption kinetics of pentachlorophenol on eggshell. As shown, the contact time needed for the PCP solutions to reach equilibrium is approximately 10 min. Almost no remarkable improvement was observed after a longer contact time. After this equilibrium period, the amount of PCP adsorbed did not change significantly with time.

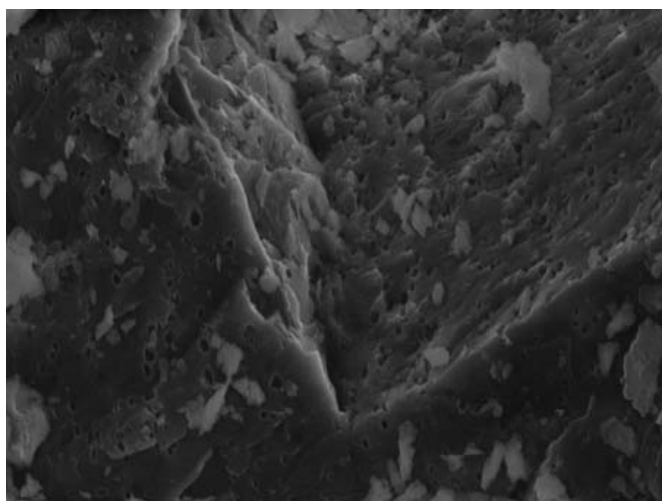
The Lagergren (1898) pseudo-first order equation and the pseudo-second order model (Ho and McKay 1999) were used to fit the experimental results obtained herein. These models are given under by the following equations:

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

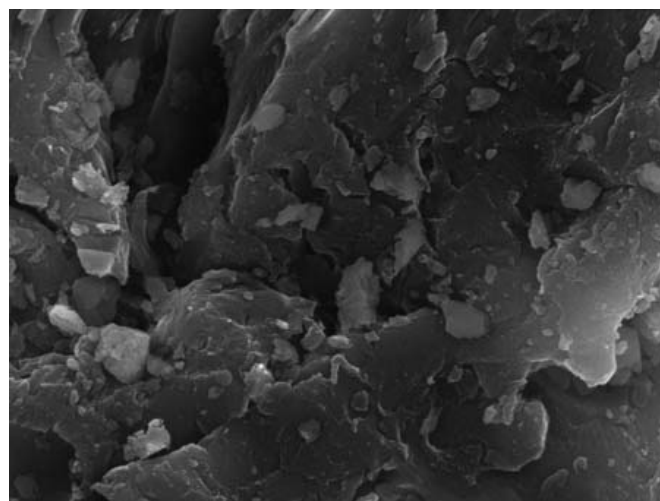
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_t is the adsorption capacity (mg/g) at any time t , k_1 (1/min) is the pseudo-first order adsorption rate constant, and k_2 (g/mg min) is the pseudo-second order adsorption rate constant. The values of the k_1 and k_2 were determined from the linear plots of the graph and their values are given in Table 1.

For the same amount of adsorbent, the adsorption rate decreased with the increase of initial PCP concentration in solution. The higher value of R^2 calculated in the case of pseudo-second order kinetic model indicates better fitness of the data and indicates that the adsorption follows pseudo-second order kinetics. Table 1 shows also that the calculated q_e is much closer to experimental q_e in the case of pseudo-second order model. A similar observation was reported for adsorption of PCP on fungal biomass (Mathialagan and Viraraghavan 2009) and activated carbons (Abdel-Ghani et al. 2015). The opposite results were reported for the adsorption kinetics of phenol on eggshell, where the pseudo-first order model was more reasonable than the second-order one (Daraei et al. 2013). However, the values of R^2 obtained for both kinetic models were very similar (Daraei et al. 2013).



a) X 5000



b) x 10000

Fig. 1. Selected SEM images of eggshell

The intra-particle diffusion model (Weber and Morris 1963) was also applied to explain PCP adsorption mechanism on eggshell. The mathematical expression for this model is:

$$q_t = k_i t^{1/2} + C_i \quad (5)$$

where k_i is intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$) and C_i describes the boundary layer thickness (mg/g).

The plots of q_t vs. $t^{1/2}$ (Fig. 2b) were non-linear over the whole time range indicating that adsorption process takes place in two main steps. The first step represents rapid surface adsorption of PCP molecules via boundary layer diffusion, in which adsorbate molecules move from bulk solution to the external surface of adsorbent. The second step describes the diffusion of the adsorbate from the external surface into the pores of the adsorbent. The multi-linearity indicates that more than one process affected the adsorption. Moreover, the lines did not pass through the origin hence intra-particle diffusion was not the only rate limiting mechanism.

Adsorption isotherm

The adsorption isotherm of the pentachlorophenol on untreated powdered eggshell is presented in Fig. 3. The experimental data for the removal of PCP were tested with different isotherm models including Langmuir, Freundlich, Sips and Redlich-Peterson (Rangabhashiyam et al. 2014). All model parameters were calculated by a nonlinear least-squares method using OriginPro 7.5 software. The isotherm equations and the calculated adsorption constants are presented in Table 2. The goodness of fit of the isotherm models was assessed by computing the normalized standard deviation (Δq) with the following equation:

$$\Delta q = 100 * \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{cal}}) / q_{\text{exp}}]^2}{N - 1}} \quad (6)$$

where N is the number of data points. It was considered that the adsorption isotherm model with the lower Δq as well as the higher correlation coefficient (R^2) better fitted the experimental data.

By comparing the R^2 and Δq values, it can be concluded that the Langmuir, Sips and Redlich-Peterson isotherm models adequately fitted the adsorption process of PCP. The Freundlich isotherm equation was less suitable than other models ($R^2 = 0.982$, $\Delta q = 7.444\%$).

The adsorption capacity of eggshell was found to be 0.127 mg/g by using the Langmuir model. The maximum adsorption capacities for PCP removal onto various adsorbents as previously reported in the literature were as follows: 40.2 mg/g for fungal biomass (Mathialagan and Viraraghavan 2009), 12.9 mg/g for commercial activated charcoal (Abdel Salam and Burk 2010), 8.2 mg/g for multi-walled carbon nanotubes (Abdel Salam and Burk 2010), 9.1 mg/g for coconut shell-based activated carbon (Abdel-Ghani et al. 2015), 5.3 mg/g for activated carbons prepared from corn cobs (Abdel-Ghani et al. 2015), 7.1 mg/g for activated carbons from corn nodes (Abdel-Ghani et al. 2015) and 2.5 mg/g for fly ash (Estevinho et al. 2007).

The Freundlich constants K_F for adsorption of PCP on eggshell was found to be $0.028 (\text{mg/g}) \cdot (\text{dm}^3/\text{mg})^{1/n}$. For comparison, the values of K_F were: 0.21 for pine bark (at $\text{pH} = 7$) (Bras et al. 2005), 0.075 for almond shell (Estevinho et al. 2006), 0.056 for spent mushroom compost (Law et al. 2003) and $0.042 (\text{mg/g}) \cdot (\text{dm}^3/\text{mg})^{1/n}$ for peat-bentonite

Table 1. The pseudo-first order and pseudo-second order kinetic parameters for PCP adsorption on eggshell

PCP	$q_{e(\text{EXP})}$ (mg/g)	pseudo-first order			pseudo-second order		
		k_1 (1/min)	$q_{e(\text{CAL})}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e(\text{CAL})}$ (mg/g)	R^2
5 mg/dm ³	0.033	0.166	0.016	0.826	65.87	0.034	0.999
10 mg/dm ³	0.063	0.082	0.047	0.843	45.88	0.064	0.999

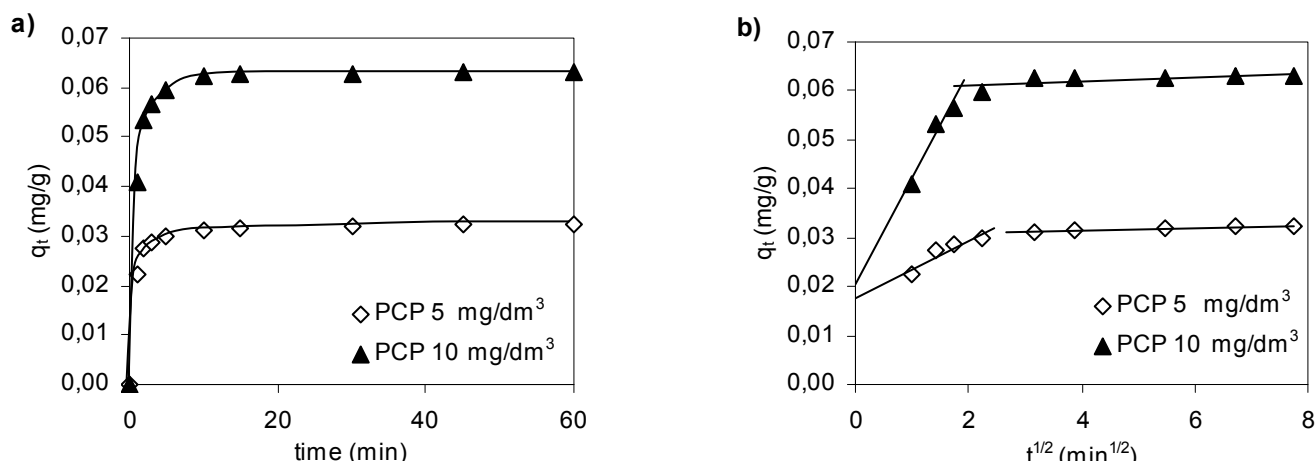


Fig. 2. Adsorption kinetics of PCP (a) and the intra-particle diffusion model for the adsorption of PCP on eggshell (b)

Table 2. The isotherm model parameters for adsorption of PCP on eggshell

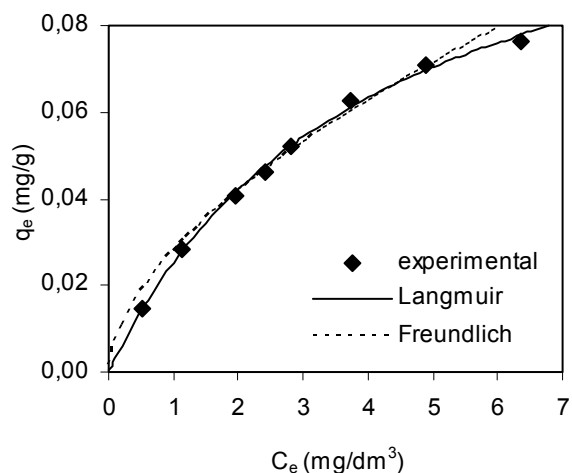
Adsorption model	Equation	Parameter	Value
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_m (mg/g)	0.127
		K_L (dm ³ /mg)	0.249
		R^2	0.997
		Δq (%)	2.162
Freundlich	$q_e = K_F C_e^{1/n}$	K_F ((mg/g) (dm ³ /mg) ^{1/n})	0.028
		n	1.718
		R^2	0.982
		Δq (%)	7.444
Sips	$q_e = \frac{q_m K_S C_e^m}{1 + K_S C_e^m}$	q_m (mg/g)	0.124
		K_S (dm ³ /mg)	0.254
		m	1.017
		R^2	0.997
		Δq (%)	2.383
Redlich-Peterson	$q_e = \frac{A C_e}{1 + B C_e^\beta}$	A (dm ³ /g)	0.029
		B (dm ³ /mg)	0.179
		β	1.114
		R^2	0.997
		Δq (%)	2.806

mixture (Viraraghavan and Slough 1999). As can be seen, the adsorption capacity of eggshell is lower in comparison with other adsorbents.

Effect of pH and ionic strength

The solution chemistry, especially the solution pH and ionic strength, is a very important factor which influences the adsorption process.

The effect of pH on the removal of PCP was investigated and the results are presented in Fig. 4a. The adsorption experiment of PCP was performed in 4–10 pH range because over the range of pH the solubility of calcium carbonate (the main component of the eggshell) is low (below 1%) (Flores-Cano et al. 2013). The percentage of CaCO₃ dissolved doubles while the solution pH is reduced from 4 to 3 and increases considerably at pH below 3 (Flores-Cano et al. 2013). The maximum adsorption of the PCP was achieved at pH 4 (0.057 mg/g). The adsorption amount decreased slowly after pH 5 and it was approximately constant in the pH range of 6–10. The percentage removal decreased from 81% to 65% when increasing the pH from 4 to 10. The solution pH plays an important role in controlling the surface charge of the adsorbent as well as the degree of ionization of the adsorbate in the solution. The pentachlorophenol has a pKa value of 4.75. Thus, PCP will be mainly in protonated form at pH < pKa and in deprotonated (ionic) form at pH > pKa. The point of zero charge (pH_{pzc}) of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. The pH_{pzc} of eggshell was found to be 11.2 and was comparable to the values reported in previous paper 11.4 (Flores-Cano et al. 2013). When the solution pH is greater than pH_{pzc} the surface of eggshell is negatively charged. At lower pH values (pH < pH_{pzc}) the surface charge of

**Fig. 3.** Adsorption isotherm of PCP eggshell

the adsorbent may get positively charged. The results showed that the non-dissociated form of PCP was preferred by the positively charged surface of the eggshell. Based on these facts as well as the literature data (Abdel-Ghani et al. 2015), one could expect the large reduction in the PCP adsorption at highly basic conditions (above the pH_{pzc}) as a result of electrostatic repulsion between the negatively charged eggshell and the dissociated PCP molecules.

The effect of ionic strength is another important parameter in adsorption studies due to the fact that the presence of salts in the solution can modify the strength of the adsorbent-adsorbate electrostatic interactions. When the electrostatic interaction between the adsorbent surface and the adsorbate is repulsive, or the surface concentration is sufficiently high, the

adsorption will increase with the increased ionic strength. On the other hand, when the electrostatic interaction is attractive, and the surface concentration is sufficiently low, an increase in the ionic strength will decrease the adsorption. The effect of the sodium sulfate concentration on the adsorption of PCP on the eggshell is presented in Fig. 4b. The experimental data indicate that the presence of salt in the solution improves the adsorption capacity of the eggshell. The q_e value increased with an increase in sodium sulfate concentration in the solution from 0.046 mg/g (distilled water) to 0.058 mg/g (0.1 mol/dm³

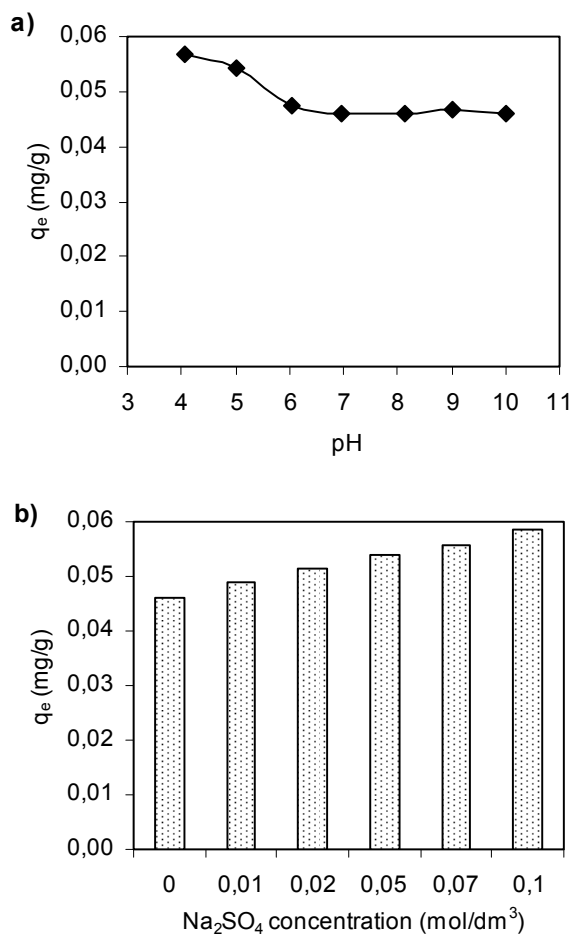


Fig. 4. Effects of initial solution pH (a) and ionic strength (b) on equilibrium adsorption of PCP on eggshell. Initial concentration of PCP = 7 mg/dm³

Table 3. Adsorption and desorption of PCP on eggshell

C_0 (mg/dm ³)	Adsorption (%)	Desorption (%)
2	12.90	7.16
4	28.65	7.41
6	32.42	7.09
7	34.11	7.21
8	35.23	7.70
10	37.36	7.80
12	40.86	7.78
14	45.48	7.89

Na₂SO₄). The values of the Langmuir (q_m) and Freundlich (K_F) constants obtained for the adsorption of PCP on eggshell in the electrolyte solutions (0.1 mol/dm³) were 0.140 mg/g and 0.041 (mg/g)·(dm³/mg)^{1/n} respectively, and were slightly higher than those obtained in water (0.127 mg/g and 0.028 (mg/g)·(dm³/mg)^{1/n}, respectively). A similar dependency, enhanced adsorption of chlorophenol in salt presence, was observed for the adsorption of 4-chlorophenol on F-400 activated carbon (Kuśmierk and Świątkowski 2015).

Desorption studies

The results obtained in the adsorption/desorption experiments are presented in Table 3. As can be seen, the adsorption of PCP increased with an increase of the initial concentration of adsorbate in the solution, however, the desorption was more or less constant. The desorption percentages were not high. The total desorption efficiency of eggshell was found to be from 7.09 to 7.89%. 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. The results suggest that the force of attraction existing between adsorbate and adsorbent are of almost the same strength as chemical bonds and that the removal of the PCP from water on eggshell takes place by means of chemisorption rather than physisorption.

Conclusions

In this paper, the removal of pentachlorophenol from aqueous solutions by adsorption on untreated powdered eggshell was investigated. The effects of adsorbent dosage, initial pH and ionic strength on the adsorption of PCP were studied. The adsorption characteristics of PCP onto eggshell were evaluated in terms of kinetic and equilibrium parameters. Rapid adsorption occurred within the first 2 min and equilibrium was reached within 10 min. The adsorption kinetics of PCP on eggshell followed the pseudo-second order kinetic model rather than the Langergen model. The Langmuir ($R^2 = 0.997$), Freundlich ($R^2 = 0.982$), Sips ($R^2 = 0.997$) and Redlich-Peterson ($R^2 = 0.997$) isotherms were fitted to describe the equilibrium of PCP adsorption process.

References

- Abdel Salam, W. & Burk, R.C. (2010). Thermodynamics and kinetics studies of pentachlorophenol adsorption from aqueous solutions by multi-walled carbon nanotubes, *Water, Air, & Soil Pollution*, 210, pp. 101–111.
- Abdel-Ghani, N.T., El-Chaghaby, G.A. & Zahran, E.M. (2015). Pentachlorophenol (PCP) adsorption from aqueous solution by activated carbons prepared from corn wastes, *International Journal of Environmental Science and Technology*, 12, pp. 211–222.
- Ali, I., Asim, M. & Khan, T.A. (2012). Low cost adsorbents for the removal of organic pollutants from wastewater, *Journal of Environmental Management*, 113, pp. 170–183.
- Bras, I., Lemos, L., Alves, A. & Pereira, M.F.R. (2005). Sorption of pentachlorophenol on pine bark, *Chemosphere*, 60, pp. 1095–1102.
- Carvalho, J., Araujo, J. & Castro, F. (2011). Alternative low-cost adsorbent for water and wastewater decontamination derived from eggshell waste: An overview, *Waste and Biomass Valorization*, 2, pp. 157–167.

- Chowdhury, S. & Saha, P.D. (2012). Utilization of a domestic waste – eggshells for removal of hazardous Malachite Green from aqueous solutions, *Environmental Progress & Sustainable Energy*, 31, 3, pp. 415–425.
- Chowdhury, S., Chakraborty, S. & Saha, P.D. (2013). Removal of Crystal Violet from aqueous solution by adsorption onto eggshells: equilibrium, kinetics, thermodynamics and artificial neural network modeling, *Waste and Biomass Valorization*, 4, pp. 655–664.
- Czaplicka, M. (2004). Sources and transformations of chlorophenols in the natural environment, *Science of the Total Environment*, 322, pp. 21–39.
- Daraei, H., Mittal, A., Noorisepehr, M. & Daraei, F. (2013). Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, *Environmental Science and Pollution Research*, 20, pp. 4603–4611.
- Dmitruk, U., Zbieć, E. & Dojlido, J. (2006). Occurrence and assay of chlorophenols in aquatic environment, *Ochrona Środowiska*, 32(3), pp. 25–28. (in Polish)
- Estevinho, B.N., Martins, I., Ratola, N., Alves, A. & Santos, L. (2007). Removal of 2,4-dichlorophenol and pentachlorophenol from waters by sorption using coal fly ash from a Portuguese thermal power plant, *Journal of Hazardous Materials*, 143, pp. 535–540.
- Estevinho, B.N., Ratola, N., Alves, A. & Santos, L. (2006). Pentachlorophenol removal from aqueous matrices by sorption with almond shell residues, *Journal of Hazardous Materials*, B137, pp. 1175–1181.
- Flores-Cano, J.V., Leyva-Ramos, R., Mendoza-Barron, J., Guerrero-Coronado, R.M., Aragón-Pina, A. & Labrada-Delgado, G.J. (2013). Sorption mechanism of Cd(II) from water solution onto chicken eggshell, *Applied Surface Science*, 276, pp. 682–690.
- Guru, P.S. & Dash, S. (2014). Sorption on eggshell waste – A review on ultrastructure, biomineralization and other applications, *Advances in Colloid and Interface Science*, 209, pp. 49–67.
- Ho, Y.S. & McKay, G. (1999). Pseudo-second-order model for sorption processes, *Process Biochemistry*, 34, pp. 451–465.
- Koumanova, B., Peeva, P., Allen, S.J., Gallagher, K.A. & Healy, M.G. (2002). Biosorption from aqueous solutions by eggshell membranes and *Rhizopus oryzae*: equilibrium and kinetic studies, *Journal of Chemical Technology and Biotechnology*, 77, pp. 539–545.
- Kuśmierek, K. & Świątkowski, A. (2015). The influence of an electrolyte on the adsorption of 4-chlorophenol onto activated carbon and multi-walled carbon nanotubes, *Desalination and Water Treatment*, 56, pp. 2807–2816.
- Lagergren, S. (1898). The theory of so-called adsorption of soluble substances, *Vetenskapsakademien Handlingar*, 24, pp. 1–39.
- Law, W.M., Lau, W.N., Lo, K.L., Wai, L.M. & Chiu, S.W. (2003). Removal of biocide pentachlorophenol in water system by the spent mushroom compost of *Pleurotus pulmonarius*, *Chemosphere*, 52, pp. 1531–1537.
- Leyva-Ramos, R., Bernal-Jacome, L.A., Mendoza-Barron, J. & Hernandez-Orta, M.M.G. (2009). Kinetic modeling of pentachlorophenol adsorption onto granular activated carbon, *Journal of the Taiwan Institute of Chemical Engineers*, 40, pp. 622–629.
- Mathialagan, T. & Viraraghavan, T. (2009). Biosorption of pentachlorophenol from aqueous solutions by a fungal biomass, *Bioresource Technology*, 100, pp. 549–558.
- Michałowicz, J. (2005). The occurrence of chlorophenols, chlorocatechols and chlorinated methoxyphenols in drinking water of the largest cities in Poland, *Polish Journal of Environmental Studies*, 14, pp. 327–333.
- Michałowicz, J., Stufka-Olczyk, J., Milczarek, A. & Michniewicz, M. (2011). Analysis of annual fluctuations in the content of phenol, chlorophenols and their derivatives in chlorinated drinking waters, *Environmental Science and Pollution Research*, 18, pp. 1174–1183.
- Oke, I.A., Olorinoye, N.O. & Adewusi, S.R.A. (2008). Adsorption kinetics for arsenic removal from aqueous solutions by untreated powdered eggshell, *Adsorption*, 14, pp. 73–83.
- Proudfoot, A.T. (2003). Pentachlorophenol poisoning, *Toxicological Reviews*, 22, pp. 3–11.
- Rangabhashiyam, S., Anu, N., Giri Nandagopal, M.S. & Selvaraju, N. (2014). Relevance of isotherm models in biosorption of pollutants by agricultural byproducts, *Journal of Environmental Chemical Engineering*, 2, pp. 398–414.
- Tsai, W.T., Yang, J.M., Lai, C.W., Cheng, Y.H., Lin, C.C. & Yeh, C.W. (2006). Characterization and adsorption properties of eggshells and eggshell membrane, *Bioresource Technology*, 97, pp. 488–493.
- Viraraghavan, T. & Slough, K. (1999). Sorption of pentachlorophenol on peat-bentonite mixtures, *Chemosphere*, 39, 9, pp. 1487–1496.
- Weber, Jr., W. & Morris, J. (1963). Kinetics of adsorption on carbon from solution, *Journal of the Sanitary Engineering Division*, 18, pp. 31–42.
- Zulfikar, M.A. & Setiyanto, H. (2013). Study of the adsorption kinetics and thermodynamic for the removal of Congo Red from aqueous solution using powdered eggshell, *International Journal of ChemTech Research*, 5, 4, pp. 1671–1678.
- Zulfikar, M.A., Mariske, E.D. & Djajanti, S.D. (2012). Adsorption of lignosulfonate compounds using powdered eggshell, *Songklanakarinn Journal of Science and Technology*, 34, 3, pp. 309–316.
- Zulfikar, M.A., Novita, E., Hertadi, R. & Djajanti, S.D. (2013). Removal of humic acid from peat water using untreated powdered eggshell as a low cost adsorbent, *International Journal of Environmental Science and Technology*, 10, pp. 1357–1366.

Adsorpcja pentachlorofenolu na skorupkach jaj

Streszczenie: Dokonano oceny przydatności niemodyfikowanych skorupki jaj jako taniego adsorbentu do usuwania pentachlorofenolu (PCP) z roztworów wodnych.

Zbadano najważniejsze parametry mające wpływ na proces adsorpcji, między innymi wpływ pH oraz siły jonowej roztworu. Zbadano zarówno kinetykę adsorpcji PCP jak i adsorpcję równowagową. Do opisu kinetyki zastosowano równania kinetyczne pseudo-pierwszego i pseudo-drugiego rzędu oraz model dyfuzji wewnątrzcząstkowej. Izotermy adsorpcji były analizowane za pomocą równań Langmuira, Freundlicha, Sipsa oraz Redlicha-Petersona.

Kinetyka adsorpcji PCP na skorupkach jaj przebiegała zgodnie z modelem pseudo-drugiego rzędu. Maksymalna pojemność adsorpcyjna skorupki jaj w stosunku do PCP, wyznaczona na podstawie równania izotermy Langmuira, wynosiła 0,127 mg/g.

Wyniki badań pokazały, że skorupki jaj są interesującym adsorbentem do usuwania pentachlorofenolu z roztworów wodnych.