THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 1 - 2022, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2022.1.07

REMOVAL OF DRUG POLLUTANTS FROM AQUEOUS MEDIA USING CLAM SHELLS WASTE

Petronela NECHITA, Marilena CRĂCIUN, Carmen Elena OCHIROȘI
"Dunarea de Jos" University of Galati, Department of Environmental, Applied Engineering and Agriculture, Romania
e-mail: petronela.nechita@ugal.ro

ABSTRACT

The pharmaceutical products represent a serious environmental issue in the municipal wastewaters and waste water treatment plants (WWTP). Due to their resistance to biological degradation, the elimination of these pollutants is difficult. In the last years, paracetamol has been detected in higher concentrations in wastewaters. In order to avoid disturbing the aquatic life, economically viable procedures should be identified for removing these types of pollutants. In this context, the present paper has evaluated the efficiency of clam shells waste for retaining paracetamol molecules dispersed in aqueous solutions. The obtained results showed that high removal efficiency is obtained for 60 minutes adsorption duration and a ratio of about 1:100 clam shells: aqueous solution.

KEYWORDS: wastewater treatment, paracetamol, clam shells, adsorption

1. Introduction

The pharmaceutical products represent a serious environmental issue in the municipal wastewaters (MWW) and waste water treatment plants (WWTP). Due to their resistance to biological degradation, the elimination of these pollutants is difficult.

Residual concentrations of pharmaceutical compounds in post-treated MWW can bio-accumulate and cause ecotoxicological damages and indirect acute and chronic toxicity to humans.

In 2018, the European Environmental Agency (EEA) reported that pharmaceuticals are responsible for endocrine-disrupting effects on animals and humans and inhibit photosynthesis or plant growth [1].

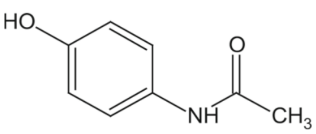


Fig. 1. *Chemical structure of paracetamol (N-acetyl-p-aminophenol)*

The occurrence of pharmaceutical products in MWW may be associated with pharmaceutical and hospital effluents, human and animal excretions, improper disposal of pharmaceutical products, and previously contaminated ground or freshwater used as a primary source for the production of freshwater for human consumption (Table 1).

Paracetamol (PAR) is the priority drug in the aquatic environment based on criteria of toxicity and persistence in the environment (Figure 1) [2].

Paracetamol is commonly disposed into the aquatic environment and can cause hepatotoxicity and nephrotoxicity towards aquatic animals, which eventually results in aquatic death or affects the next level of consumers [2, 3].

In the last years, paracetamol has been detected in higher concentrations in wastewaters. In order to avoid disturbing the aquatic life, economically viable procedures should be identified for removing these types of pollutants.

However, efficient and low-cost methods to deal with the environmental and health problems of paracetamol must be implemented.

Adsorption is extensively used for the removal of PAR from the environment usually at concentrations lower than ppm [4]. Compared to the advanced oxidation process (AOP), adsorption is less costly and less energy consuming. The adsorption can be considered a more advantageous removal method, as it is less complex, easy to apply, and can use cheap, naturally occurring adsorbent materials, even of the biomass waste type.

Activated carbon is one of the best adsorbents to remove common synthetic pollutants from water, and

N°. 1 - 2022, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2022.1.07

was proved to be efficient up to concentrations lower than ppm, which is solely due to its highly developed microporosity and surface area [4].

Clam shells (mussels, clams) have the ability to efficiently remove pollutants from wastewater (metal ions), due to the presence of aragonite, a biogenic form of calcium carbonate, which exhibits ion exchange properties (Table 2).

Table 1. *The concentration of several common analgesic and antipyretic drugs found in the aquatic environment* [3]

Type of drug	**Concentration, µg/dm^3**			
	Municipal wastewaters	**Treated wastewaters**	**Surface water**	**Drinking water**
Ibuprofen	0.28-6.1	0.11-0.125	0.0045-0.15	< 0.003
Diclofenac	0.46-4.41	0.12-2.89	0.001-0.5	< 0.0025
Paracetamol	45-163	3-16	10-15.5	< 0.298
Salicylic acid	0.9-1.48	0.35-0.47	0.007-0.25	-
Naproxen	0.9-321	0.5-2.4	11-25	-

Table 2. *Physico-chemical characteristics of shellfish waste [5]*

Content of $CaCO_3$, %	**Particle size, mm**	**Volumetric density, g/cm^3**	**Specific surface, m^2/g**
95.6-96.8	0.85-1.18	1.46	2.13

Clam shells contain aragonite, a mineral that has a good ion exchange capacity and can be an alternative to synthetic ion exchangers [5].

In addition, by calcination at 600-800 °C, clam shells have a higher yield in the adsorption of other pollutants as calcium carbonate is converted to calcium oxide [6].

The reactivity of different types of natural calcium carbonates decreases in order: *dolomite < chalk < marble < shell limestone*.

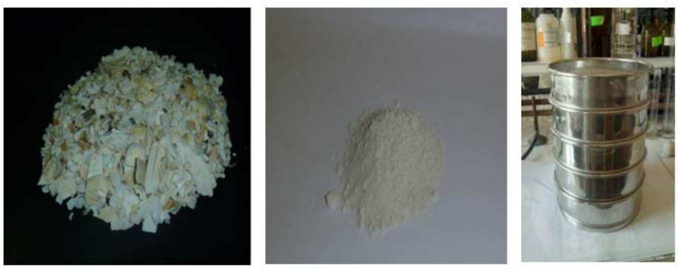
In the present paper, the efficiency of clam shell waste was evaluated for the retention of paracetamol (PAR) pollutants from aqueous solutions.

2. Experimental

2.1. Materials

Clam shells - in powder form with particle diameter between 100 and 250 µm, obtained by grinding for 5 h in a ceramic ball mill with diameter = 1 cm. After grinding, the material was subjected to the dry grading process on the sieves with mesh diameters of 500 µm, 200 µm, 100 µm, 50 µm, and 20 µm (Figure 2) [6].

Para-acetyl-aminophenol (Paracetamol) 500 mg tablets as 0.15 g/L solution in distilled water (PAR).



a) b) c)

Fig. 2. *Clam shells: a) initial state; b) after grinding; c) Granular material sieving equipment*

N°. 1 - 2022, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2022.1.07

2.2 Methods

The particle size distribution of the ground clam shells was determined in the laboratory by a dry grading process on a sieve with a mesh diameter of 500 µm, 200 µm, 100 µm, 50 µm, and 20 µm (Figure 2c).

The static adsorption method is performed by mixing the adsorbent material with paracetamol solution for a specified time and filtering the mixture on filter paper [6].

Determining the content of PAR in solution was performed using the analysis method of oxidizable organic substances. This method consists of analysing the specific parameter for determining the concentration of organic compounds in wastewater as chemical oxygen consumption (CCO). This is a parameter that estimates the degree of chemical oxidisability of compounds dissolved in water. The content of organics was determined by measuring the amount of $KMnO_4$ reduced by oxidizable substances in the aqueous solution, where the excess of potassium permanganate oxidizes organics from water in acidic and high temperature conditions [1, 2].

The pH of the solutions was measured using colorimetric methods.

The retention degree of PAR from the aqueous solution was determined by measuring the concentration of organic substances in the solution before and after the clam shell treatment and was calculated with the formula [6]:

$$\varepsilon = \frac{Ci - Cf}{Ci} x100, \%, \quad (1)$$

where: Ci - initial pollutant concentration; Cf - concentration of pollutant after treatment.

2.3 Description of the experimental programme

2.3.1. Determination of the optimal duration of adsorption

Parameters:

- concentration of PAR = 0.15 g/L;
- adsorption ratio ($m_{clamshells}$:V_{sol}) = 1:100 (g:mL): 1 g clam shells powder to 100 mL solution of PAR;
- adsorption duration = 5, 10, 15, 20, 30, 60, 120 minutes.

Working procedure: 1 g of clam shell powder was added to 100 mL of PAR solution (0.15 g/L) using an Erlenmeyer flask. The mixture is shaken for 5, 10, 15, 20, 30, 60, and 120 minutes and then filtered through filter paper (at least 2 samples are taken in parallel for each duration).

Before and after treatment the amount of organic substances in the solution has been analysed.

2.3.2. Ratio optimization $m_{clamshells}$:V_{sol}

Parameters:

- concentration of PAR = 0.15 g/L;
- adsorption duration = 60 min;
- adsorption ratio ($m_{clamshells}$:V_{sol}) = 1.5:100, 2:100, 2.5:100.

Working procedure: 1.5 g, 2 g, 2.5 g of clam shell powder was added to 100 mL PAR solution (0.15 g/L) using an Erlenmeyer flask. The mixture is shaken for 60 minutes and then filtered through filter paper (at least 2 samples are taken in parallel for each duration).

Before and after treatment, the amount of organic substances in the solution has been analysed.

3. Results and discussions

3.1. Particle size distribution of clamshells

It is revealed that these materials have particle diameters between 100 µm and 500 µm (Figure 3).

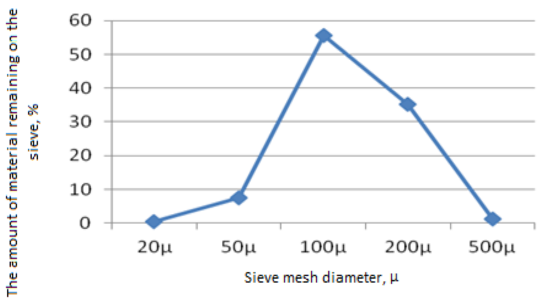


Fig. 3. *The size distribution of clam shells particles*

3.2 Optimal adsorption time determination

The results obtained from the experiments, expressed in terms of adsorption efficiency are presented in Figure 4 as the adsorption efficiency of the organic pollutants on the clam shell substrate versus the adsorption duration. The increase in adsorption efficiency is observed with contact duration of up to 60 min. After this duration, the adsorption efficiency worsens. This can be explained by reaching adsorption equilibrium when the adsorbent material is exhausted and needs to be regenerated. In Figure 5, it can be observed that at the same contact time the maximum amount adsorbed by 1 g of clamshells is 148.52 mg of organic substance.

N°. 1 - 2022, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2022.1.07

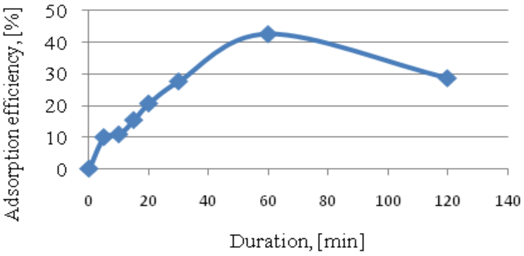


Fig. 4. *The influence of contact time on the efficiency of the organic pollutants' adsorption*

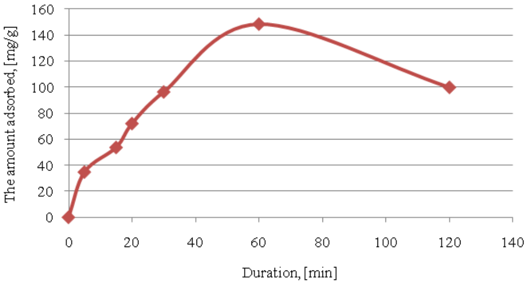


Fig. 5. *The influence of contact time on the amount of organic pollutants adsorbed by 1 g of clam shells*

3.3. Ratio optimization $m_{clamshells}$:V_{sol}

The results obtained under the conditions of the parameters presented in 2.3.2 are shown in Figures 6, 7 where it can be seen that the best adsorption efficiency of organic substances was obtained at a ratio $m_{clamshells}$:V_{sol} of 1:100.

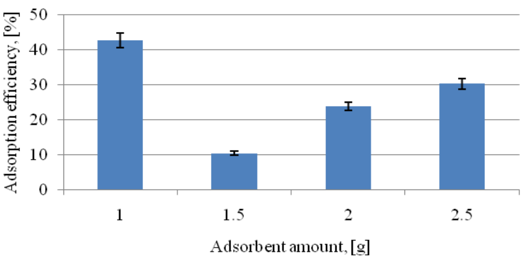


Fig. 6. *The influence of the adsorbent quantity on the adsorption efficiency*

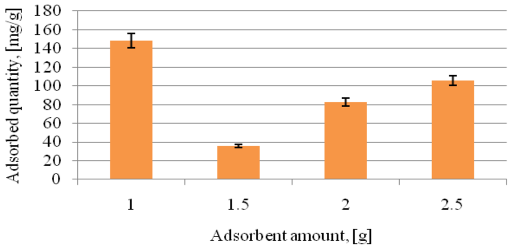


Fig. 7. *The Influence of the quantity of adsorbent on the quantity of organic pollutant retained*

4. Conclusions

The obtained results on the evaluation of paracetamol removal from aqueous solutions using clam shell waste as adsorbent material led to the following conclusions:

- The static adsorption used to retain paracetamol on clamshell waste particles resulted in high yields for an adsorption time of 60 minutes and a ratio of $m_{clamshells}$:$V_{solution}$ of 1:100.
- The method uses cheap and available adsorption materials (biomass waste) and can be an alternative to advanced oxidation methods for the removal of drugs from wastewater, which are relatively expensive and complex and have a negative impact on the environment.
- The future research will be aimed at the study of all factors that could influence the process as well as the study of adsorption isotherms and process kinetics in order to determine the exact conditions of using these wastes in the process of organic pollutant retention from aqueous media.

References

[1]. Hamoudi S. A., Brahimi M., *et al.*, *Removal of paracetamol from aqueous solution by containment composites*, www.degruyter.com, Published online, February 4, 2021.

[2]. Lee W. J., Goh P. S., Lau W. J., Ismail A. F., *Removal of Pharmaceutical Contaminants from Aqueous Medium: A State-of-the-Art Review Based on Paracetamol*, Published online, 6 March 2020.

[3]. Shraim A., Diab A., Alsuhaimi A., Niazy E., *Analysis of some pharmaceuticals in municipal wastewater of Almadinah Almunawarah*, Arabian Journal of Chemistry, 10, S719-S729, 2017.

[4]. Nechita P., *Procese şi echipamente pentru protejarea şi epurarea apelor*, Ed. Europlus, Galaţi, p. 72-78, 2014.

[5]. Tudor H. E. A., Gryte C. C., Harris C. C., *Sea shells : Detoxifying agents for metal-contaminated waters*, Water, Air, and Soil Pollution, 173, p. 209-242, 2006.

[6]. Nechita P., *Natural Additives Used in Adsorption of Pollutants from Textile Wastewaters*, American Journal of Environmental Engineering, 5(2), p. 39-42, DOI: 0.5923/j.ajee.20150502.01, 2015.