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Comparison of cadmium adsorption process on barley straw in batch and flow reactors

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ABSTRACT

The aim of the study was to determine an influence of reactor types used in the cadmium adsorption process from aqueous solutions. During the study, a barley straw with the size in the range of 0.25–0.63 mm was used as a adsorbent. The adsorption was carried out in glass reactors with a capacity of 400 cm^3 for the stationary process and in the plastic burettes with a capacity of 30 cm^3 as flow reactors. The initial concentration of the solution was in the range of 5–30 mg/dm^3. It was found that the optimum pH value for those reactions is 7 and the time necessary to achieve an adequate degree of purification is about 90 min for flow reactors and 2 h in the case of batch reactors. It was also found that for the process conducted in flow reactors, degrees of purification compared with batch reactors are much higher, and in the case of solutions with the pH 5, these differences can be up to 30%. Maximum cadmium removal from solution with the initial concentration 30 mg/dm^3 was observed in the flow reactor at the pH of 7 and it was equal to 74.1% and for batch reactors that value was only 56.7%.

Keywords: Cadmium adsorption; Straw adsorbents; Flow reactors; Batch reactors

1. Introduction

Heavy metals contamination is one of the most important environmental problems in developed countries and in those whose economies are largely based on heavy industry and metallurgy. One of the most significant sources of toxic heavy metals, such as cadmium, are wastewaters generated in plants involved in the aforementioned industries [1]. Along with the wastewater heavy metals are getting into sewage treatment plants, where they can be removed through the accumulation process in biomass of activated sludge [2]. However, in the case when the dose of heavy metals in wastewater is higher than a certain level of toxicity, it may lead to the death of some of the activated sludge micro-organisms and thereby the efficiency of the purification process start to decrease [3,4]. Therefore, the standards and laws concerning the industrial plants must strictly determine maximum concentrations of heavy metals in the industrial wastewater that are discharged to the sewer [5]. Consequently, entrepreneurs

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are forced to build a special internal wastewater treatment plant that is specializing in the removal of some specific groups of contaminants.

That is why, finding of cheap and effective way of heavy metals removal from wastewater that are brought to the surface waters, is one of the most important aspects in the fight against the environmental health hazards. Methods that are nowadays applied to the industrial wastewater treatment are based mainly on the chemical precipitation of sparingly soluble heavy metal compounds [6,7]. However, the main drawback of these methods is the necessity of introducing to the wastewater additional quantities of chemical compounds, which are often toxic and harmful to the environment [8]. Therefore, many scientific centers are working on the development and implementation of the alternative, more environmentally friendly methods of heavy metal removal from aqueous solutions. An alternative for a chemical method can be various kinds of biotechnological methods, such as the adsorption process on the biomass based on the removal of heavy metals by non-toxic natural sorbents. The process consists of a removal of some specific compounds by the molecules adsorption on the surface of a specially prepared natural sorbent. That is why, adsorption on biomass can effectively remove contaminants from aqueous solutions, without the need of using any additional compounds including some toxic chemicals [9,10]. Another advantage is the ability of using a cheap and easy method in obtaining materials as sorbents, for example, agricultural wastes.

In the world scientific literature, the majority of reports related to the adsorption process of heavy metals are associated with studies that were carried out using batch reactors [11–13]. It is associated primarily with the simple design and principle of operation of this type of reactors. By fully stirring of the mixture, there is no concentration gradient inside the reactor, which simplifies the analysis of the process. However, a significant drawback of the batch reactors is the necessity to separate mixture phases after the adsorption process. It is due to relatively small particle sizes of sorbents that are often eluted from the reactor together with purified solution. Therefore, there is a need to improve the whole process by an additional separation process such as filtration or centrifugation of the mixture at the end of the adsorption reaction [14,15]. Mentioned complications can be avoided by using flow reactors, wherein the biomass sorbent is packed in the special column, in which the heavy metals solutions flow as a mobile phase. It is because the filtrate leaking from the flow reactor with the packed biomass sorbent column is free from any particulate matter [16]. This property may be especially desirable if the filtrate is directed to the further steps of treatment, for example, pumping systems since the presence of those solid particles may lead to clogging of the installation elements.

To summarize, the aim of the conducted study was to analyze the influence of reactor and process type at the performance of adsorption process, using cadmium as a representative of highly toxic heavy metals. Better understanding of these aspects would make it possible to develop some appropriate technologies for the removal of heavy metals from industrial wastewater.

2. Materials and methods

2.1. Chemical reagents and adsorbents used during the study

Cadmium ions were added to the initial solutions in the form of cadmium nitrate by diluting the standard solutions from Merck with the concentration equal to 1.000 ± 0.002 g/dm^3. pH of the initial solutions was set to the value 3, 5, and 7, by adding appropriate amounts of sodium hydroxide, to analyze adsorption process for different pH of reaction. Concentrations of the initial cadmium solutions, used during the study, had a cadmium concentration ranging from 5 to 30 mg/dm^3.

The adsorbent used during the study was a barley straw, which was an agricultural waste sourced from Raciborz, a small city in Poland. In order to remove possible surface contaminants, straw was first washed with distilled water and then after drying at 60˚C it was cut in a lab mill. After milling, straw was sieved on analytical sieve to obtain a fraction with a selected particle size in the range of 0.63–1 mm. Next, the straw was soaked in distilled water and the pH of the resulting mixture was determined at the level corresponding to the solutions for which it was used, by adding a suitable amount of sodium hydroxide. After stabilization of the pH value, straw was dried again at 60˚C. Moreover, the humidity of the prepared straw was analyzed and it was equal to 3.4%. In order to simplify the description in all further considerations, default concentrations are expressed per gram of dry weight of straw. To determine the amount of the cadmium in straw that could pass to the purified solution and affect the obtained results, the measurement of cadmium concentration in straw was conducted. After mineralization of sample weight, about 0.1 g cadmium concentration was found at the level of 683 μg/kg which demonstrates that the possible amounts of cadmium embedded in the straw structure is so low that it will not affect the results obtained during adsorption.

Previously prepared straw was weighed and added to reactors in a ratio of 1 g per 300 cm^3 of solution. The process was conducted in glass reactors with a stirrer with a volume of 400 cm^3 for batch reactors and in the case of flow reactors in a plastic column with a volume of 30 cm^3. The elution rate for flow reactors was 3.6 cm^3/min. For batch reactors, it was found that the time after which no further changes in cadmium concentration were observed was 120 min. Each of the measurements were made in triplicate and results presented in further considerations are always the mean value of obtained data.

2.2. Results of preparation and data analysis

For each solution, the cadmium concentration was analyzed by using the atomic absorption spectroscopy at the spectrometer SpectrAA Varian 880, by a flame method. To accurately determine the adsorption abilities of straw for both types of reactors two different, basic mathematical models of adsorption were used. The first model was a Langmuir theory, which assumes the formation of monolayers during the adsorption process on the surface of a heterogeneous adsorbent. The equation, used in this model describes the adsorption isotherm, has the following form [17]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \times C_e} \quad (1)$$

where q_e—amount of adsorbate adsorbed at the surface of the adsorbent at the adsorption equilibrium [mg/g]; C_e—cadmium concentration remaining in the aqueous solution at the adsorption equilibrium [mg/dm^3]; q_{max}—capacity of the adsorption monolayer [mg/g]; b—dimensionless constant value in the Langmuir isotherm equation.

The second isotherm used to determine the properties of the adsorption was a Freundlich isotherm. It is a modified, empirical version of the Langmuir isotherm. This type of adsorption isotherm often fits better with obtained results than the Langmuir isotherm, especially for the adsorbents with highly heterogeneous energy surfaces. The form of Freundlich isotherm which allows one to find the linear relationship between the equilibrium concentration and mass of the adsorbed cadmium is described by the equation [17].

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_f) \quad (2)$$

where K_f—Freundlich constant (also known as Freundlich capacitive ratio); $1/n$—Freundlich exponent, defining the degree of heterogeneity of the adsorbent energy.

After creating both presented models for the collected during the experiment data, it was checked which one better describes the analyzed adsorption process for each type of the reactor. The compatibility of the model to laboratory results was determined by comparing the coefficients of determination R^2.

3. Results and discussion

Before starting the main tests, the preliminary analysis had been conducted to determine the optimum pH of the starting solution during adsorption of cadmium in the batch and flow reactors. During these studies, the results of cadmium removal on a barley straw were compared for solutions with pH ranging from 3 to 7. After further alkalization of the solutions, at a pH above 7, the turbidity occurred due to the precipitation of sparingly soluble forms of cadmium from an aqueous solution. Therefore, it was decided that the pH of 7 would be the maximum of analyzed values. The results of the preliminary study are presented graphically in the diagram (Fig. 1).

According to the data shown in the figure (Fig. 1), the adsorption process in the batch reactors depends strongly on the pH of the solution. The highest degree of cadmium removal for both types of reactors was observed at the pH of 7, that is why this value was considered to be optimal for further research. The percentage removal of cadmium, with the corresponding duration of process was presented in Table 1.

The time required to carry out the adsorption for 300 cm^3 of the starting solution in the flow reactors was 83 min. Consequently, in flow reactors, the cadmium concentration after 90 min of the process was identical with the cadmium concentration in the final filtrate. The analysis of data in Table 1 indicates clearly on a higher final removal of cadmium for flow reactors. A difference in cadmium concentration, between the flow and batch reactors, after 90 min of process was 20%. However, in the case when the process in a batch reactor was carried out until the maximum degree of cadmium removal, the difference decreased to 17.4%. On the basis of carried measurements, the correlation between the amount of adsorbed cadmium and equilibrium concentration of the solution was shown in Fig. 2.

Based on the adsorption isotherms (Fig. 2) it was found that for both types of reactors, the isotherms had a clear logarithmic character ($R^2 = 0.98$ for batch

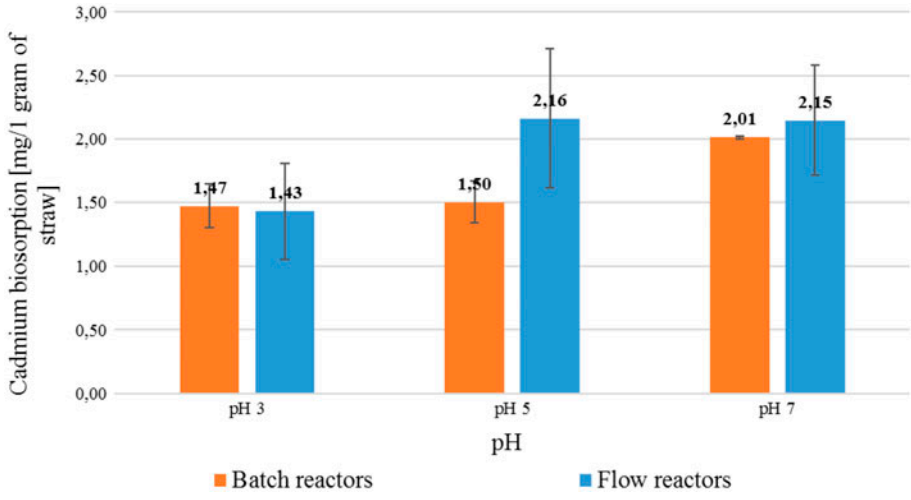

Fig. 1. The average cadmium adsorption on barley straw for batch and flow reactors, at different pH values, and appropriate standard deviations (n = 3).

Table 1
The percentage removal of cadmium with time of process per gram of straw, depending on the type of reactor used

	Percent removal of cadmium				
	15 min	30 min	60 min	90 min	120 min
Batch reactor	46.6%	50.2%	52.3%	54.1%	56.7%
Flow reactor	98.8%	95.7%	85.2%	74.1%	–

reactors and $R^2 = 0.97$ for continuous). The analysis of the two curves, especially in the initial phase, indicates a much stronger influence of the cadmium equilibrium concentration to the adsorption amount for the flow reactors. This observation seems to confirm previous results which showed significantly better performance of adsorption in the initial phase for the process performed in flow reactors. In order to properly interpret the obtained results, data were also described using the Langmuir adsorption isotherm, which was depicted in a linearized form in Fig. 3.

The linearized form of the Langmuir isotherm once again indicates that there is higher adsorption efficiency for flow reactors. This fact is also confirmed by the values of the slopes of the both isotherms. For flow and batch reactors the slopes values were, respectively, 0.193 and 0.164. In addition, the coefficients of determination R^2 for both types of reactors were identical and amounted to 0.992, which indicate that there is a very good fitting of the Langmuir isotherm with

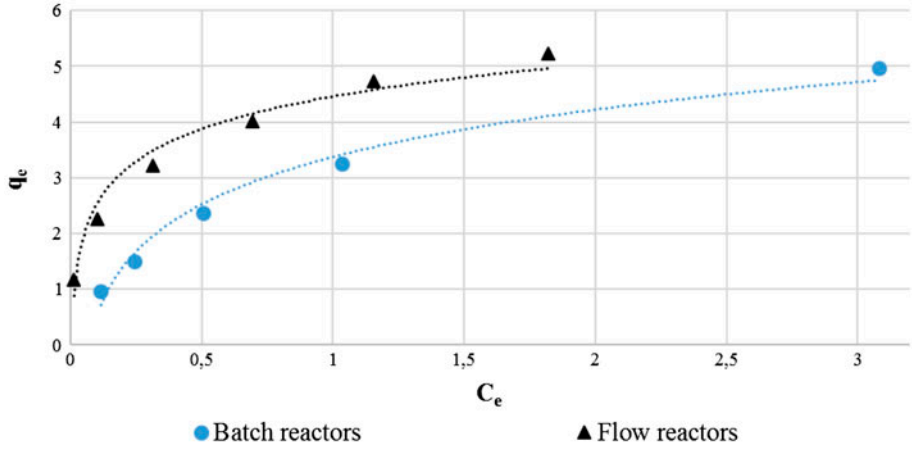

Fig. 2. Adsorption isotherms for batch and flow reactors.

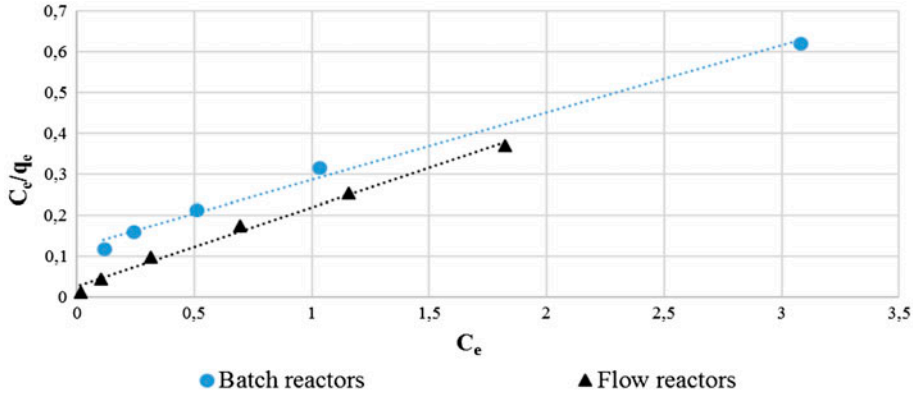

Fig. 3. Linearized form of Langmuir isotherm for the process performed in both types of reactors.

obtained results of the study. The results obtained during the study were also described using the Freundlich isotherm and the course of its linear form was shown in Fig. 4.

For this type of isotherm, the R^2 coefficient of determination is lower for batch reactors than the Langmuir isotherm and amounts to 0.987. In the case of flow reactors, R^2 value is 0.999 which indicates an almost perfect fit of the model with obtained data. However, for both types of reactors, the coefficient of determination exceeds 0.95, which demonstrates that the Freundlich isotherm describes the adsorption process very well. Based on the slopes and y-intercepts of the obtained Freundlich and Langmuir isotherm lines, the basic parameters of the models were determined for both types of reactors. The values of those parameters were shown in Table 2.

Conducted studies show that barley straw can be used as an efficient adsorbent in the process of cadmium removal from aqueous solutions. Calculated values of maximum sorption capacity were in the range from 5.17 to 6.08 mg/g, depending on the reactor type. Obtained efficiency of the adsorption process is competitive when compared to other widely studied adsorbents. For example, for rice straw the result was about 8–10 mg/g and for dried biomass from *Pythium torulosum* it was 6.75 mg/g [18,19]. When the aqueous solutions of cadmium were treated by using yeast, *Saccharomyces cerevisiae*, the maximum capacity was 3.1 mg/g [20].

Moreover, the analysis of presented in the table results show that in the case of batch reactors, the value of monolayer adsorption capacity (q_{max}) is higher. Therefore, in accordance with the Langmuir theory, straw used in those kinds of reactors can

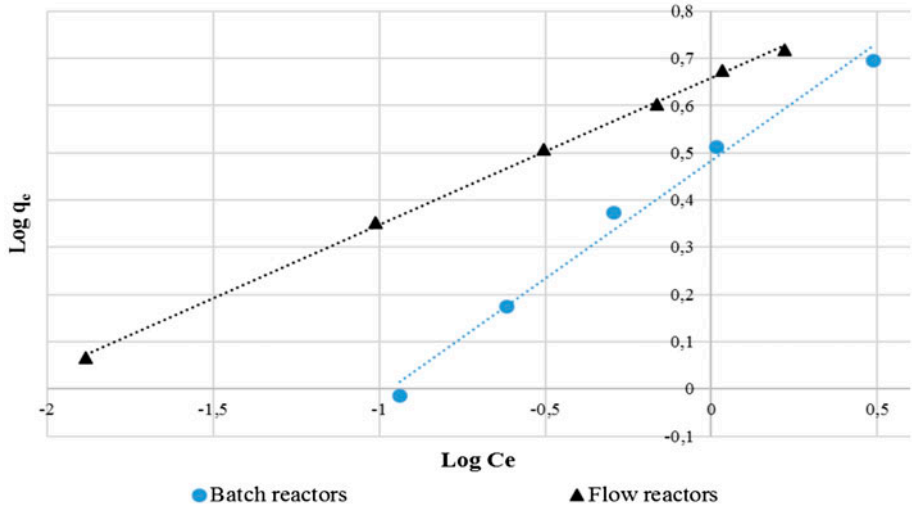

Fig. 4. Linear form of Freundlich adsorption isotherm for the process carried out in batch and flow reactors.

Table 2
The values of the parameters of equations describing the Langmuir and Freundlich isotherms for batch and flow reactors

	Freundlich isotherm			Langmuir isotherm		
Parameter	K_f	n	R^2	q_{max}	b	R^2
Batch reactors	0.48	2	0.987	6.08	1.34	0.992
Flow reactors	0.66	3.21	0.999	5.17	7.24	0.992

adsorb more cadmium from solution. Although in both types of reactors used, the adsorbent was the same but Freundlich exponent values are different. This means that the heterogeneities in the energetic structure of the surface was higher, when the flow reactors was used. This suggests that not only the efficiency of the process, but also a physicochemical characteristic of process changes together with the reactor type.

The exact binding mechanism of cadmium on the straw was not studied, but in the scientific literature related to this topic, there are two basic binding mechanisms. The first one is a ion-exchange mechanism, where Cd binds to anionic sites by displacing protons from acidic groups or existing alkali metals like Ca^{2+} or Na^{+} present at the surface of straw [21,22]. Therefore, as many literature sources report, adsorbents having on their surface a greater amount of alkali groups are usually characterized by substantially improved adsorption properties with respect to cadmium than adsorbents poorer in those groups [23]. The second adsorption mechanisms assumed complexing of the cadmium by some chemical groups, present at the surface of the straw, for example, carboxyl groups, ammonium, phosphate, etc. In those cases, cadmium present in the solution is bound by the coordination with mentioned functional groups to complex formation, where cadmium is a central atom and surrounded functional groups are the ligands [19,24]. Nevertheless, since in reactions conducted in both types of reactors the same absorbent was used, and the chemical and physical properties of those adsorbents must be the same. Therefore, it can be assumed that the mechanisms of cadmium binding on the surface of the straw were also the same, irrespective of the reactor type.

4. Conclusions

Although determined on the basis of Langmuir isotherm capacity of adsorption monolayer was larger for batch reactors, the actual degree of cadmium removal was higher when continuous reactors were used. Mentioned divergence may be a consequence of differences between the actual process and the assumptions of the ideal Langmuir isotherm model. On the other hand, the Freundlich capacitive factor is higher when the adsorption process was carried out in flow reactors. It indicates that this type of reactor provides enhanced removal of cadmium ions from the solution. It was considered that obtained sorption capacity for both models was similar and the main difference, which might determine the choice of optimal reactor type, may be the time needed to obtain the desired degree of purification. In this respect, flow reactors are much better since in the same time intervals the removal of cadmium was much higher than that in batch reactors. An additional advantage of using those flow reactors is the ability of constantly monitoring the cadmium concentration in the filtrate. It allows one to interrupt the process, if the cadmium concentration in the filtrate would exceed the limit value. To sum up, our studies have shown that despite a similar level of cadmium removal from aqueous solutions, the adsorption process conducted in flow reactors is much more favorable and allows for a better control of the process.

Finally, an important aspect of the presented study was the fact that they were conducted by using pure cadmium solutions. Provided that similar research is carried out at real industrial wastewater, with high cadmium concentration, some significant differences might be expected in relation to studies on model solutions. The most important reason of those differences can be a possible influence of other ions and active chemical groups present in actual wastewater. Therefore, it appears advisable to conduct further research in this direction using real industrial wastewater.

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