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Removal of cadmium ions from polluted waters using low-cost adsorbents: process optimization study

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ABSTRACT

In this study, attempts were made to optimize the sorption process of cadmium ions by a mixture of low-cost adsorbents such as poultry litter and char. The optimization study was performed using the response surface methodology and the central composite design (CCD). The parameters such as the initial concentration of cadmium ions (c_o), the initial pH and the weight ratio of poultry litter to char were selected as variables in the CCD. The introduced data allowed the creation of a model of the dependence of the sorption capacity of cadmium ions with initial parameters. Thanks to the developed model, optimal values of the sorption process were obtained at the level of pH = 5.05, c_o = 105 mg/L and a poultry litter/char ratio of 0.79 (w/w). The optimal sorption values for the obtained parameters were tested for four types of samples: deionized water, river water and water extracts from waste and soil. The obtained results indicated high compliance of the cadmium ion sorption predicted by the model in the case of the model sample (deionized water). In the remaining cases, the sorption capacity of the adsorbent decreased depending on the sample used, in the following order: soil water extract > river water > waste water extract. The research showed the potential of the mixture of poultry litter and char as a low-cost adsorbent.

Keywords: Sorption; Response surface methodology; Cadmium; Design of experiments; Low-cost adsorbent; Water pollution; Optimization

1. Introduction

Cadmium is an element naturally occurring in low concentrations, for example, in soil (0.06–1.1 mg/kg) and in sea waters (0.07–0.11 ug/L) [1]. It is estimated that approx. 10% of cadmium emissions to the environment originate from natural sources. The remaining part is attributed to anthropogenic sources, which correspond to 38 × 10^6 kg/y of cadmium emissions [2]. The main sources of anthropogenic cadmium emissions to waters and soils include mining, refining of zinc ores and plastics industry. Particular attention should be paid to the possibility of cadmium contamination in agricultural soils [3]. Cadmium contamination in agricultural soils arises mainly from phosphate fertilizers and liming materials [1]. It poses a considerable challenge as cadmium shows high mobility and a high degree of bioaccumulation in plants. Thus, it can easily enter the trophic chain [4]. From the toxicological perspective, cadmium and its compounds are considered highly toxic and carcinogenic [5,6]. Cadmium enters the body directly in two ways, by ingestion and inhalation, and indirectly through the consumed food and water. The toxic effect of cadmium on human health manifests itself mainly by gastric and prostate cancer or osteoarticular system disfunction

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[1], including the infamous itai-itai disease [7]. Due to its high toxicity, cadmium and its compounds are classified as a carcinogen of the Carc class. 1B [8] and a priority hazardous substance [9]. Monitoring of cadmium concentrations in water, foodstuff as well as in soil and ambient air is strongly recommended. The WHO recommends that maximum cadmium concentration should not exceed 3 μg/L in water and 5 ng/L in the air, respectively, and the maximum cadmium consumption in foods should be 25 μg/kg body weight per month [10]. For this reason, the harmful effects of cadmium and its compounds should be minimized. The priority is to remove cadmium from the water medium. There are many remediation methods available for water treatment based on chemical precipitation, coagulation, and membrane filtration. Recent research shows higher efficiency of methods based on combining membrane with electrochemical techniques [11] or using microorganisms [12,13]. Nevertheless, the removal of cadmium from natural water and wastewaters was examined using low-cost adsorbents such as wastes from food industry, that is, rice shell, sugarcane bagasse, sunflower stalk [14,15] or materials developed from agricultural biowaste, for example, biochar [16,17]. In the case of remediation of soil, low-cost absorbents can be used for heavy metal immobilization [18] or as an aid for phytoremediation technologies.

Poultry litter and the products derived from it offer interesting materials for the agricultural and reclamation purposes. The production of poultry litter in Poland at approx. 4.5×10^6 Mg [19] presents a real problem to be solved. [20]. Due to its properties, poultry litter meets the definition of a "biosorbent" [21], which allows us to hypothesize about its possible use in the techniques of immobilization of metal ions from the water environment. Due to its properties, such as possible presence of the pathogens (e.g., *Salmonella*) as well as heavy metal contamination, the use of poultry litter for water and soil remediation purposes is limited [22]. One of the main issues with poultry litter use, for water and soil remediation purposes, is the negative effect of dissolved organic matter on heavy metal mobility [23–27]. There are known methods that can lead to minimizing the negative effect of dissolved organic matter, such as composting [28,29], chemical modification [30], pyrolysis [31,32], modifiers addition [33–36]. Char (unburned coal) derived from coal combustion ashes offers a useful additive to enhance the sorption process of poultry litter. Separated from ashes, char concentrates mainly consist of carbon (amorphous, organic, graphitic). Mineral phases are dominated by silicon and aluminum oxides (amorphous quartz SiO_2, mullite $3Al_2O_32SiO_2/2Al_2O_3SiO_2$) [37]. There are few reports about its sorption capacity against organic compounds [38]. The described char properties can be useful for the adsorption of dissolved organic matter derived from poultry litter.

Research using Fourier-transform infrared spectroscopy (FT-IR) techniques indicates the participation of ion exchange in the sorption process. Apart from the dominant role of carboxyl groups on the surface of poultry manure, the process of removing cadmium ions from aqueous solutions is also influenced by the precipitation of insoluble organic matter derivatives with cadmium ions [27]. The present study aims to investigate the effect of low-cost modifier addition on the percentage of cadmium removal by poultry litter. Optimal sorption conditions such as poultry litter/char ratio, initial cadmium concentration and initial pH were examined. To simulate the impact of selected parameters, on cadmium removal percentage, central composite design was used. Finally, optimal cadmium removal percentage was studied for selected samples (deionized water, river water, wastewater).

2. Experimental procedures

2.1. Materials and methods

The poultry litter used in the research came from a poultry farm near Mikołów (Silesian Voivodeship), Poland. Raw poultry litter was prepared and stored according to the procedure described elsewhere [27]. Preparation of raw poultry litter included drying for 48 h at 70°C, followed by milling in knife mill. Ground and dried poultry litter was stored at <5°C. The char used in the experiment was obtained by separation of the fraction of unburned carbon from power plant slag, according to Wierzchowski et al. [39]. Poultry litter and char samples were characterized using the FT-IR method (Nicolet iS50) in the range of 400–4,000 cm^{-1}. The obtained spectra were processed using Origin Pro 8.1 software (OriginLab Corp., US). FT-IR spectra of poultry litter and char samples were shown in Fig. 1. Both spectra are characterized by wide bands in the range of 3,100–3,500 cm^{-1}, related to the presence of hydroxyl –OH groups bound by the OH. O hydrogen bond. In both

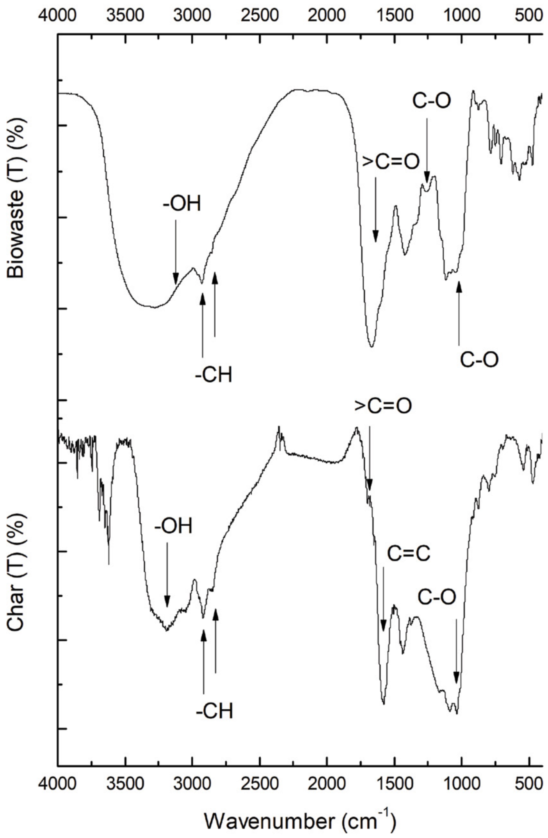

Fig. 1. FT-IR spectra of poultry litter (top) and char (bottom) samples.

cases, the presence of vibrations originating from the C–O bond in the range of 1,300–950 cm^{-1} was found. Bands in the range of 2,920; 2,849; 1,436 and 1,374 cm^{-1} are associated with the stretching and bending bonds of the aliphatic CH_2 and CH_3 groups. The absence of clearly marked bands above 3,000 cm^{-1} indicates the absence of a C–H bond in the aromatic compounds. The low intensity of the bands at the wavenumber of 1,500 and 1,485 cm^{-1} also proves the low content of C–C aromatic bonds in the sample. Char samples are characterized by bands related to the presence of inorganic substances located approx. 3,689; 3,669; 3,619; 543 and 472 cm^{-1}. The char sample is characterized by bands related to the presence of inorganic substances located at approx. 3,689; 3,669; 3,619; 543 and 472 cm^{-1}, and by a high-intensity band of approx. 1,580 cm^{-1} due to the stretching vibration of the unsaturated C=C bond. In contrast to the poultry litter sample, the presence of weak bands around 1,700 cm^{-1}, originating from the vibration of C=O bonds, was found, which indicates a low intensity of carboxyl groups.

Natural water (W) was collected from the Olza River above Szotkówka River. Water extracts were prepared according to PN-EN 12457-2:2000. Two types of materials were used to obtain water extracts: soil (S) collected near zinc smelter "Miasteczko Śląskie", Poland. The waste (E) characterized as fluidized bed reactor sands. The selected parameters of natural water (W) and water extracts are (S and E) shown in Table 1.

Initial cadmium concentration was obtained by spiking water samples by 1,000 mg/L cadmium ion stock solution. The stock solution was prepared by dissolution of 2.7442 g of $Cd(NO_3)_2{\cdot}4H_2O$ (analytical grade, EUROCHEM BGD, Poland) in 1 L of deionized water. Cadmium, sodium, potassium, magnesium and calcium concentrations in the samples were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5300, USA) according to PN-EN ISO 11885:2009. The pH-value and conductivity were determined by potentiometric method (Elmetron CX-701 with IJ44CT and EC-60 electrode, ELMETRON, Poland) according to PN-EN ISO 10523:2012 and PN-EN 27888:1999, respectively.

2.2. Design of experiment and response surface methodology

Design of experiment (DOE) and further response surface studies were conducted by applying Statistica 12 software (StatSoft, Poland). Optimization of cadmium removal percentage by biowaste/char mixture was conducted using response surface methodology (RSM) [40]. RSM is a statistical model that helps find optimal values for a designed process, that is, sorption, with a minimum number of approaches [41–46]. RSM comprises three stages: DOE, response surface modeling, and model optimization/validation. Experiments were prepared based on the central composite design (CCD). Three input parameters ($k = 3$) were adopted as independent variables: initial pH and initial cadmium concentration of the initial solution as well as biowaste/char ratio. A number of runs (N) were calculated by Eq. (1).

$$N = 2^k + 2k + n_o \tag{1}$$

The total number of runs was calculated as sum of 2^k orthogonal design points, $2k$ axial design points and number of replicates ($n_o = 2$). The variance between the cadmium removal percentage (R_{obs}) of n_o points determines an experimental error. As a result of the above-mentioned calculations, 16 experiments were determined. The variability of the independent parameters was originally established at x_1 (initial pH, 3.5–5.5), x_2 (initial cadmium concentration (50–150 mg/L), and x_3 (poultry litter – char mass ratio 0.25–0.75), respectively After taking into account $\alpha = 1.6818$ (for rotatability) and $\alpha = 1,2872$ (for orthogonality), the variability of the independent parameters of the experiment was, respectively x_1 (2.82–6.18), x_2 (15.9–184.1 mg/L), x_3 (0.08–0.92).

The response surface modeling stage consists of creating a mathematical model of the relation between independent parameter variables and the observed response (R_{obs}). As a result of modeling, second-order response surface is created Eq. (2):

$$Y = \beta_o + \sum_{i=1}^{k}\beta_i x_i + \sum_{j=1}^{k}\sum_{i=1}^{k}\beta_{ij}x_i x_j + \sum_{i=1}^{k}\beta_{ii}x_i^2 + \varepsilon \tag{2}$$

where Y (R_{pred}) – predicted response, β_o – offset value, $x_i x_j$ – value of the input parameter, β_i, β_{ii}, β_{ij} – linear, quadratic and interaction effect coefficient, ε – statistical error. The validity of the mathematical model was determined by analysis of variance (ANOVA).

Table 1
Properties of sorption solution matrices

i	S	$\pm U(i)$	W	$\pm U(i)$	E	$\pm U(i)$
pH	6.15	0.2	7.7	0.2	14	0.2
Electrical conductivity, uS/cm	83.7	16.0	601	30	9840	490
Cd, mg/L	0.5	0.17	<0.001	–	<0.001	–
Na, mg/L	1.05	0.10	48.1	4.8	2.34	0.47
K, mg/L	2.01	0.04	5.47	1.09	4.3	0.9
Mg, mg/L	<0.12		10.5	1.1	<0.12	
Ca, mg/L	30.1	3.0	58.9	5.9	1640	160

$\pm U$ – expanded uncertainty ($k = 2$) with 95% confidence interval.

2.3. Experiment setup

Cadmium removal percentage (R_{obs}) was investigated under static conditions (temperature, amount of adsorbent used). The batch sorption study was conducted using 55 mL centrifuge tubes containing 50 mL of the test solution and 0.200 ± 0.002 g of the sorbent. Parameters of test mixtures are collected in Table 2.

Resulting mixtures were shaken in an overhead shaker at the equilibrium time of 23 h (50 rpm, 22°C ± 2°C). After 23 h, resulting solutions were centrifuged (15,000 rpm, 15 min) and filtered through Whatman 0.45um filter (Merck, Germany). For further analysis, the samples were diluted and acidified accordingly with nitric acid (65%, Merck, Germany). The residual cadmium concentrations were determined by CP-OES. Cadmium removal percentage of poultry litter/char mixture to cadmium ion sorption were calculated using Eq. (3):

$$R_{obs} = \frac{c_0 - c_x}{c_0} \times 100\% \quad (3)$$

where R_{obs} – cadmium removal percentage (%); c_o – initial cadmium concentration (mg/L); c_x – cadmium concentration after sorption study (mg/L). Uncertainty of cadmium removal percentage was calculated according to Eurachem/CITAC guide [47].

3. Results and discussion

3.1. Response surface model fitting

The decrease in the concentration of cadmium ions in the solution, expressed as cadmium removal percentage (R_{obs}), is shown in Table 2. The obtained results served as input data for the multiple regression analysis. Mathematical representation of the cadmium removal percentage (Y) depending on the selected variables: x_1 (initial pH), x_2 (initial cadmium concentration), x_3 (poultry litter – char mass ratio) is presented:

$$Y = 82.8434 + 1.0646x_1 - 12.1324x_2 + 32.8191x_3 - 8.2482x_1^2 + 0.6614x_2^2 - 14.3646x_3^2 - 2.2250x_1x_2 - 1.4750x_1x_3 + 11.4250x_2x_3 \quad (4)$$

The correctness of a given model was confirmed by ANOVA of regression variables of the calculated response surface quadratic model (Table 3). The high degree of

Table 2
Design of experiment and response values

Run no.	pH	c_o, mg/L	Biowaste/char, m/m	R_{obs}, %	±$U(R_{obs})$, %
	x_1	x_2	x_3	Y	
1	3.50	50.0	0.25	63.6	3.2
2	3.50	50.0	0.75	85.7	4.3
3	3.50	150.0	0.25	44.4	2.2
4	3.50	150.0	0.75	87.1	4.4
5	5.50	50.0	0.25	74.7	3.7
6	5.50	50.0	0.75	91.6	4.6
7	5.50	150.0	0.25	48.8	2.4
8	5.50	150.0	0.75	90.8	4.5
9	2.82	100.0	0.50	54.1	2.7
10	6.18	100.0	0.50	84.1	4.2
11	4.50	15.9	0.50	93.1	4.7
12	4.50	184.1	0.50	70.3	3.5
13	4.50	100.0	0.08	30.6	1.5
14	4.50	100.0	0.92	90.3	4.5
15	4.50	100.0	0.50	82.2	4.1
16	4.50	100.0	0.50	84.2	4.2

Table 3
Analysis of variance (ANOVA) for the response surface for cadmium removal degree

Effect	Analysis of variance; DV: R_{pred}				
	Sums of (Squares)	df	Mean (Squares)	F	p-value
Regress.	5,532.007	1	5,532.007	427.9300	<0.000001
Residual	180.983	14	12.927		
Total	5,712.990				

Table 4
Estimated regression coefficients

Factor	Effect estimates; Var.: *R*, %; *R*-sqr = 0.96832; Adj.: 0.9208 (DOE in Workbook1) 3 factors, 1 blocks, 16 runs; MS Residual = 30.16385 DV: *R*, %									
	Effect	Std. Err.	$t(6)$	p	–95, % (Cnf.Limt)	+95, % (Cnf.Limt)	Coeff.	Std. Err. (Coeff.)	-95, % (Cnf.Limt)	+95, % (Cnf.Limt)
Mean/Interc.	82.843	3.872	21.394	<0.001	73.368	92.318	82.843	3.872	73.368	92.318
pH (L)	11.064	2.972	3.722	0.009	3.791	18.337	5.5323	1.486	1.895	9.168
pH (Q)	–8.248	3.608	–2.285	0.062	–17.078	0.582	–4.124	1.804	–8.539	0.291
c_o, mg/L (L)	–12.132	2.972	–4.081	0.006	–19.405	–4.859	–6.066	1.486	–9.702	–2.429
c_o, mg/L (Q)	0.661	3.608	0.183	0.860	–8.169	9.491	0.330	1.804	–4.084	4.745
Biowaste/char, m/m (L)	32.819	2.972	11.041	<0.001	25.546	40.092	16.409	1.486	12.773	20.046
Biowaste/char, m/m (Q)	–14.365	3.608	–3.980	0.007	–23.195	–5.534	–7.182	1.804	–11.597	–2.767
1L by 2L	–2.225	3.883	–0.572	0.587	–11.727	7.277	–1.112	1.941	–5.863	3.638
1L by 3L	–1.475	3.883	–0.379	0.717	–10.977	8.027	–0.737	1.941	–5.488	4.013
2L by 3L	11.425	3.883	2.941	0.025	1.922	20.927	5.712	1.941	0.961	10.463

F-value (427.9300) and a correspondingly low value of probability (*p*-value < 0.000001) suggest the significance of model terms for the regression model.

Values of the determination coefficient *R*-squared (*R*-sqr = 0.96832) and adjusted *R*-squared (Adj. = 0.9208) indicated a high correlation between predicted and observed results (Table 4). To visually assess the fitness of the proposed mathematical model with experimental data, a graph was created (Fig. 2). The clustering of points along a simple regression indicates a good fit for the proposed model for empirical data.

The analysis of *p*-value ($p > 0.05$) showed the significance of linear (first-order) effects of initial pH (L), initial cadmium concentration c_o (L) and, especially, biowaste/char ratio (L). Further analysis showed the significance of quadratic (second-order) effect of biowaste/char ratio (Q) and linear interaction between biowaste/char ratio and initial cadmium concentration (2 L by 3 L). The *p*-values of the other factors were not significant (Fig. 3.).

3.2. 3D response surface plot description

The obtained mathematical model was used to create a series of 3D plots showing the change in the degree of cadmium removal depending on the selected parameters. Fig. 4 represents a 3D plot of the BW/char mass ratio and the initial cadmium concentration in the model solution. The initial pH value was constant at 4.5.

The relationship presented in the diagram clearly shows the dominant role of poultry litter in the process of cadmium ion sorption. In the case of the sorption process, the relationship between the cadmium ion removal degree and the initial cadmium concentration in the solution should initially reach the plateau. As the concentration of cadmium ions increases further, the cadmium ion removal degree should decrease. This behavior is explained by two processes. The first is the achievement of a specific state of equilibrium between the concentration of cadmium ions in the test solution and the cadmium adsorbed on the active sites of poultry litter. The second process is related to the gradual saturation of the sorption active sites of poultry manure.

In the case of the discussed sorption system, the removal of cadmium ions reaches a plateau around the initial cadmium concentrations of 1–50 mg/L [27]. The cadmium ions removal degree in the considered range was at the level of 90%. Along with the increase in the initial concentration of cadmium ions in the test solution (c_o, mg/L), a decrease in the degree of cadmium removal (*R*, %) was found, respectively for c_o = 100 (79.83), 150 (65.00), 400 (47.15), for poultry litter alone. The results obtained based on the DOE method show a significant increase in the degree of cadmium ion removal in the presence of coke breeze, compared to our previous findings. As mentioned before, the effect of poultry manure/char ratio plays a dominant role in the mathematical model of cadmium ion sorption. That effect is clearly visible in Fig. 4. With the increasing share of char, the degree of cadmium removal decreases substantially. The mass ratio of char, not exceeding 50%, leads to significant growth of poultry litter/char mixture cadmium ion removal ratio. This confirms the supportive role of char for cadmium ion sorption.

On the second 3D plot (Fig. 5), the interaction between cadmium removal percentage and two variables (poultry litter/char ratio; initial pH) was presented. The initial cadmium concentration value was set at 100 mg/L. The choice of c_o as the middle of the range in the design of the experiment was dictated by our previous research. As mentioned earlier, from the value of 100 mg/L, there is a visible decrease in the value of the degree of cadmium removal. Taking this value into account makes it possible to capture the impact of the modification of chicken litter with char. The dependence presented in the graph shows a clear decrease in the ability to remove cadmium ions with a decrease in pH. The decrease in *R* yield is drastically influenced by the change in the mass ratio of poultry manure/char. According to the data presented in Fig. 3, the linear effect of initial pH on *R* is relatively high (3.722524).

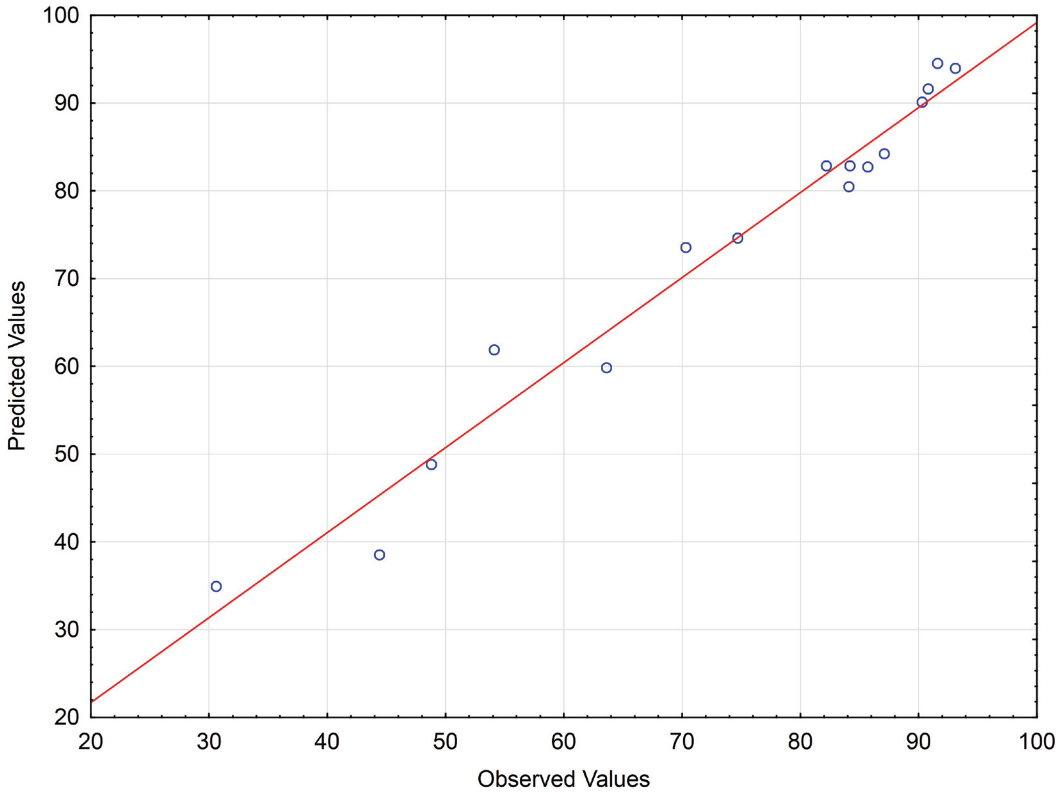

Fig. 2. The correlation between predicted and observed values of removal percentage (*R*, %).

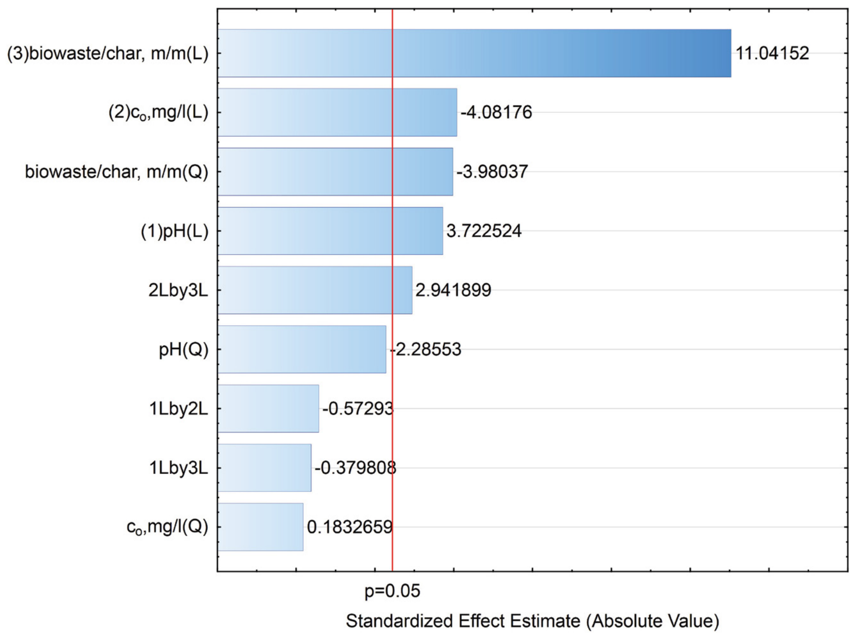

Fig. 3. Pareto chart—the absolute value of standardized assessment of the effects.

Similar observations were reported in many studies in the field of cadmium ion biosorption [14,21,28,48,49]. It was noted that the change in pH may affect as follows: surface charge of sorbent, degree of functional groups protonation and the cadmium ion speciation in water solution. For this reason, the effect of pH change on poultry litter/char mixture can be explained in two ways. Firstly, the carboxyl groups (RCOO–) contained in the poultry litter

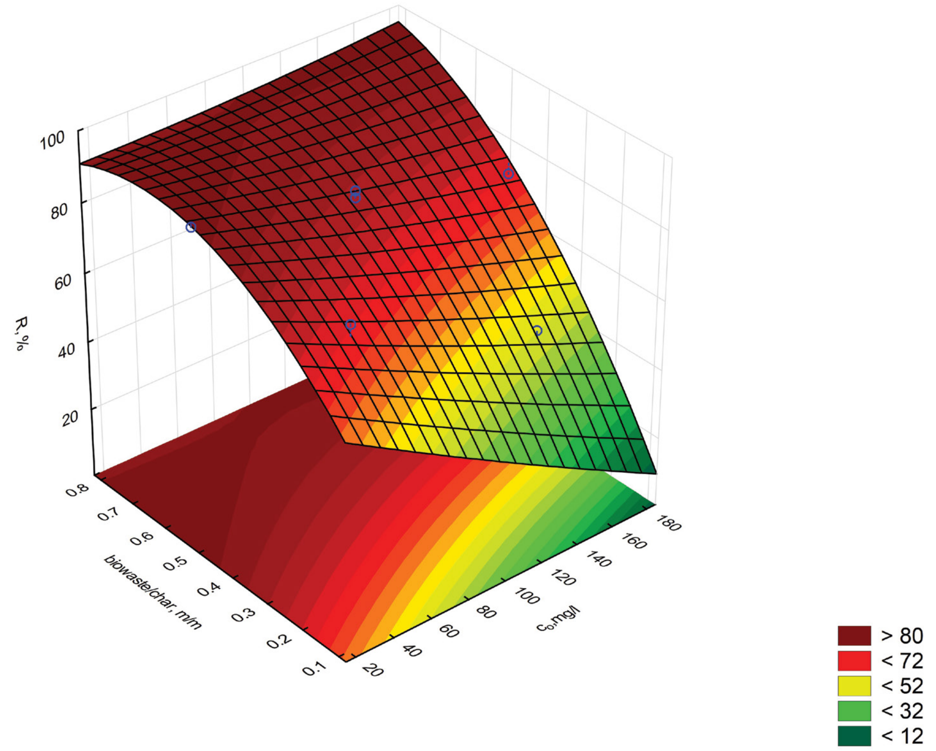

Fig. 4. 3D response surface plot. Interaction plot of Cd^{2+} initial concentration (c_0, mg/L) and mass ratio of sorbent substrates (biowaste/char, m/m).

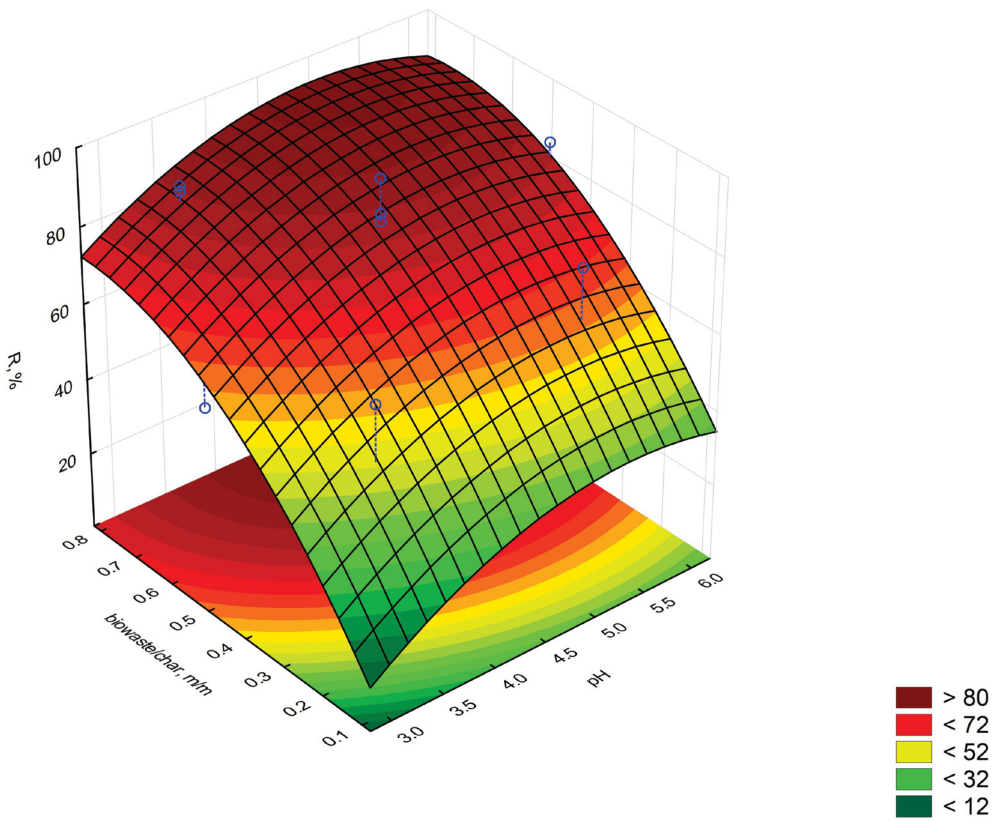

Fig. 5. 3D response surface plot. Interaction plot of initial pH and mass ratio of sorbent substrates (biowaste/char, m/m).

absorb cadmium ions by ion exchange. The pKa value of the weakly acidic carboxyl group is about 3.5–5.0 [21]. At about pH 5.0–5.5, *R*-value reaches its peak then starts to decrease. Characteristic optimum of sorption at pH 4.0–6.0 was widely noted in the research of the so-called biosorbents. Jayakumar et al. [48] performed optimization of Cd ion removal by green alga *Caulerpa scalpelliformis*. The result obtained using Box–Behnken design provides optimal pH for Cd sorption at 4.9 (removal degree 78.7%). Significant reduction of cadmium removal percentage was noted at highly acidic conditions. This phenomenon is explained by the affinity of carboxyl groups for the sorption of hydrogen cations at low pH levels. Tan et al. [49] investigated influence of pH change on cadmium removal by wheat stem, corncob, and rice husk. The maximum sorption efficiency was set within the range of pH = 4.5–6.0. Ding et al. [50] research led to similar conclusions. Sorption of cadmium ion was effective in the range of pH = 2.0–6.0. Ion exchange between Cd^{2+} and H^+, Na^+, Mg^{2+} and Ca^{2+} ions was assumed as the main process responsible for sorption. López-Sotelo et al. [28] investigated the effect of pH on cadmium and lead ion removal degree by poultry litter/poultry hatchery waste compost. The research results showed a similar relationship between *R*-value and pH to the data presented in this study. Cadmium removal percentage increased sharply at pH range 2–3 then reached a plateau (*R* about 50%), at pH > 5 minimal decreases in *R*-value were noticed. Decreasing the degree of cadmium removal at pH < 6.0 may be related to the decomposition of organic matter in poultry litter. This phenomenon was identified as the second way of influencing the pH on the sorption process of the considered sorption system. Studies of the sorption process using chicken manure indicate interactions between dissolved organic carbon and initial cadmium concentration [27]. The initial concentration of dissolved organic carbon (DOC) in the test solution was 370 mg/L. During batch sorption test, DOC concentration was decreasing. DOC concentration was 338 and 250 mg/L for initial cadmium concentration respectively 100 and 1,000 mg/L. At a higher pH range, DOC may increase because of the solubilization of humic-like substances from poultry litter. This reduces the sorption capacity of the poultry manure. The organic carbon fractions released into the aqueous solution may form soluble complexes with cadmium ions. A similar effect of pH on the degree of cadmium ion removal is shown in Fig. 6. The presented relationship was determined for a constant poultry litter/char ratio of 0.5. The discussed 3D plot presents maximum cadmium ion removal degree at the range of pH = 4.5–6.0 and low initial cadmium concentration (<40 mg/L). At low pH values, the ion exchange equilibrium shifts towards the sorption of hydrogen ions at the expense of cadmium

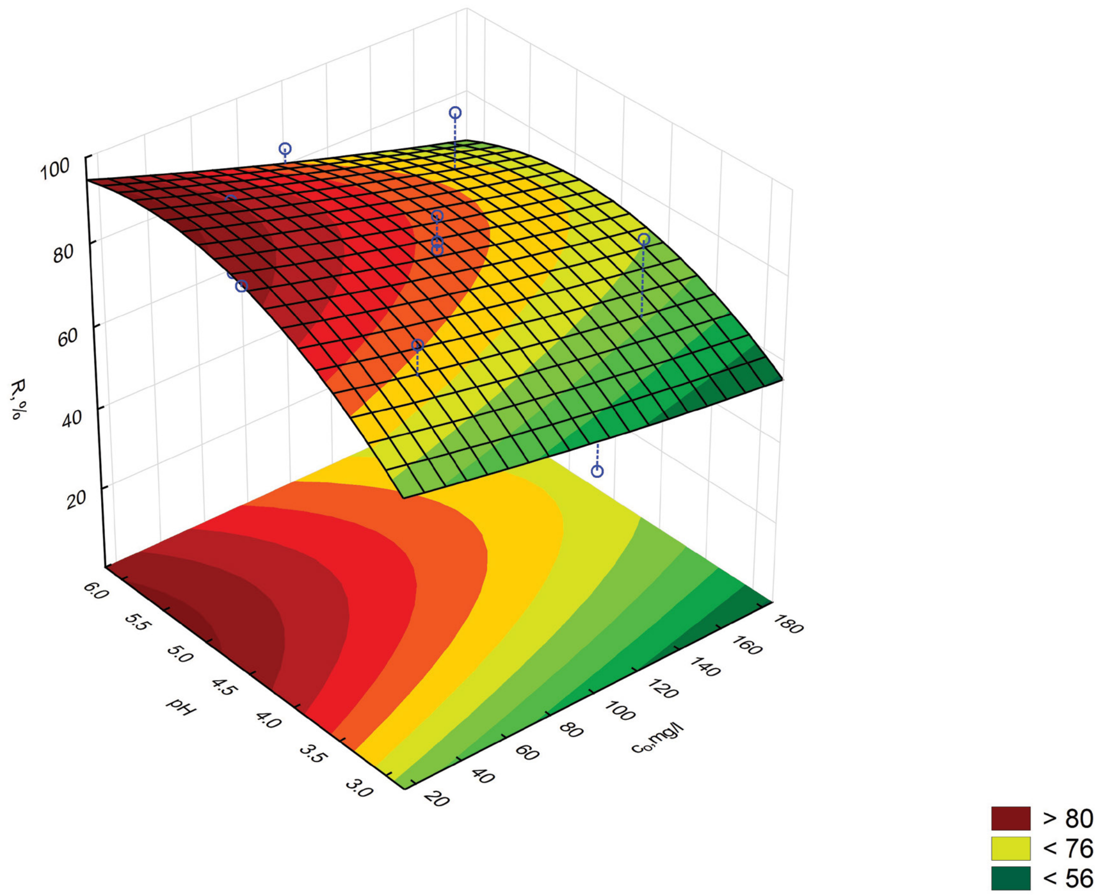

Fig. 6. 3D response surface plot. Interaction plot of Cd^{2+} initial concentration (c_o, mg/L) and pH.

ions. To determine the range of pH values in which the sorption of cadmium ions is inhibited, additional tests were performed under the conditions of poultry litter/char ratio 0.5; initial cadmium concentration was 100 mg/L and initial pH was 2.0; 2.3. In both cases, R-value was marginal, <0.1 and 0.33%, respectively.

3.3. Response surface model validation

The fitted square model Eq. (4) allowed for the determination of the optimal parameters of the sorption process. Optimal cadmium removal conditions of poultry litter/char ratio, initial pH and cadmium concentration were 0.79, 5.05 and 105 mg/L, respectively. Alternatively, the initial cadmium concentration was lowered to 20 mg/L. The correctness of the determined parameters was checked for the model solution (DW) and selected matrices: river water (W), soil extract (S), waste extract (E). The obtained results were collected in Table 5. The degree of compliance of the obtained results to the predicted value of cadmium removal was represented by the E_n value.

$$E_n = \frac{\left|R_{\text{predicted}} - R_{\text{observed}}\right|}{\sqrt{u\left(R_{\text{predicted}}\right)^2 + u\left(R_{\text{observed}}\right)^2}} \quad (5)$$

where $u(R_i)$ is calculated as expanded uncertainty ($k = 2$; 95% confidence level) of predicted and observed values.

Traditionally E_n is used to compare two different values with uncertainties given. In general $E_n < 1$ testifies to the good compliance of the results within the limit ranges set by the uncertainty of the results [51]. E_n values for observed cadmium removal percentage characterize good compliance with predicted values in case of model solution (DW) and soil water extract (S). For river water (W) compliance is questionable. The highest E_n level was found in the case of waste water extract (E). The degree of compliance of the observed result corresponds with electrical conductivity of samples (Table 1). As electrical conductivity increases, the degree of cadmium removal from the aquatic environment decreases. For electrical conductivity, approx. 1,640 μS/cm cadmium removal percentage is two times lower concerning the theoretical value. The increase in electrical conductivity value is related to the increase in the concentration of Na^+, K^+, Ca^{2+} and Mg^{2+}. The increase in ionic strength resulting from the increase in the total concentration of ions in the solution significantly reduces the adsorption capacity of cadmium ions. The influence of the ionic strength resulting from the concentration of ions in the solution on the adsorption capacity of biosorbents is relatively well-known. The increase in ionic strength causes the effect of competition between cadmium ions and matrix ions, thus reducing the adsorption capacity of biomaterials. The type of ions present in the solution also affects the decrease in the sorption capacity of the biosorbent. Ma et al. [52] investigated the adsorption capacity of cadmium ions for corn stalk pyrolysis products. It was found that the sorption capacity decreased in relation to selected ions in the order $Ca^{2+} > NH_4^+ > Na^+$, respectively. Aranda-García et al. [53] reached similar conclusions in their research on the sorption capacity of nickel ions on an adsorbent obtained from acorn shell of the oak *Quercus crassipes* Humb. & Bonpl. The research showed a greater influence of the divalent Ca^{2+} and Mg^{2+} ions, compared to Na^+ and K^+ ions, on the reduction of the adsorption capacity of Ni^{2+} ions.

Table 5
Comparison of cadmium removal percentage for selected matrices

Value	c_o, mg/L	R, %	±$U(R)$, %	E_n
Predicted	105.0	93.5	4.8	–
	20.0	94.5	4.8	–
Observed				
W_20,0	20.0	83.9	4.2	1.7
W_20,0	20.0	84.2	4.2	1.6
W_105	105.0	84.2	4.2	1.5
W_105	105.0	83.8	4.2	1.5
S_20,0	20.0	90.7	4.5	0.6
S_20,0	20.0	90.5	4.5	0.6
S_105	105.0	87.9	4.4	0.9
S_105	105.0	89.1	4.5	0.7
DW_20,0	20.0	91.5	4.6	0.5
DW_20,0	20.0	92.8	4.6	0.3
DW_105	105.0	88.2	4.4	0.8
DW_105	105.0	87.7	4.4	0.9
E_20,0	20.0	64.6	3.2	5.2
E_20,0	20.0	65.1	3.3	5.0
E_105	105.0	41.9	2.1	9.8
E_105	105.0	41.3	2.1	10.0

4. Conclusions

In this study cadmium ion removal process optimization was conducted using RSM with CCD. The proposed empirical model was characterized by good agreement with the obtained (R_{obs}) results. Adjusted R^2 and predicted R^2 values were 0.9208 and 0.96832 respectively. Statistical analysis showed a significant influence of the factors as follows, poultry litter/char ratio, initial cadmium concentration (c_o) and initial pH. The following optimal values of the process parameters were determined: poultry litter/char ratio (0.79), initial cadmium concentration (105 mg/L) and initial pH (5.05). The obtained values were characterized by the excellent consistency in the case of the model solution.

The obtained results indicate the usefulness of the poultry litter/char, as a low-cost absorbent, for the removal of cadmium from different water samples such as river water, sewage and landfill leachate. However, the studies have shown a poor selectivity of the sorption process. Therefore electrical conductivity and ionic strength of samples should be taken into account in further investigations.

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