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OPTIMIZATION OF PROCESS PARAMETERS FOR RETENTION OF Cd(II) IONS ADSORPTION FROM AQUEOUS SOLUTIONS ON CLAY MATERIALS

BY

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Abstract. Globally, heavy metal pollution is classified as serious environmental problem. Cd(II) ions are commonly encountered pollutants that are toxic to human life, even at low concentration and adsorption is one of the most suited process for this heavy metal ions removal from aqueous solutions. Clay materials have risen as potential options in contrast to conventional adsorbents. The adsorption properties of clay in retention of Cd(II) from aqueous solutions have been studied in batch technique. The amount of adsorbed heavy metal ions was determined for the adsorption systems as a function of adsorbent dose, initial solution pH, initial ion concentration, contact time and temperature. Based on the obtained experimental results, the optimal values of the process parameters are: initial solution pH 7.0, 4.0 g adsorbent·L^{-1}, 60 minutes of contact time and ambient temperature. These conditions ensure a maximum removal efficiency of Cd(II) ions of 93%.

Keywords: water pollution, heavy metals, cadmium ions, clay materials, adsorption

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1. Introduction

Various fields of anthropogenic activities such as extracting, mining, use of fertilizers, battery production, metallurgical engineering, electroplating or geochemical natural processes generate various types of heavy metal pollutants in wastewater effluent (Roberts, 2014). The contamination of water resources by heavy metal like chromium, cadmium, nickel, lead, arsenate is an important worldwide concern due their toxicity, high storage capacity and low biodegradability. When transferred to humans through the food chain, these metals could be accumulated in various body organs and tissues causing life-threating illness (Morais *et al.*, 2012).

Cd(II) is a highly toxic pollutant that can be released to the environment from natural sources such as volcanic activity, weathering of Cd-containing rocks, sea spray or from industrial activities (smelting, refining, dyeing etc.) (Roberts, 2014). This heavy metal is known to be a great concern due to very high-water solubility, high bioaccumulation, non-biodegrading properties and high toxicity even at low concentration (Long *et al.*, 2021). Cadmium in drinking water should not exceed the limit value of 0.003 mg/L (WHO, 2019) and from anthropogenic activities the discharged concentration should be lower than 2 mg/L (Basu *et al.*, 2017). Contamination with this toxic metal ions, exceeding those values, can cause cadmium poisoning described by renal dysfunction, osteoporosis, cancer (Bashir *et al.*, 2014).

In order to remove these hazardous pollutants, many treatment technologies are being proposed globally. Several procedures such as chemical precipitation, biological method, electrodialysis, ion exchange, membrane (Kurniawan *et al.*, 2006). These technologies have shown interesting removal efficiencies at laboratory scale and upscaling to real cases has been hindered by several limitation such as high capital and exploitation costs, very sensitive operational condition, the use of large amounts of chemicals and the production of secondary sludge that has to be sustainably handled (Cui *et al.*, 2014).

Adsorption is the most widely employed because of its flexibility and reversibility (Fu *et al*., 2011). Also, this method is both simple to use and effective even at low concentration (Kwikima *et al.*, 2021). Other advantages are high selectivity, practicality, ease of operation, low environmental risk, low start-up and installation costs, resistance to toxic components and significant potential for removal of unsafe contaminants (Pyrzynska, 2019). Many low-cost adsorbents have been well studied for the removal of Cd(II) such as zeolites, clays, algae, coal, mosses, chitosan, biochar, eggshell, sunflower, peanut shell, brewed tea waste (Szende *et al.*, 2022).

Clay proposed as adsorption materials fulfil all requirements for low-cost chemical precursors for industrial application. Clay materials are mainly composed of silica, alumina and water, having a particle size less than 2 µm (Usman *et al*., 2020). Also has a high specific surface area which contain a large variety of exchangeable cations and anions. In most of the cases, the surface of the clay is negatively charged and can contain Ca^{2+}, Mg^{2+}, H^{+}, K^{+}, NH^{4+}, Na^{+}, SO_4^{2-}, Cl^{-}, PO_4^{3-}, NO^{3-}, these ions could be easily exchange with other ions while the mineral structure of clay is not affected (Srinivasan, 2021). For this reason, this adsorbent is an excellent option for retention metal cation from water. Also, clay material has a high binding performance due to porous surface which determined strong attractive force and many active binding sites (Uddin, 2017).

In this study, a local clay material was used as a natural adsorbent for the removal of Cd(II) ions from aqueous solutions. Batch adsorption studies were conducted, where the most influencing parameters were investigated (initial solution pH, adsorbent dosage, initial Cd(II) ions concentration, contact time and temperature).

2. Experimental section

2.1. Materials

The clay material used in experimental studies was collected from Vladiceni, Iaşi, Romania. The samples were gathered from the surface horizon (10 - 40 cm), dried in air at 60°C for 6 hours, grounded, mortared and sieved to pass only particles grain size lower than 0.5 mm and after stored in desiccators and used in adsorption process.

All the chemical reagents used in this study were of analytical grade and were used without further purifications. Solution of hexamethylenetetramine 5%, pH = 6 was prepared by dissolving an appropriate amount of solid reagent in distilled water. The pH was adjusted with HNO_3(2N). A stock solutions of Cd(II) ions (566.0514 mg $Cd(II)\cdot L^{-1}$) was obtain by dissolving an exact weight quantity of cadmium nitrate in distilled water. All working solutions (22.48 - 157.37 mg $Cd(II)\cdot L^{-1}$) were prepared from stock solution by dilution with distilled water and HNO_3 solutions were used to adjust the initial pH.

A digital spectrophotometer (S 104 D) with a 1 cm glass cell was used to analyse and determine the concentration of Cd(II) ion from aqueous solutions in the following condition: absorbance of each solutions was measured at $\lambda = 570$ nm against blank solution using xylenol-orange as colour reagent.

2.2. Adsorption studies

Adsorption studies of Cd(II) ions onto clay material were performed in batch systems, at room temperature (20 ± 2°C). A given quantity of clay adsorbent (0.1 g) was mixed with volume of 25 mL of aqueous solutions with known Cd(II) ion concentration, known initial solution pH, in 100 mL Erlenmeyer flasks, with intermittent stirring. The range of variation of the experimental parameters for each type of experiment is summarised in Table 1.

Table 1
The range of variation of the experimental parameters in the adsorption experiments

Experiment	pH	Adsorbent dosage [g·L^{-1}]	Cd(II) concentration [mg·L^{-1}]	Contact time [min]	Temperature, [°C]
Effect of initial solution pH	2.0 - 7.0	4.0	22.70	1440	20.5
Effect of adsorbent dosage	7.0	4.0 - 20.0	22.70	1440	21
Effect of initial Cd(II) concentration	7.0	4.0	22.48 - 157.37	1440	19.1
Effect of contact time	7.0	4.0	22.70	5 - 180	20
Effect of temperature	7.0	4.0	22.48 - 157.37	180	8.2; 26; 50

After 24 hours, the sample were separated through filtration and Cd(II) ions concentration in filtrate was determined. The adsorption capacity of clay material (q, [mg·g^{-1}]) and the percent of Cd(II) ions removal (R, [%]), were calculated using following equations:

$$q = \frac{(C_0 - C) * (V/1000)}{m} \quad (1)$$

$$R = \frac{c_0 - c}{c_0} * 100 \quad (2)$$

Where c_0 and c are the initial and equilibrium Cd(II) ions concentration [mg·L^{-1}], V is the volume of solution [mL], and m is the mass of clay material [g].

3. Results and discussions

3.1. Effect of initial solution pH

The effect of initial aqueous pH on Cd(II) removal efficiency was performed under the experimental conditions presented in Table 1. The experimental results showed that the removed amounts increased with the increase of the pH solutions (Fig. 1). For the initial pH of 2.0, the adsorbed amount of Cd(II) was 0.185 mg·g^{-1}. At pH of 7.0, this parameter reached 5.21 mg·g^{-1} which is about 28 times higher than the value obtained for an initial pH of 2.0. This fact could be explained by the clay surface charge, which is positive at lower pH solutions causing the repulsion of the cationic metals. At this pH range, abundant H^+ ions in the solution will compete with Cd(II) ions over the adsorption site. As the pH of the initial solution increases, the dissociation degree of the surface functional groups increases and the adsorbent surface of the clay materials carry more negative charges and will consequently favor Cd(II) ions adsorption through electrostatic reactions. When Cd(II) ions concentration is constant, the values of q are almost the same (Fig. 1).

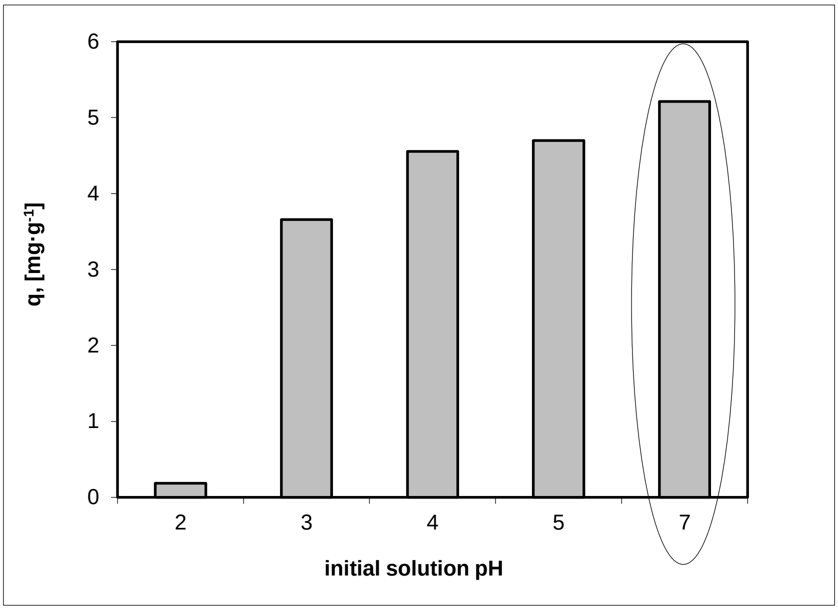

Fig. 1 – Effect on initial solution pH on Cd(II) ion adsorption on clay adsorbent.

Therefore, under these conditions, the best performance were obtained at initial solutions pH of 7.0 and this value was considered optimal for the removal of Cd(II) ions from aqueous solutions by adsorption on clay materials and used in all further experiments.

3.2. Effect adsorbent dosage

The impact of adsorbent dose on Cd(II) removal from aqueous solution was studied using different amount of clay material (see Table 1), while the other experimental parameters were maintained constant. The experimental results are presented in Fig. 2 and indicate that the increase of the adsorbent dosage between 4.0 and 20.0 $g·L^{-1}$ determined a decrease of adsorption capacity from 4.99 to 1.08 $mg·g^{-1}$. Also, can be observed that the values of R increase very slowly from 91.83 to 96.57%, in opposite variation with q. This fact may be the consequence of the decrease of number of active sites as the adsorbent dose increased due to particles agglomeration process (Azanfire *et al.*, 2020). Such high removal efficiencies observed for relatively low clay dose is a real asset for larger applications at industrial levels.

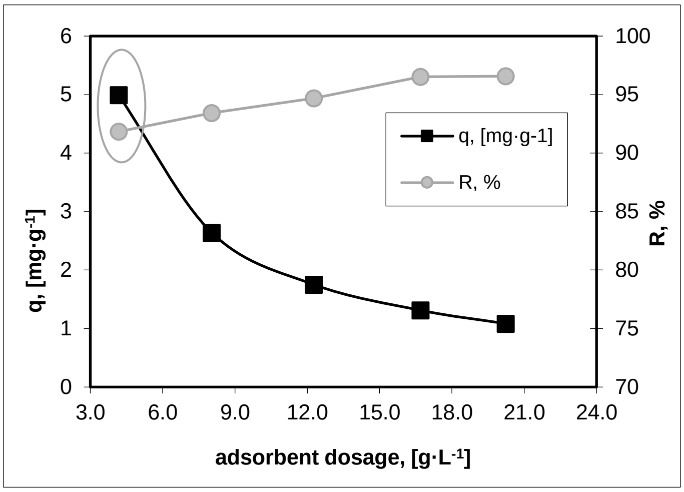

Fig. 2 – Effect on adsorbent dosage on Cd(II) ion adsorption on clay adsorbent.

In conclusion, a dosage of clay material of 4.0 $g \cdot L^{-1}$ of can be considered optimal for the removal of Cd(II) ions from aqueous solutions and this value was used in all experiments.

3.3. Effect of contact time

The influence of contact time on the adsorption efficiency of clay material for the removal of Cd(II) ions from aqueous media was analyzed in the time interval between 5 and 180 min (see Table 1). The experimental results are presented in Fig. 3.

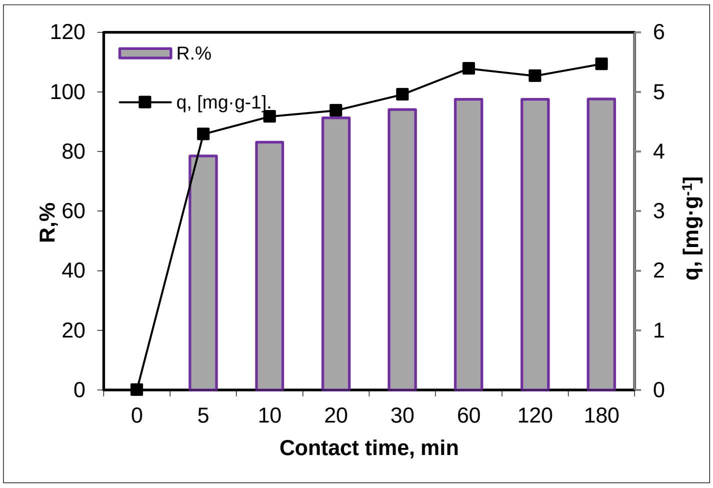

Fig. 3 – Effect on adsorbent dosage on Cd(II) ion adsorption on clay adsorbent.

As you can see in Fig. 3, the adsorption capacity increases very fast with the increasing of contact time in the first 60 minutes, from 0 to 5.39 $mg{\cdot}g^{-1}$, after which the values of q increase very slowly, reaching a maximum adsorption capacity 5.46 $mg{\cdot}g^{-1}$ at 180 minutes. The adsorption process can be considered at equilibrium after 60 minutes of contact time for economic reasons, the differences between the values of adsorption capacities obtained for 60 and 180 minutes are very small. The presence of a large number of adsorption sites on the surface of clay material which are initially free and can easily bind the heavy metal ions determined a short time to reach the balance. Also, the removal percent of Cd(II) ions are very high (R ≅ 97.46%) at low initial Cd(II) ions concentration 22.70 $mg{\cdot}L^{-1}$. A contact time of 60 minutes was considered sufficient and was used in other experimental studies.

3.4. Effect of initial Cd(II) ions concentration

The adsorption efficiency of Cd(II) ions on clay material were investigated at various initial concentration via batch adsorption method (see Table 1.) In equilibrium, results showed (Fig.4) that the adsorption capacity q increased from 4.85 to 33.52 $mg{\cdot}g^{-1}$ as the initial concentration of Cd(II) increased from 22.70 to 158.94 $mg{\cdot}L^{-1}$, indicating that the adsorption process is a quantitative one regardless of the value of the initial concentration. A high concentration of Cd(II) free ions was observed at neutral pH (pH = 7.0), they were adsorbed on clay surface, binding to the functional group. Also, the removal percent R increases with the increase of initial heavy metal concentration, reaching a maximum of 92.81%.

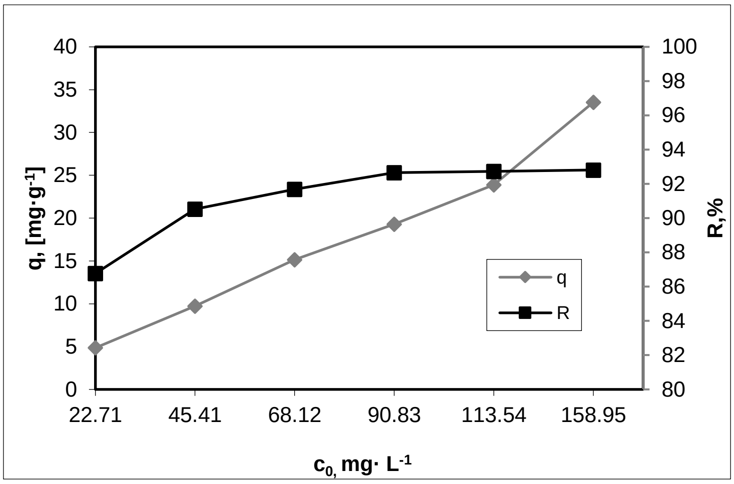

Fig. 4 – Effect of initial Cd(II) concentration on the adsorptive performance of clay material.

3.5. Effect of temperature

In order to understand the influence of temperature on adsorption process on clay material, the experimental studies were conducted at three different values of temperature (8.2, 26, 50°C), under optimized experimental conditions (see Table 1). The obtained experimental results are presented in Fig. 5.

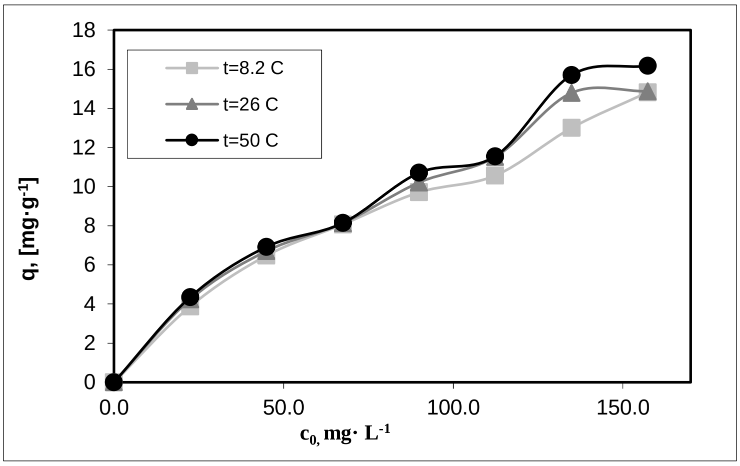

Fig. 5 – Effect of initial metal ions concentration and temperature on Cd(II) ion adsorption on clay material.

According to these curves (Fig. 5), the values of adsorption capacity q at equilibrium increase as the Cd(II) metal ions concentration increases, until the clay surface became saturated with basic groups from solutions. At 26°C, an increase of initial Cd(II) concentration from 22.48 to 157.37 mg·L^{-1} determined the increase of q values from 4.23 to 14.87 mg·g^{-1}. High values of the adsorption capacity were determined by the collision between Cd(II) ion and superficial functional group from clay surface, process conducted by raised values of initial heavy metal concentration. It can be also seen from Fig. 5 that temperature is not an influencing factor in adsorption mechanism. An increase in temperature from 8.2 to 50°C determine a small improvement of adsorption capacity of clay adsorbent from 14.82 to 16.16 mg·g^{-1}. Economically speaking, this behavior is a big advantage because the adsorption process can be conducted at ambient temperature, without cooling or heating the solutions.

4. Conclusions

In this study was examined the retention of Cd(II) ions from aqueous media using as adsorbent a low-cost clay material. The adsorption experiments were performed in batch system and the obtained results have indicated that the highest adsorption capacity of clay material is reached at initial solution pH of 7.0, 4.0 g·L^{-1} adsorbent dosage, 60 minutes of contact time and ambient temperature. The obtained results indicate that the clay material can be used with success in retention of Cd(II) ions from aqueous media.

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OPTIMIZAREA PARAMETRILOR ÎN PROCESUL DE REȚINERE A IONILOR METALICI Cd(II) DIN MEDII APOASE PE MATERIALE ARGILOASE

(Rezumat)

La nivel global, poluarea cu metale grele este tratată ca o problemă serioasă în ceea ce privește mediul înconjurător. Ionii de Cd(II) sunt o serie de poluanți frecvent întâlniți care sunt foarte toxici pentru organismul uman chiar și în concentrații foarte mici și adsorbția este una dintre cele mai eficace metode de îndepărtare a acestora din medii apoase. În ultimul timp, materialele argiloase au stârnit un interes ridicat comparativ cu alte materiale adsorbante convenționale datorită suprafeței specifice mari, structurii poroase, capacitații de adsorbție ridicate, stabilității chimice, disponibilității în cantități ridicate în multe regiuni din întreaga lume, operațiilor preliminare simple. Proprietăţile adsorbante ale materialelor argiloase implicate în procesul de reținere a ionilor de Cd(II) din medii apoase au fost studiate în condiții statice. Cantitatea de ioni metalici adsorbiți a fost analizată în funcție de doza de adsorbent, pH-ul soluției inițiale, timpul de contact și temperatură. Rezultatele experimentale obținute indică o eficiență crescută a procesului de îndepărtare a ionilor de Cd(II) din soluții apoase la un pH al soluției inițiale egal cu 7,0 și o cantitate de 4,0 $g \cdot L^{-1}$ de material argilos. De asemenea, echilibrul procesului de adsorbție se atinge foarte rapid, timpul de contact fiind foarte mic, 60 de minute, la temperatura ambientală indicându-ne faptul că procesul de adsorbție este unul economic. În aceste condiții, procesul de reținere a ionilor de Cd(II) este de peste 93% într-un interval de concentrație inițială cuprins între 11,0 și 160 $\mu g \cdot mL^{-1}$ Cd(II). Conform acestui studiu, materialele argiloase pot fi folosite cu succes ca și materiale adsorbante pentru îndepărtarea ionilor de Cd(II) din efluenții industriali și reprezintă o alternativă promițătoare pentru procesele de reținere a metalelor grele.