Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2022.29001

276 (2022) 142–149
November

Characterization and isothermal studies of Cd removal from aqueous solutions using sludge-based activated carbon

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Received 26 May 2022; Accepted 3 October 2022

ABSTRACT

Generated sewage sludge by wastewater treatment plants is carbonaceous in nature and rich in organic materials, therefore, it has the potential to be converted into activated carbon. In this study, the sludge-based activated carbon was obtained using sewage sludge from Volkovo wastewater treatment plant in Skopje by chemical activation under controlled conditions. Prepared sludge-based activated carbon was characterized using scanning electron microscope and X-ray diffractometer, and was studied its application as adsorbent for cadmium removal from aqueous solutions. The experimental results performed to determine the efficiency of the sludge-based activated carbon for cadmium removal from aqueous solutions, shows that the removal of Cd was 73.91%. The effects of parameters such as pH, mass of adsorbent, contact time and initial cadmium ion concentration were investigated and presented in this study. The sludge-based activated carbon's maximum capacity was determined in equilibrium studies. Experimental data were fitted to adsorption models and better fit was obtained with the Langmuir adsorption isotherm.

Keywords: Cadmium; Sewage sludge; Adsorption isotherm; Adsorption capacity; WWTP Volkovo

1. Introduction

Sludge management, a by-product of wastewater treatment, is becoming a serious problem both in our country and in the world. In terms of volume and method of valorization, sewage sludge continues to cause environmental issues. While the focus throughout the world is on discovering ways to make sludge recyclable, in our country, sludge is usually disposed of in landfills. In the past few years, European Union promoted the ecological management of such wastes by introducing directives regarding sewage sludge management and therefore classical methods, such as storage, are being replaced by methods leading to waste stabilization and safe recycling [1]. There are several methods for sewage sludge treatment such as: anaerobic co-digestion [2], composting [3], incineration [4], co-incineration [5] and cementing [6]. Thermal treatment of sewage sludge is considered as an attractive method in reducing sludge volume which at the same time produces reusable by-products.

Sludge, as a by-product during the process of sewage treatment, is difficult to handle because it is characterized by high water content, loose structure, a large amount of organic matter, and poisonous and harmful substances (such as microorganism, heavy metal, and poisonous organism) [7]. On the other hand, sludge is rich in nutrients such as nitrogen and phosphorus, and contains organic

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matter that is especially useful for soils prone to erosion. Also, sewage sludge is carbonaceous in nature, therefore, it has the potential to be converted into activated carbon [8]. Converting sewage sludge into activated carbon based on its high content of organic components not only solve the disposal problem of sewage sludge, but also turn solid waste into useful material in producing adsorbent for wastewater treatment. The raw material of sludge-based activated carbon is cheap and easy to obtain, and its adsorption ability to some pollutants is better than that of commercial activated carbon or other potential adsorbents [9].

The Republic of North Macedonia is rich in inorganic materials with a wide range of potential application as adsorbents, including trepel [10,11], diatomaceous earth [12,13], perlite [14] and zeolite-bearing tuff [15], but using sludge-based activated carbon as adsorbent also achieve the goal of waste utilization.

Sludge-based activated carbon can be prepared by direct pyrolysis method [16,17], physical activation process [18,19], chemical activation process [20,21], physical–chemical activation process [22], microwave activation [23], etc. These methods can be used to produce porous carbon-adsorbing materials. This material is a black amorphous carbon material generated from activated sludge from water treatment, which is created through blending, carbonization, activation, etc. It has the characteristic of a dense pore, complex pore structure, and large specific surface area, as well as a high absorbability [7].

The sludge-based activated carbon could be utilized to remove organic matter [24], heavy metal [25,26] and gas pollutants [27]. Sludge-based activated carbon can be used alone or in combination with other water treatment technologies to expand its application potential while lowering operational costs. Sludge-based activated carbon, when combined with a membrane bioreactor to treat waste leachate, improved the characteristics and structure of the cake layer on the membrane surface, resulting in improved filtration performance and water permeability.

The removal of heavy metal ions with sludge-based activated carbon is mainly achieved through chemical adsorption, physical adsorption and ion exchange reaction [7]. Heavy metal ions can generate an exchange reaction on the surface of activated carbon. The surface of sludge-based activated carbon can be introduced to the special groups to strengthen the absorption of heavy metal ions after adding a reagent or remodification of sludge-based activated carbon. The sludge-based activated carbon adsorption of heavy metals is mainly chemical adsorption, but also, adsorption mechanisms that occur are surface precipitation and ion exchange.

The application of sludge-based activated carbon for heavy metal ions removal are described by some authors. Tan et al. [25] used sludge-based activated carbon for adsorption to Pb, Zn, Cu, and Cd and obtained that the adsorption using sludge-based activated carbon had higher adsorption capacity than that of commercial activated carbon. The authors prepared sludge-based activated carbon under 900°C by anaerobic pyrolysis. At high level of pH, the heavy metal ions were converted into hydroxide and precipitated on the surface of adsorbent, but at low pH, in addition to producing a very small amount of precipitation, a large number of heavy metal ions were exchanged with Ca^{2+} and subsequently adsorbed by adsorbent.

Hanfeng [26] studied the process of adsorption of heavy metals, such as, Cu(II), Pb(II), Cr(VI), and Cd(II) by sludge-based activated carbon. The equilibrium adsorption efficiencies of studied heavy metals are much higher than that of commercial activated carbon, which is possibly attributed to the fact that the content of the acid group in sludge-based activated carbon is too high that it affects the adsorption of heavy metal ions.

Heavy metal ion pollution in water is an important environmental issue due to carcinogenicity and toxicity properties. Cadmium is a heavy metal with an extremely high ability to inhibit enzymes. Cadmium is relatively rare, but low concentrations are very toxic to plants, animals and humans [28]. Cadmium is a toxic metal that ranks 7 on the US Agency for Toxic Substances & Disease Registry's priority list of hazardous substances [29], a prioritization of substances based on a combination of their frequency, toxicity, and potential for human exposure.

The aim of this study is preparation of activated carbon from sewage sludge from Volkovo wastewater treatment plant in Skopje, Republic of North Macedonia and its application for cadmium removal from aqueous solutions.

2. Materials and methods

2.1. Preparation of sludge-based activated carbon

Activated carbon was obtained using sewage sludge from Volkovo wastewater treatment plant in Skopje, Republic of North Macedonia. Table 1 shows the characteristics of the used sludge, which were obtained as average values from four separate analyses conducted at different times of the year.

The sewage sludge contained around 51% inorganic matter 49% of organic matter. Table 1 shows the content of heavy metals in sewage sludge from a municipal wastewater treatment plant. Qiu et al. [30] described a process

Table 1
Physico-chemical properties of sewage sludge

Dry matter content, %	Organic matter content, %	Inorganic matter content, %	Relative density, kg/m^3	Electrical conductivity, μs/cm	pH	
23	48.66	51.34	9.325	160.5	7.81	
Mn, mg/kg	Ni, mg/kg	Co, mg/kg	Pb, mg/kg	Cd, mg/kg	Fe, mg/kg	Zn, mg/kg
0.342	0.076	0.012	0.020	0.0014	2.088	0.860

for preparation sludge-based activated carbon. The raw sewage sludge was dried at 105°C for 24 h, to achieve constant weight, then comminuted and sieved into a uniform size of 80 mesh (0.175 mm). The 50 g of dehydrated sewage sludge was soaked stilly with 100 mL 10% HCl solution in 2,000 mL laboratory beaker for 24 h at room temperature. Then, it was soaked again stilly with 100 mL 25% $ZnCl_2$ solution in 2,000 mL laboratory beaker for 24 h at room temperature. It was then dried at 105°C for 8 h to achieve a constant weight, and then carbonized in a muffle furnace for 50 min at 600°C. The obtained product, sludge-based activated carbon, was used for adsorption experiments.

2.2. Characterization of sludge-based activated carbon

2.2.1. Scanning electron microscope

The surface morphology of the sludge-based activated carbon was studied using a scanning electron microscope VEGA3 LMU produced by Tescan. This particular microscope is also fitted with an Inca 250 energy-dispersive X-ray analysis (EDS) system. EDS is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X-rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons.

2.2.2. X-ray diffraction

X-ray diffractometer (XRD) 6100 produced by Shimadzu was used to investigate the mineralogical structure of natural raw material samples. This technique is based on observing the scattering intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The X-ray diffractometer was equipped with a Cu anode with a radiation wavelength of CuKα = 1.54178 Å. The operating voltage was U = 40.0 kV and current intensity I = 30.0 mA. Samples were examined within 10.0–80.0 with 2.0 s on each step in a controlled rotational mode at 60.0 rpm. The data were compared to the International Centre for Diffraction Data database, to identify the material in the solid samples.

2.3. Application of sludge-based activated carbon

The obtained sludge-based activated carbon from sewage sludge from Volkovo wastewater treatment plant in Skopje was studied for cadmium removal from aqueous solutions. The experiments were performed to determine the efficiency of the sludge-based activated carbon through study the effect of the pH value of the solution, the effect of the added mass of the adsorbent and the effect of the initial metal concentration in solution.

Contact time is one of the most important parameters that influence the adsorption process. For this reason, all experiments were performed within certain time intervals.

Adsorption of cadmium on sludge-based activated carbon was performed with different initial concentration (1.58, 3.82, 4.60, 5.42, and 7.70 mg/L) of synthetic single ion solutions of cadmium ions. Synthetic single component solutions of these metals were prepared by dilution Merck Cadmium Standard Solution Traceable – SRM from NIST $Cd(NO_3)_2$ in HNO_3 0.5 mol/L 1,000 mg/L Cd Certipur®. The pH of the prepared solutions was adjusted using solutions of HCl (0.1 M) and NaOH (0.1 M) and controlled by a HQ40D Portable Multi Meter by Hach. The initial pH of the tested solutions was 3, 5, 7 and 12. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers using 1, 2, 3 and 4 g of the sludge-based activated carbon in 100 mL of cadmium single ions solution. A magnetic stirrer was used for agitation at 120 rpm, up to 1,440 min, at temperatures of 25°C. After a predetermined time, the suspension was filtered and the filtrate's concentration of metal ions in solution was analysed by high-performance VIS spectrophotometer with RFID technology for reliable and traceable measurement results of routine analysis and user applications Hach DR 3900.

The removal efficiency E (%) and the equilibrium adsorption capacity q_e (mg/g) of sludge-based activated carbon on cadmium were calculated using Eqs. (1) and (2):

$$E = \frac{C_0 - C_e}{C_0} 100(\%) \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} (\text{mg/g}) \tag{2}$$

where q_e represent the amount of metal adsorbed in mg per g of sludge-based activated carbon at equilibrium conditions, C_0 and C_e are initial and equilibrium concentration of cadmium in solution (mg/L), respectively, V is the volume of solution (L) and m is the mass of sludge-based activated carbon (g).

2.4. Equilibrium studies

Equilibrium studies generally involve the determination of the adsorption capacity of a given material. This determination is critical in determining the material's potential as an economically and commercially viable absorber. The adsorption of sludge-based activated carbon was predicted by fitting the experimental data to conventional adsorption mathematical models, namely the Freundlich and Langmuir models.

2.4.1. Langmuir model

The Langmuir isotherm model [31], based on monolayer coverage of adsorbent surfaces by the adsorbate at specific homogeneous sites within the adsorbent, is represented as:

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \tag{3}$$

where q_m (mg/g) is the amount of solute adsorbed per unit mass of adsorbent corresponding to complete coverage of available sites, K_l (L/mg), is the Langmuir adsorption coefficient, this constant is related to the affinity between the adsorbent and solute, which is evaluated by linearization of Eq. (4):

$$\frac{1}{q_e} = \frac{1}{K_l q_m C_e} + \frac{1}{q_m} \quad (4)$$

The essential characteristics of the Langmuir isotherm can be described by a dimensionless constant called the equilibrium parameter, R_L, which is usually defined by:

$$R_L = \frac{1}{\left(1 + K_l C_0\right)} \quad (5)$$

where K_l is the Langmuir constant that indicates the nature of adsorption. The value of R_L indicates if the adsorption isotherm is irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$).

2.4.2. Freundlich model

The Freundlich isotherm model [32], based on monolayer adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat, is represented as:

$$q_e = k_f C_e^{1/n} \quad (6)$$

where k_f and n are empirical Freundlich constants that are dependent on experimental conditions. k_f is an indicator of adsorption capacity, while n is related to the adsorption intensity or binding strength. Their values were determined from the linear form of the Freundlich equation:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \quad (7)$$

where $1/n$ is the heterogeneity factor. Values of $1/n < 1$ indicate heterogeneous adsorbents, while values closer to or equal to 1 indicate a material with relatively homogeneous binding sites [33].

3. Results and discussions

3.1. Scanning electron microscope

Micrographs of sludge-based activated carbon samples obtained from scanning electron microscope (SEM) analysis are given in Fig. 1. The micrographs clearly show a number of macropores in the sludge-based activated carbon structure.

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis (Fig. 2) and the elemental composition of sludge-based activated carbon are presented in Table 2.

Results of EDS analysis showed the high concentration of Zn and Cl in all studied samples, but that was expected because the activation of the samples was made with $ZnCl_2$. Also, the obtained results showed that the predominant exchangeable cations in sludge-based activated carbon structure were Ca^{2+}, Mg^{2+} and K^+. High concentration of these ions, especially Ca, indicate that ion-exchange may be occur in addition of adsorption.

3.2. X-ray diffraction

The mineralogical structure of the sludge-based activated carbon was investigated using X-ray diffraction. The XRD results, (Fig. 3) as expected, confirm that the sludge-based activated carbon does not have well define peaks indicating that it is an amorphous material. Graph also illustrated that sludge-based activated carbon has a weak

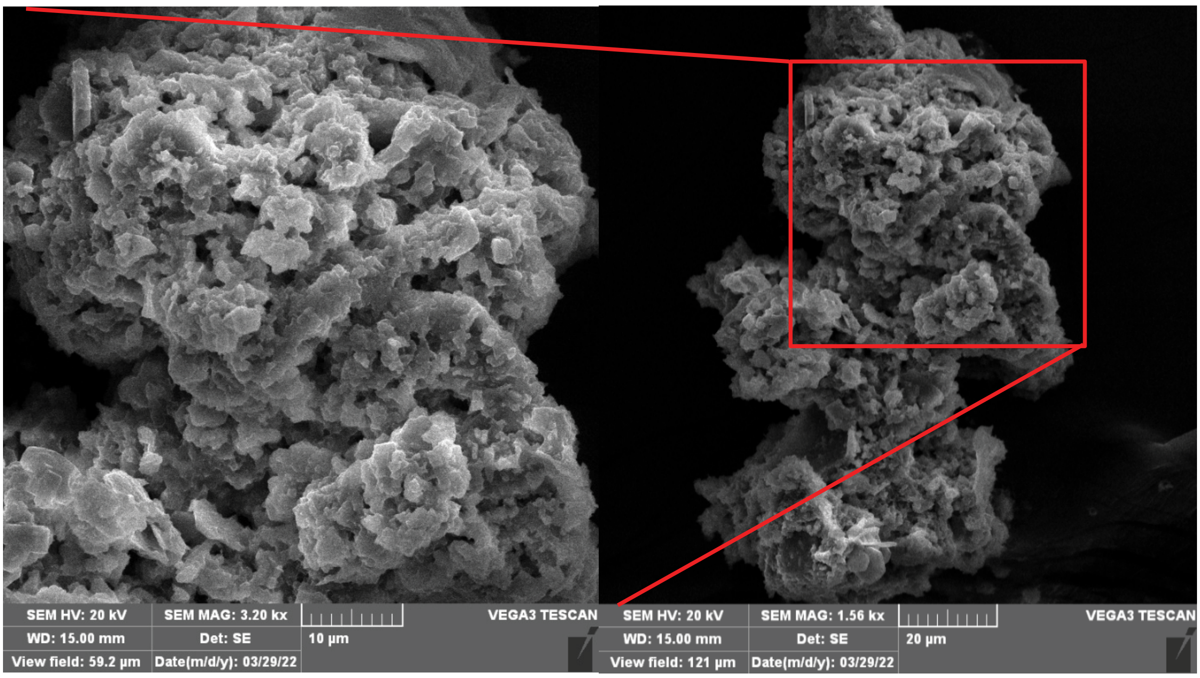

Fig. 1. Micrograph of sample obtained from SEM analysis.

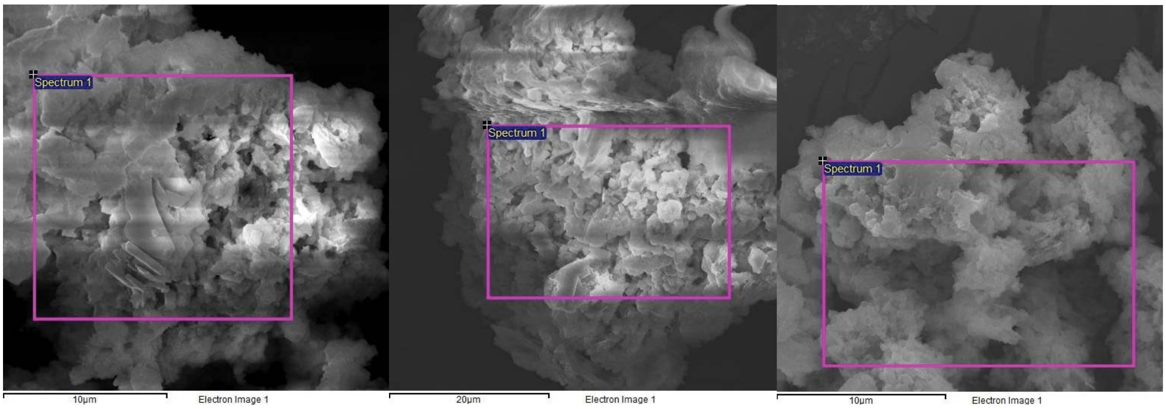

Fig. 2. Micrographs of sample for EDS analysis.

Table 2
Elemental composition of sludge-based activated carbon

Element	Weight (%)			
	Sample 1	Sample 2	Sample 3	Average
C	0.00	7.54	9.99	5.84
O	36.64	39.80	33.10	36.51
Mg	0.71	1.03	0.00	0.58
Al	2.80	2.20	2.24	2.41
Si	5.21	5.07	5.32	5.20
P	2.28	2.04	1.04	1.79
Cl	23.79	16.36	18.79	19.65
K	0.63	0.82	0.68	0.71
Ca	8.53	7.94	10.60	9.02
Fe	2.16	4.31	4.23	3.57
Zn	17.25	12.59	14.01	14.62
Ti	0.00	0.30	0.00	0.10
Totals	100.00	100.00	100.00	100.00

crystal structure with low concentration of portlandite and graphite. The sludge-based activated carbon has amorphous nature from 2θ° of 10° to 20°, which characterize the activated carbon [34].

3.3. Effect of contact time

The efficiency of the sludge-based activated carbon obtained by chemical activation process using sewage sludge from Volkovo wastewater treatment plant in Skopje were studied for cadmium removal from aqueous solutions. Contact time is one of the most important parameters that influence the adsorption process. For this reason, all experiments were performed within certain time intervals, such as, 30, 60, 120, 240 and 1,440 min. The results shows that the adsorption process is very rapid. The adsorption rate of cadmium ions increases sharply at short contact time and slowed gradually as equilibrium was approached. Therefore, the equilibrium time was 240 min. It could be because there are a huge number of vacant surface-active sites for adsorption at first, and the adsorption rate is quite quick. Due to repulsive forces between metal ions adsorbed on solid surfaces and metal ions from solution, filling vacant sites becomes difficult as equilibrium is approached [35].

3.4. Effect of mass of sludge-based activated carbon

The effect of the mass of the adsorbent was investigated by contacting 1, 2, 3, and 4 g of sludge-based activated carbon, at pH 7, with the 4.6 mg/L Cd solution. An increase in the adsorbent mass should increase the adsorption of cadmium ions, because more adsorption sites are available per unit mass of adsorbent. The results confirmed that an increase in the adsorbent mass slightly increased the adsorption of cadmium ions (Fig. 4) and the adsorption of cadmium ions was 58.7% with 1 g of adsorbent and almost 74% using 4 g of adsorbent.

3.5. Effect of initial pH of the solution

The pH of the solution plays an important role in the whole adsorption process and particularly on the adsorption

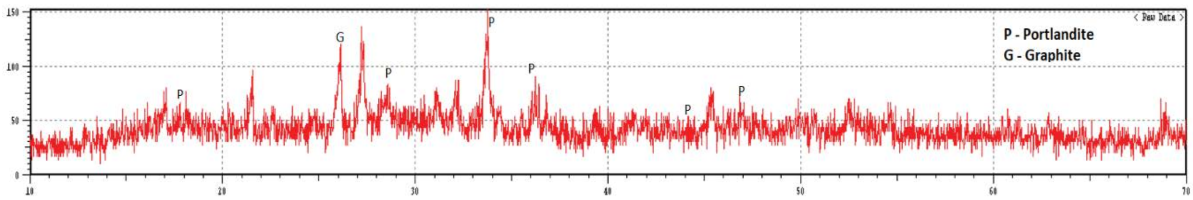

Fig. 3. X-ray diffraction of sludge-based activated carbon (2θ° vs. intensity, (cps)).

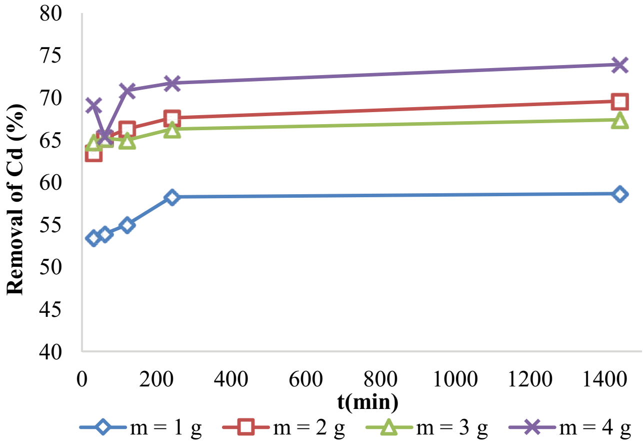

Fig. 4. Adsorption of cadmium ions over time for differing mass of adsorbent.

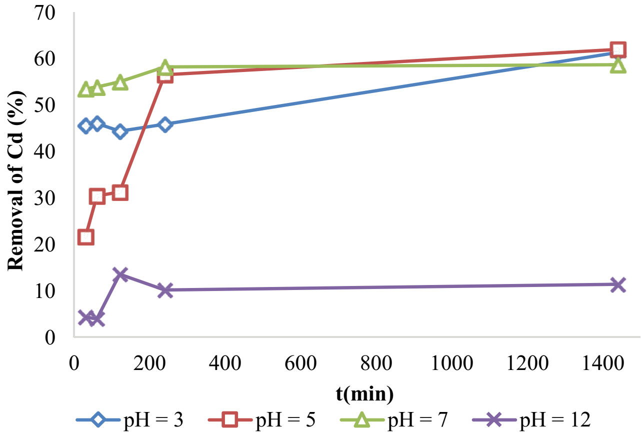

Fig. 5. Adsorption of cadmium ions over time for different initial pH of solution.

capacity as the sorbent surface creates positive or negative charge on its surface depending on the solution pH. The effect of the initial pH of the solution was investigated by contacting 1 g of sludge-based activated carbon at four pH values (3, 5, 7 and 12), with the 4.6 mg/L Cd solution.

The obtained results show that adsorption capacity of sludge-based activated carbon is higher at lower pH value, such as 3 and 5, slowly decreases at pH 7, but significantly is decreased at pH 12 (Figs. 5 and 6). This was expected because similar data were obtained from Xue et al. [36] and Givianrad et al. [37] that optimal pH for Cd removal is between 3 and 6. Xue et al. [36] used mesoporous ceramic functional nanomaterials as adsorbent and obtained that adsorption capacity increased with increasing pH value between 3 and 6. According to Givianrad et al. [37] removal of Cd using silica aerogel and activated carbon increases with increasing pH and a maximum value was found at pH 6.0.

It is known that pH may affect the adsorption of cadmium by influencing the hydrolysis of Cd ions, the exchange between Cd ions and H^+, the type of adsorptive complexing surface, the charge on adsorptive surface and the distribution coefficient of cadmium in the competitive system. The competitive adsorption of H^+ and Cd ions occurred in the solution under the low pH value and the hydrated hydrogen occupied the adsorption sites resulting in smaller adsorption capacity. However, with increasing pH value, the competitive adsorption effect of H^+ decreased, and the negative charge on the adsorbent surface increased, which weakened the electrostatic repulsion of the absorbent surface to Cd ions, while the adsorption capacity and the removal rate of Cd ions increased. Metal ions precipitated with OH^- when pH value was greater than 7. Therefore, the optimal pH for adsorption was 6.

3.6. Effect of initial metal concentration in solution and equilibrium studies

The effect of the initial metal concentration was investigated by contacting 1 g of the sludge-based activated carbon, at pH 7, with different concentrations of the single-component solutions (1.58, 3.82, 4.60, 5.42, and 7.70 mg/L Cd ions). These experiments were also used for equilibrium studies to determine the maximum capacity of sludge-based activated carbon for removal of cadmium ions from solution.

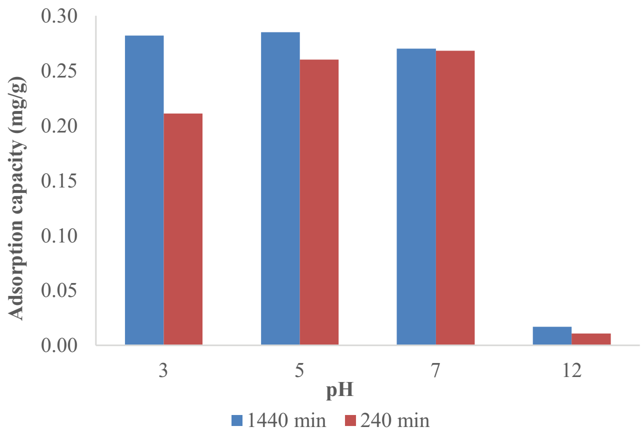

Fig. 6. Adsorption capacity for different initial pH of solution at equilibrium.

An increase in concentration generally results in an increase in the amount of metal adsorbed. This may be due to more collisions between the reactants, leading to an observed increase in reaction rate and capacity [38]. Increasing the initial metal concentration in solution until the system reaches a saturation point will increase the amount adsorbed (q_e) (Fig. 7 and Table 3).

The experimental data obtained from these experiments was fitted to the Langmuir and Freundlich adsorption isotherms (Fig. 8 and Table 4).

According to Freundlich model, values of the heterogeneity factor 1/n, indicate that sludge-based activated carbon is heterogeneous adsorbent, because the value of heterogeneity factor is <<1. Based on the correlation coefficients (R^2), the adsorption isotherms can be better described by the Langmuir model. The R_L values reported in Table 4, confirmed that the behaviour of Cd ions adsorption onto used adsorbent was favorable ($0 < R_L < 1$).

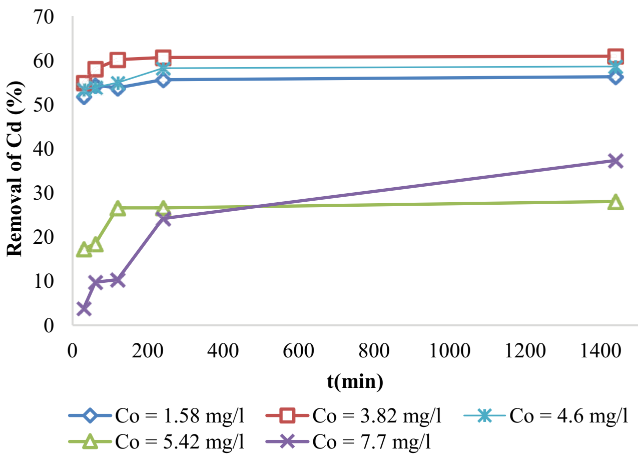

Fig. 7. Adsorption of cadmium ions over time for differing initial ion concentrations.

Table 3
Effect of initial ions concentration on the adsorption capacity of adsorbent

Initial concentration C_o (mg/L)	Percentage adsorbed (%)	Amount adsorbed q_e (mg/g)
1.58	56.33	0.09
3.82	60.99	0.24
4.60	58.70	0.27
5.42	28.04	0.15
7.70	37.40	0.29

4. Conclusion

This study was encouraged because sewage sludge generated from wastewater treatment plants continue to create environmental problems and because European Union promoted the ecological management of such wastes by introducing directives regarding sewage sludge management, such as recycling.

The sewage sludge generated by Volkovo wastewater treatment plant in Skopje, Republic of North Macedonia was successful converted to sludge-based activated carbon using method of chemical activation.

The obtained sludge-based activated carbon is characterized by a macroporous structure and exchangeable cations that makes it a suitable as adsorbent for wastewater treatment. The results, also shows that sludge-based activated carbon successful can be used as adsorbent for cadmium removal from aqueous solution, because the adsorption of cadmium ions from aqueous solution occurs efficiently. It is the most effective at lower concentration of cadmium ions, higher mass of adsorbent and pH of the solution between 3 and 6. The maximum capacity of sludge-based activated carbon for removal of cadmium ions from solution was determined fitting the experimental data to the Freundlich and Langmuir adsorption models. In general, comparing the obtained results, the Langmuir adsorption isotherm is better fitted with results obtained from experiments.

Knowing the efficiency of sludge-based activated carbon to remove cadmium from a one-component solution, as a suggestion for future research is to study cadmium removal from multi-component solution.

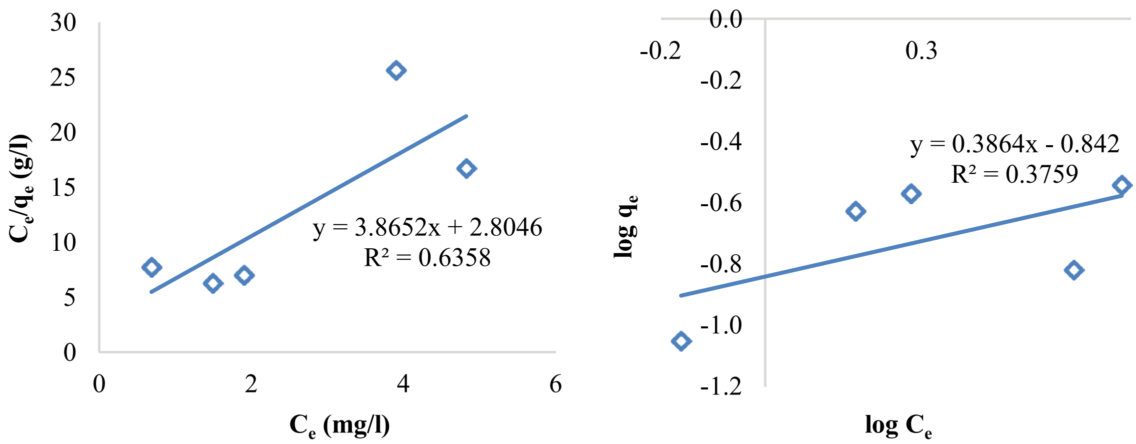

Fig. 8. Adsorption isotherms: (a) Langmuir and (b) Freundlich isotherm.

Table 4
Calculated equilibrium adsorption isotherm constants for the uptake of cadmium from solution by sludge-based activated carbon

Element	Experimental		Langmuir				Freundlich			
	q_e (mg/g)	C_e (mg/L)	q_m (mg/g)	K_l (L/mg)	R^2	R_L	k_f	$1/n$	n	R^2
Cd	0.288	4.82	0.2587	1.3782	0.6358	0.09	0.1439	0.3864	2.5880	0.3759

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