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Dry Biosolids Reuse as Costless Biodegradable Adsorbent for Cadmium Removal from Water Systems

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ABSTRACT
The recycling of untreated dry biosolids, as costless biodegradable adsorbent for the removal of cadmium from aqueous phase was characterized. The adsorption of cadmium was reported to depend on initial pH, adsorbent dose, agitation time, and initial Cd concentration. The results of the batch experiments revealed that the maximum adsorption capacity of the untreated dry biosolids was 39.22 mg g^{-1} under optimum operating conditions (i.e. pH: 5, adsorbent dose: 2 g l^{-1}, contact time: 16h). Adsorption reaches equilibrium after 16h, which can be attributed to both external surface adsorption ($R^2 = 0.86$) and intraparticle diffusion ($R^2 = 0.98$). The Langmuir isotherm model best described cadmium adsorption ($R^2 = 0.99$) and the pseudo-second-order kinetic model was obeyed, suggesting that the mechanism involved was chemisorption. Biodegradability would make the recovery of adsorbed Cd an environmentally friendly process. Comparing the obtained findings with the related published results, it can be concluded that treating biosolids might be an unnecessary and costly procedure for recycling biosolids as an adsorbent for cadmium.

Keywords: adsorption, Cd-contaminated environment, untreated biosolids, intraparticle diffusion model, Langmuir isotherm model.

INTRODUCTION

Pollution of water systems with cadmium (Cd) can cause several environmental problems that might negatively impact human health as well as ecological systems (Wang and Chen, 2009). Cadmium can be discharged into the environment through its mining and smelting processes as well as by other anthropogenic means, such as the application of phosphate fertilizers, land application of biosolids, and diverse industrial uses, e.g. nickel-cadmium batteries.

According to Rahimzadeh et al. (2017), long-lasting exposure to cadmium through air, water, soil, and food leads to cancer and organ system toxicity. A provisional tolerable weekly intake (PTWI) from food of 7 μg Cd kg^{-1} body weight was identified by the WHO, which is equivalent to a daily tolerable intake level of 70 and 60 μg Cd for the average 70-kg man and 60-kg woman, respectively (WHO, 1992).

The WHO has recommended a limit of 0.003 mg dm^{-3} as a drinking-water guideline value for cadmium based on an allocation of 10 % of the PTWI to drinking-water (WHO, 1993).

Several materials have been investigated to remove cadmium ions from water systems by adsorption, including *Arundo donax* leaves, *Cyperus laevigatus* shoots, paper solid waste, and algal tissues (*Hydrodictyon reticulatum*) (Ammari, 2014; Ammari et al., 2015; Ammari, 2016; Ammari et al., 2017). Adsorption was considered in these studies for being inexpensive in addition to requiring minimum skills for implementation.

Biosolids are a kind of colloidal sediment waste produced from the treatment of municipal wastewater. According to the German Corporation for International Cooperation (GIZ, 2020), there are about 31 domestic wastewater treatment plants in Jordan. Only one plant uses biosolids to generate energy. All the remaining treatment facilities do not utilize biosolids properly. Therefore, biosolids have become an ecological, environmental, and financial burden. In other parts of the world, biosolids are reused in landfilling, in forestry, in sea dumping, as soil improver, etc. (Ishikaw et al., 2007; El-Deen and Zhang, 2016). In addition, biosolids have been utilized to prepare useful adsorbing materials with prospective applications in environment using chemical (Rio et al., 2006; Ros et al., 2006; Anfruns et al., 2009; Nageeb et al., 2017) as well as physical activation methods (Otero et al., 2009; Monsalvo et al., 2011; AbdelAziz et al., 2017).

In the current study, (1) the adsorption performance of untreated dry biosolids (BS) was investigated in terms of cadmium removal from aqueous phase, (2) different key parameters including initial pH, initial concentration, dose, and contact time were investigated to understand the adsorption of cadmium ions onto untreated dry biosolids collected from the Wastewater Treatment Plant of Wadi Shueib, and (3) adsorption kinetics and isotherm modeling were also discussed.

MATERIALS AND METHODOLOGY

Preparation of the untreated dry biosolids

Dry biosolids, brought from the Wastewater Treatment Plant of Wadi Shueib, were repetitively washed using tap water followed by distilled water. The purpose was to decrease the electrical conductivity of these samples to values around 100 μS cm^{-1}, which were, further, dried in an oven at 105°C. The oven-dried biosolids were ground with a ceramic mortar and pestle and sieved to obtain the particles between 250 and 355 μm in size.

Characterization of the BS

The Fourier transform infrared (FTIR) analyses

The FTIR analyses using thermo Nicolet nexus 670 were carried out by using the KBr pellet technique, before and after adsorption, on the BS materials using the Fourier Transform Infrared Spectroscopy to define the functional groups involved in adsorbing Cd^{2+}. The spectra of FTIR of BS were determined in a 400–4000 cm^{-1} spectral domain and a resolution of 4 cm^{-1}.

Energy dispersive X-ray spectrum (EDX)

The EDX spectrum using Scanning Electron Microscope (SEM) (FEI quanta 600, Thermo Fisher) was conducted to reveal the elemental composition of the BS material. In this technique, the samples were excited by a highly focused, high-energy primary electron beam and X-rays are emitted from the samples.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) and derivative thermogravimetry analysis (DTA) before and after adsorption were conducted to investigate the thermal characteristics of the BS material using a thermal analyzer (Netzsch STA 409 PG/PC) with a heating rate of 10°C /min, under nitrogen flow at a rate of 30 ml/min.

Aqueous phase and analytical procedure

Cadmium standard and aqueous solutions with concentrations ranging from 20 to 100 mg l^{-1} were prepared using a certified Cd reference solution (Cd metal in 2% HNO_3, USA). All solutions were prepared in 0.01 mol l^{-1} $NaNO_3$ (UK). Diluted NaOH (Germany) or HNO_3 (China) was used to modify the pH of these solutions. All chemicals were of analytical reagent grade. The flame atomic absorption spectrophotometer (A Varian model AA-6650 flame AAS, Shimadzu, Japan) was used to measure the concentrations of Cd in solutions at 228.8 nm wavelength.

Adsorption experimental setup

Effect of solution pH

The solutions containing 20 mg l^{-1} of Cd and 2 g l^{-1} BS were used to investigate the effect of pH at the ambient temperature of the laboratory (approx. 25±1°C). The initial pH of solutions was 2, 3, 4, 5, 6, 7, and 8. The BS-Cd solutions were agitated on an orbit shaker for a period of 24 h. This experiment was conducted in PE-bottles, previously washed with acid (Alemayehu and Lennartz, 2009) onto which no sorption of Cd was detected.

Effect of BS Dose

Different doses of BS (2, 3, and 4 g l^{-1}) were added to the pH 5.0 modified solutions of 100 mg l^{-1} Cd. The BS-Cd solutions were agitated for 16 h.

Effect of Contact Time

The kinetics of the adsorption process were investigated by agitating the pH 5.0 modified solutions that contain 20 mg Cd l^{-1} and 2.0 g l^{-1} BS for 1, 5, 30, 60, 180, 360, 960, 1200, and 1440 min.

Effect of Initial Concentrations of Cd

The optimal adsorption conditions (in terms of pH and BS dose) were considered to study the effect of different initial concentrations of Cd. Two g l^{-1} BS were added to the pH 5.0 modified solutions of 20, 40, 60, 80, and 100 mg l^{-1} Cd.

The BS-Cd solutions were agitated for 16 h, filtered via 0.45 µm filters, and analyzed for the equilibrium concentration of Cd by flame AAS. The efficiency and capacity of adsorption were expressed using the following equations (Eqs. 1 and 2):

$$\text{Removal efficiency (\%)} = [(C_i - C_e)/C_i] \cdot 100 \qquad (1)$$

$$q_e\ (\text{mg g}^{-1}) = [(C_i - C_e) \cdot V]/m \qquad (2)$$

where: C_i is the Cd initial concentration (mg l^{-1}),
C_e is the concentration of Cd at equilibrium (mg l^{-1}),
q_e is the capacity of adsorption at equilibrium in mg g^{-1},
V is the volume of Cd solutions in l, and
m is the BS weight in grams.

Batch adsorption experimental data

The Langmuir and Freundlich isotherm models; commonly available in the literature, were used to test the equilibrium data of Cd adsorption by BS. Isotherm variable parameters and determination coefficients (R^2) were estimated from the linearization of the above-mentioned models.

Langmuir Isotherm Model

Cadmium adsorption can be described by the Langmuir model particularly as the Cd concentration at equilibrium (C_e) becomes high (Essington, 2004). The Langmuir model is defined as (Eq. 3):

$$q_e = (K_L q_m C_e)/(1+K_L C_e) \qquad (3)$$

where: q_e is the adsorbed Cd at equilibrium [mg g^{-1}],
K_L (l mg^{-1} of adsorbent) indicates the adsorption isotherm intensity (Essington, 2004) and
q_m is the monolayer adsorption capacity (mg g^{-1}).

The Langmuir model is linearized as follows (Eq. 4):

$$C_e/q_e = 1/(K_L q_m) + [(1/q_m) \cdot C_e] \qquad (4)$$

A straight line is attained by plotting C_e/q_e versus C_e and K_L and q_m were computed. Slope and intercept of the straight line were used to estimate the values of q_m and K_L, respectively. In addition, the affinity between the adsorbate and adsorbent can be predicted using the value of R_L, i.e. dimensionless separation factor (Hall et al., 1966). R_L is expressed as (Eq. 5):

$$R_L = 1/(1+K_L C_0) \qquad (5)$$

where: K_L is previously defined and C_0 is the initial concentration of Cd (mg l^{-1}). When R_L is $0 < R_L < 1$, adsorption is favorable (Weber and Chakravarty, 1974).

Freundlich Isotherm Model

The adsorption data over the whole range of C_e can be described by the Freundlich isotherm model [20]. This model is given as (Eq. 6):

$$q_e = K_F C_e^{1/n} \qquad (6)$$

where: K_F and 1/n are the Freundlich constants that describe the capacity of sorption or the number of surface sites onto which adsorption might occur (Mustafa et al., 2004) and intensity of sorption, respectively.

The linearization of this model was carried out as follows (Eq. 7):

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (7)$$

The variables of the Freundlich model were estimated by plotting log q_e against log C_e. The slope and intercept of the straight line were used to calculate the values of 1/n and log K_F, respectively.

Kinetics of adsorption

Batch experiments were conducted to determine the equilibrium time using 100 mg l^{-1} Cd initial concentration, pH 5.0, and 2 g l^{-1} BS agitated for 1, 5, 30, 60, 180, 360, 960, 1200, and 1440 min. According to Alyuz and Veli (2009), adsorption mechanism as either mass transfer or chemical reaction, can be determined by kinetic studies. In addition, estimating the rate of adsorption is useful for the design of batch adsorption systems. Type-1 pseudo-second-order kinetic model was applied to investigate the adsorption kinetics, which is described as (Eq. 8):

$$t/q_t = (1/(k_2 q_e^2)) + t/q_e \tag{8}$$

where: k_2 (g mg^{-1} min^{-1}) is the second-order adsorption rate constant calculated from the linear plot of t/q_t against t.

Equations (9) and (10) were used to calculate the rate constant and the initial adsorption rate (mg g^{-1} min^{-1}), respectively, and were as follows:

$$k_2 = 1/(intercept \cdot q_e^2) \tag{9}$$

$$Initial\ adsorption\ rate = k_2 \cdot q_e^2 \tag{10}$$

The Intraparticle diffusion kinetic model was also applied to fit the present kinetic data, which is described as (Eq. 11):

$$q_t = K_{di} t^{0.5} + C \tag{11}$$

where: K_{di} is the rate constant (mg/g min$^{1/2}$) (Weber and Morris, 1963).

RESULT AND DISCUSSION

Characterization of BS

Energy dispersive X-ray spectrum

The EDX analysis showed that before Cd adsorption, BS consists mainly of carbon (percent by mass = 94.65 wt.%) and traces of Si, S, Mg, Ca, and P (Fig. 1). The appearance of the main characteristic peaks of Cd in the EDX spectrum of the BS sample after Cd adsorption shown in Figure 1 reveals that Cd ions have been successfully adsorbed onto BS.

Thermogravimetric analysis

The TGA and DTG for BS before and after Cd adsorption are shown in Figure 2 (a) and (b); respectively. The thermogravimetric profiles showed that Cd^{2+} adsorption caused delay in thermal degradation. In general, the mass losses occur in four phases. The first phase was observed approximately between 50°C and 175°C, in which the release of superficial absorbed water, coordinated water and possible volatile compounds occurred (Conesa et al., 1997; Masoud and Ali, 2015). The second and third phases ranged from 200°C to 540°C and were attributed to the thermal degradation of organic matter such as semi-volatile compounds, cellulose, and other organic polymers in the BS. The last phase started above 660°C, which according to Font et al., (2001), Weber et al., (2008), and Patricia et al., (2009), is associated with the decomposition of non-biodegradable polymers and possible minerals in the sample. The estimated total mass losses at 900°C

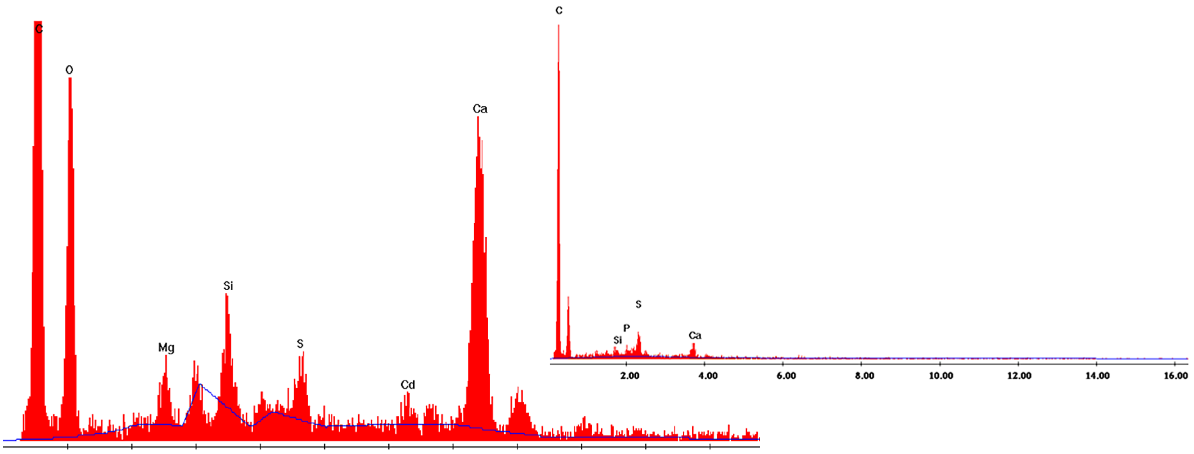

Fig. 1. EDX spectra of BS before (the left figure) and after Cd adsorption

were 67.7% and 60.9% before and after adsorption, respectively. The DTA curve of BS before adsorption showed a peak at around 125°C that is associated with water loss (Figure 2); whereas the position of this peak shifted to 105°C and its intensity decreased after Cd adsorption because Cd ions repelled the water molecules occupied by the BS.

Effect of pH

The ionization of functional groups increases along with the solution pH, consequently, the surface negative charges of certain adsorbents increase as well (Chen and Ting, 1995). Moreover, the solution chemistry of heavy metals can be influenced by the solution pH via hydrolysis (Wang, 2002).

Adsorption of cadmium onto BS, as affected by solution pH was examined by modifying the initial solution pH to 2, 3, 4, 5, 6, 7, and 8. Such pH values were selected because they might be found in municipal as well as industrial wastewater (Bond and Straub, 1974). The solutions were prepared using 0.01 M $NaNO_3$ was to simulate the actual conditions of most water systems because the ionic strength of background solutions reflects the interaction degree among ions in solutions (Sparks, 1995).

The pH-adsorption edges of Cd (II) obtained for the BS are shown in Figure 3. The results showed that the Cd removal efficiency ranged from 13.7% to 95.3% at pH 2 and 5, respectively. The obtained results are commonly in agreement with the previously published studies for sewage sludge ash (pH 6) (Elouear et al., 2009), for treated sewage sludge (pH 6) (Ait Ahasainea et al., 2017), for modified physically activated sewage sludge (Nageeb et al., 2018).

According to Hawari and Mulligan (2006) the heavy metal removal can be attributed to different causes such as (1) electrostatic attraction, (2) formation of surface complexes, and (3) precipitation. The obtained results showed that, at pH 2, the efficiency of Cd removal was lower than that at higher pH. At pH 2, the H^+ concentration increased and occupied almost all adsorption sites on the surface of the adsorbent, which limited the ability of Cd ions to move towards the surface due to charge repulsion. Protons also decrease the negative charges by protonation, i.e., association of the functional group with protons (Khalfa and Bagane, 2011). The removal percentage increases along with the pH (> 2), due to the decrease of H^+ on the surface, which results in lesser repulsion with Cd ions (Sheha and El-Zahhar, 2008). Moreover, the surface becomes progressively negatively charged, as the hydroxyl ion activity (and pH) increase, thus creating favorable conditions for specific adsorption of Cd (Zhou and Haynes, 2010).

Furthermore, the divalent Cd and $Cd(OH)^+$ are the dominant Cd species at pH less than 8 (Babic et al., 2002, Cordero et al., 2004). For the chemical composition of solutions used in our study, the free divalent Cd ranged from 97.3% of the total concentration of Cd at pH 8 to ≈98% at pH 2 as estimated by Visual MINTEQ (Data not shown). The obtained results agreed with Baes and Mesmer (1986) and Srivastava et al. (2006) who reported that the log$K$ of Cd hydrolysis reaction is equal to -10.08 or -7.9, respectively. Therefore, when pH is less than pKa, free divalent Cd ions are dominant in solutions. Consequently, Cd speciation, as affected by pH, was not responsible for the observed "adsorption envelope". It can be concluded that the magnitude of adsorption in the current study can be attributed to the functional groups and their associated ionic state. Ait Ahsainea et al. (2017) suggested that, among others, the –OH stretching vibration and the stretching

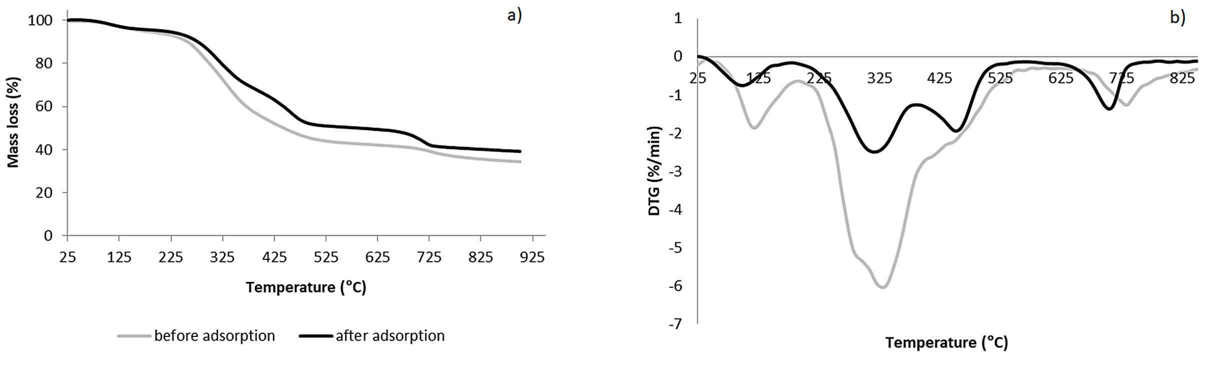

Fig. 2. a) TG and b) DTG thermograms for the BS before and after Cd adsorption

of the N–H bond of organic compounds can be responsible for the adsorption of Cd^{2+} by mesoporous treated sewage sludge. The FTIR spectra analysis of Li et al. (2018) showed that Cd (II) adsorption by live and dead biosorbents took place via the hydroxyl, amino, amide, carbonyl, and carboxyl groups. These candidate functional groups were determined by the FTIR spectra of the BS before and after adsorption (Figure 4). The peaks at 3,390, 2922 and 2852, 1,652, and 1,542 cm^{-1} are associated with several organic functional groups. The peak at 3,390 cm^{-1} is attributed to the –OH stretching vibration (Droussi et al., 2009) associated with cellulose in the BS, adsorbed water molecules (Vazquez et al., 2009), and the stretching of the N–H bond of organic compounds (Vazquez et al., 2009; El-Deen and Zhang, 2016). The peaks at 2922 and 2852 cm^{-1} are attributed to C–H stretching (Belfer et al., 2000); whereas, the peaks at 1,652 and 1,542 cm^{-1} indicated the existence of amide I (–CO– stretching vibration) and amide II (–NH bending and –CN stretching) in proteins, respectively. After adsorption, while some peaks disappeared, shifts were observed for the peaks from 3,390 and 1,652 cm^{-1} to 3,448 and 1,639 cm^{-1}, respectively, indicating that the above-mentioned functional groups might be involved in the adsorption of Cd ions. However, the increase of the band intensity observed in the region of the –OH stretching vibration when compared with the BS before adsorption could be due to the adsorbed water after adsorption. Additionally, the other bands in the region 200–2,600 cm^{-1} were relatively found to decrease in intensity after adsorption. According to Ait Ahsainea et al. (2017), this might be due to the electrostatic interactions between the related functional groups (–NH and –CO) and Cd ions, which is in agreement with (Mnahan, 1999a; Mnahan, 1999b; Gutierrez-Segura et al., 2012). Shift and disappearance of peaks suggest a binding between Cd ions and the BS surface. It can also be concluded that hydroxyls and amides are the most important characteristic functional groups in the BS participating in Cd^{2+} adsorption.

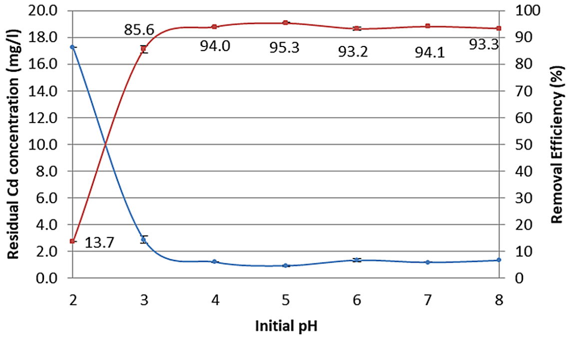

Fig. 3. Residual concentration of Cd and removal efficiency of BS as affected by pH (Adsorbent dose was 100 mg, concentration of Cd was 20 mg l^{-1}, I was 0.01 M, contact time was 24 h, n = 3, and error bars represent standard deviation)

Effect of BS Dose

The effect of BS dose on Cd adsorption was investigated and presented in Figure 5. The results showed that the removal efficiency of Cd increased along with the BS dose from 2 to 4 g l^{-1} (Figure 5). At the highest dose, the detected increase in Cd removal (%) is due to the increased surface area of the adsorbent and adsorption locations. Nevertheless, the reduction in the capacity of adsorption with the increase of BS dose (from 35.4 to 21.9 mg g^{-1}) can be attributed to the unsaturation of binding locations via the process of adsorption (Ghodbane et al., 2008). Another reason can be due to the aggregation of particles resulting from high adsorbent concentration. Such aggregation would result in reduced the total

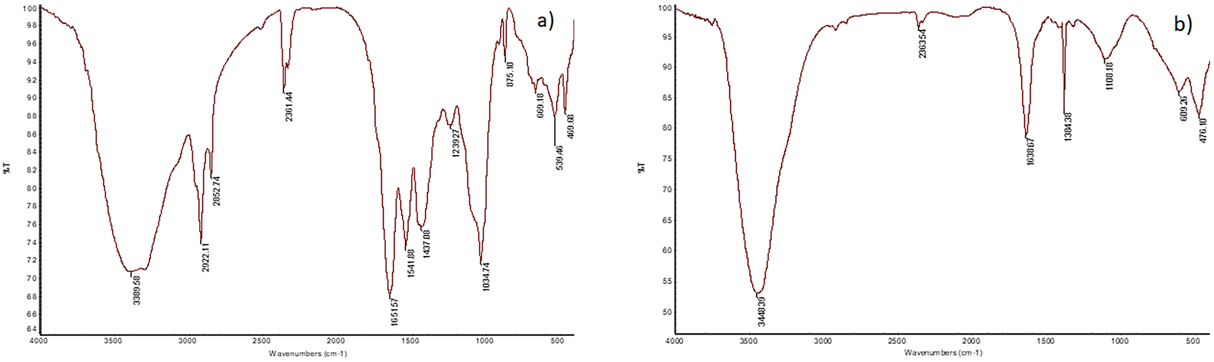

Fig. 4. FTIR spectra for BS: a) before and b) after adsorption

surface area of the adsorbent and increased diffusion path length (Zhai et al., 2004). Rao et al. (2008) found that the Cd adsorption increased along with the dose of activated sewage sludge. Hammaini et al. (2007) also showed that adsorption capacity for Cd varied with the activated sludge (biomass) dose.

Adsorption kinetics study

Effect of contact time

The binding of Cd ions on the BS as a function of contact time was investigated under optimum experimental conditions (Figure 6). Cadmium adsorption increased along with contact time and its removal efficiency gradually reached a constant value of 81% (40.4 mg g^{-1}) after 16h (Figure 6). The obtained results agree well with earlier published data concerning the relatively long equilibrium times. Luo et al. (2006) reported that the adsorption of Cu onto activated sewage sludge was up to 90% after 0.5 hour, whereas the adsorption of Cd was up to 96% after a time of 7 hours. Rashed (2006) found that the adsorption of Pb by the stones of peach and apricot increased with contact time and reached the maximum value at 3 and 4 hours, respectively. Fonseca et al. (2006) showed that the equilibrium times for manganese and cadmium onto vermiculite were 48 and 72 hours, respectively.

Kinetics of adsorption

The adsorption kinetics provide important information about the sorption mechanism (Bulgariu and Bulgariu, 2014). The kinetics of the adsorption of Cd by BS was explored by plotting t/q_t versus t (Figure 7). One of the commonly used kinetic models is the pseudo-second-order model. This model implies that the chemical interactions among ions of Cd and surface functional groups of the BS is involved, which is the rate controlling step. The agreement between the experimental and predicted values of the model was reflected by the R^2 (determination coefficient very close to 1) (Table 1), which indicates that such kinetic model effectively describes the Cd adsorption kinetics onto BS (Figure 7 and Table 1). This model indicates that chemisorption, which comprises sharing or exchange of electrons between the BS and the adsorbate ions, is the rate limiting step (Ho and McKay, 1999). From Figure 7, the estimated q_e, was calculated for the initial concentration of Cd of 100 mg l^{-1} as shown in Table 1. The value of the calculated q_e agrees well with the experimental value ($R^2 = 0.99$). Similar results were reported for different adsorbents (Hawari and Mulligan, 2006; Zhou and Haynes, 2010; Ammari, 2014; Ammari et al., 2015; Ammari, 2016; Ammari et al., 2017; Ma et al., 2018).

The Weber–Morris relationship (q_t vs. $t^{1/2}$) was applied to better understand the mechanism of diffusion (Kalavathy et al., 2005; Sheha and El-Zahhar, 2008). The plot in Figure 7 indicates a multilinear characteristic and the intraparticular diffusion rate (K_{di}) and C were calculated (Table 1). It can be seen that there are two steps that control the adsorption process: (1) the first step shows mass transfer of the Cd ions from the liquid to the solid external surface known as boundary layer diffusion and (2) the second step is the intraparticle diffusion; the movement of Cd ions within the pores begins and the equilibrium is established. Similar results were reported by Ait Ahsainea et al. (2017) who found that the adsorption

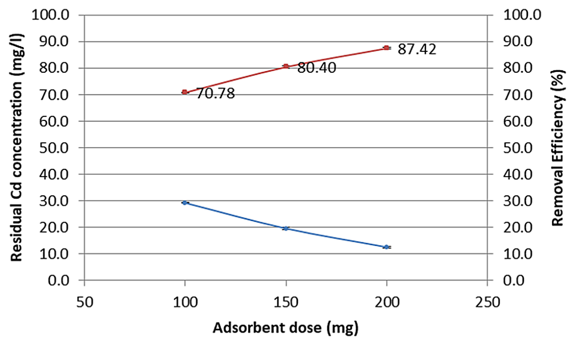

Fig. 5. Remaining Cd concentrations as affected by adsorbent dose (Contact time was 16 h, initial pH as 5.0, Cd concentration was 100 mg l^{-1}, I was 0.01 M, n = 3, and error bars represent standard deviation)

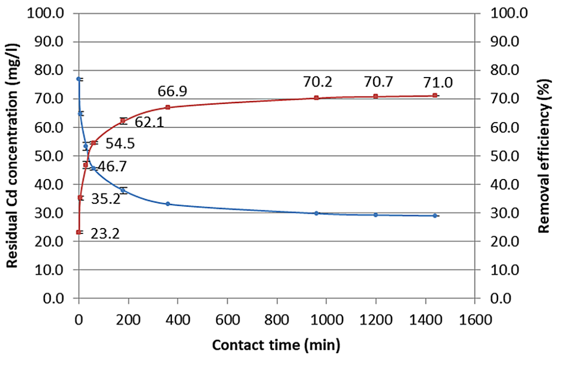

Fig. 6. Remaining Cd concentration as affected by agitation time (Adsorbent dose was 100 mg, initial pH as 5.0, Cd concentration was 100 mg l^{-1}, I was 0.01 M, n = 2, and error bars represent standard deviation)

of Cd ions onto the mesoporous treated sewage sludge is a combination of these two phases as rate-controlling steps. Such results might explain the relatively long equilibrium time obtained in the current study (16h). It might be reasonable to conclude that the intraparticle diffusion of Cd ions within the pores was evidently slow, which might delay attaining the equilibrium state.

Adsorption Isotherm Study

Specific adjustable parameters can characterize the adsorption isotherms. Such parameters describe the properties of the adsorbent surface and the affinity of the adsorbent to the adsorbed ions. As the concentration of Cd increased from 20 to 100 mg l^{-1}, a decrease in the Cd removal percentage by BS from 96.2% to 71.2% was observed, which is due to the saturation of adsorption sites on the BS when the Cd concentration exceeds a certain value, as explained by Semerjian (2010).

When equilibrium is attained, q_e of BS increased along with concentration of Cd in the solution (from 20 to 100 mg l^{-1}). These findings agree with the previously reported results of various studies (Elouear et al., 2009; Ammari, 2014; Ammari et al., 2015; Ammari, 2016; Ammari et al., 2017). With increasing initial concentrations of Cd, the observed increase in Cd ions adsorbed onto the BS can be due to the greater concentration gradient resulting from more Cd(II) available in the solution at greater concentrations of Cd. In the present study, the relation between the capacity of adsorption and the concentration of Cd at equilibrium were described and characterized by the Langmuir and Freundlich isotherm models. These isotherms are simple and able to characterize the adsorption process at the solid-solution interface. The isotherms data can be employed in designing the adsorption systems (Saygiderger et al., 2005). The constants and R^2 of the Langmuir and Freundlich isotherms are reported in Table 1. The results revealed that

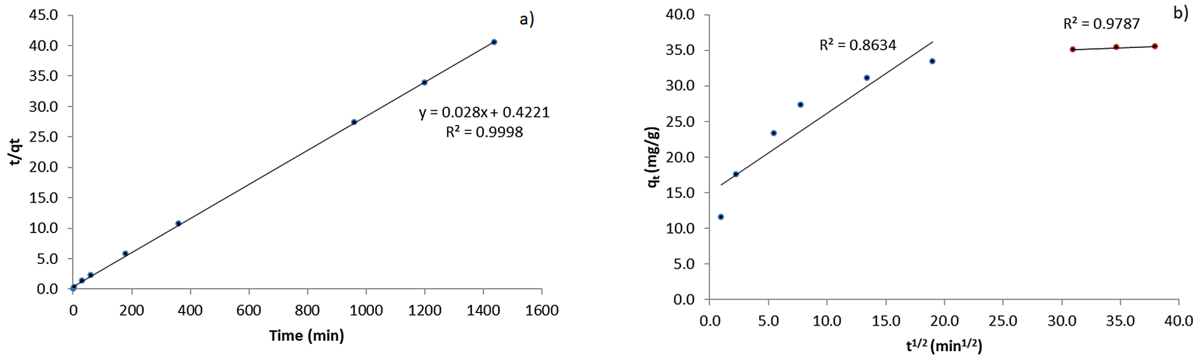

Fig. 7. Adsorption kinetics onto BS tested with: a) the pseudo-second-order kinetic model and b) the intraparticle diffusion kinetic model

Table 1. Effect of initial Cd concentration (20–100 mg l^{-1}) and 2 g l^{-1} adsorbent dose on equilibrium adsorption capacity at pH 5.0 and 0.01 *M* $NaNO_3$, the kinetic parameters for pseudo-second-order kinetic model and isotherm adjustable parameters of Cd adsorption on BS

Adsorbent	Experimental q_e [mg g^{-1}]	Pseudo-second-order kinetic model		k_2 [g mg^{-1}min^{-1}]	Initial adsorption rate [mg g^{-1}min^{-1}]	Freundlich			Langmuir			
		q_e	R^2			K_F [(mg/g).(l/mg)$^{1/n}$]	1/*n*	R^2	q_m [mg g^{-1}]	K_L [l mg^{-1}]	R^2	R_L
BS	35.1	35.7	0.99	0.00192	2.37	11.27	0.3667	0.983	39.22	0.2962	0.996	0.033 to 0.144

Intraparticle diffusion model

K_{di1} [mg/g min$^{1/2}$]	C1 [mg g^{-1}]	R^2	K_{di2} [mg/g min$^{1/2}$]	C2 [mg g^{-1}]	R^2
1.1195	14.9	0.86	0.0589	33.3	0.98

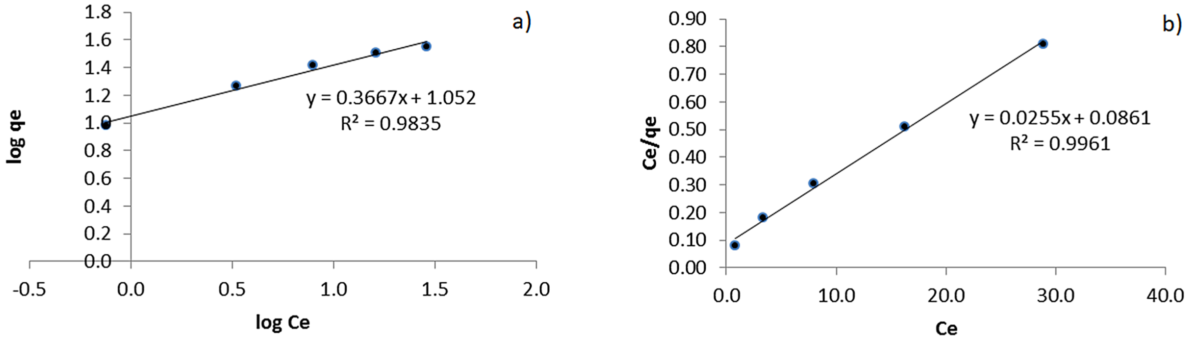

Fig. 8. a) Linearized Freundlich isotherm and b) linearized Langmuir isotherm of the BS

adsorption of Cd onto the BS better followed the Langmuir than the Freundlich isotherm model (Figure 8), indicating that the adsorption of Cd onto BS occurred on the adsorption sites; i.e. functional groups, as a monolayer adsorption. The maximum monolayer adsorption capacities (q_m) of Cd calculated from the Langmuir model were 39.22 mg g^{-1} (Table 1). Moreover, the critical characteristic of the Langmuir model, R_L, a dimensionless constant referred to as equilibrium parameter is reported in Table 1. The calculated R_L values range between 0 and 1, which refer to a favorable adsorption process.

A comparison of the values found in our study (39.22 mg g^{-1}) with commercial activated carbon (8.21 mg g^{-1}) (Azouaou et al., 2010); sewage sludge ash (7.1 mg g^{-1}) (Elouear et al., 2009) ; iron oxide coated sewage sludge (14.7 mg g^{-1}) (Phuengpraso et al., 2011); modified physically activated sewage sludge (31.44 mg g^{-1}) (Nageeb et al., 2018); mesoporous treated sewage sludge (56.2 mg g^{-1}) (Ait Ahsainea et al., 2017) revealed that the BS presented a reasonable Cd adsorption capacity from liquid phase without any kind of treatment or modification. The disposal of loaded BS with Cd ions could impose an environmental issue (Gaballah et al., 1998). Commonly, the regeneration of exhausted adsorbent materials is carried out through the desorption process, which was reported for inorganic sorbents (e.g. montmorillonite and silica gel as reported by Katsumata et al. (2003) as well as biosorbents (Abu Al-Rub et al., 2004; Bulgariu and Bulgariu, 2014). The regeneration of loaded biosolids for reuse might not be feasible or necessary because such material is increasingly generated, whereas the recovery of Cd from loaded biosolids is of environmental and industrial importance.

CONCLUSIONS

We found that dry biosolids can be recycled as costless biodegradable adsorbent for cadmium removal from polluted water systems. The removal of Cd considerably depends on the initial Cd concentration, agitation time, dose, and solution pH. The adsorption of Cd ions onto BS was characterized by the Langmuir isotherm and the pseudo-second-order model. The maximum capacity of adsorption was 39.22 mg g^{-1} under optimal experimental conditions. Equilibrium was attained after 16 h.

Comparing our findings with the related published results, treating biosolids both chemically or physically will increase the cost of biosolids recycling and might not be necessary. We showed that the adsorption capacity of untreated BS is greater than or, at least, comparable to that of commercial activated carbon, sewage sludge ash, iron oxide coated sewage sludge, modified physically activated sewage sludge, and mesoporous treated sewage sludge. Such findings will help reducing the sewage sludge recycling costs. In addition, biodegradability would make the recovery of adsorbed Cd an environmentally friendly process.

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