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INVESTIGATION OF SORPTION CHARACTERISTICS OF ANAEROBICALLY DIGESTED DEWATERED MUNICIPAL SEWAGE SLUDGE

Physical, chemical, morphological properties and sorption characteristics of anaerobically digested dewatered municipal sewage sludge have been investigated including the surface area, pore size distribution, chemical composition, surface chemistry structure, surface physical morphology, mineralogy, cation exchange capacity, heavy metal content, total solid, total volatile solid, total Kjeldahl-N, total phosphorus content of the sewage sludge. The sorption potential of sewage sludge for the removal of 4-CP and 2,4-DCP from aqueous solutions was examined by investigating their adsorption isotherms and kinetics in a lab-scale batch study. Findings of this study clearly showed that sewage sludge provides chlorophenol removal in the landfill body as disposed with solid wastes.

1. INTRODUCTION

The sludge production is too high to be disregarded. Growing concerns about the environment have resulted in the development of new environmental technologies, materials, and ways to reduce and minimize wastes [1]. One of the wastes produced by contemporary society in abundant quantity is municipal sewage sludge. Sewage sludges are produced as a result of wastewater treatment activity. Their production is expected to gradually increase through environmental necessity and legal requirements for wastewater treatment [2]. Continuous increase in the quantity of sludge produced, calls out for efficient and environmentally friendly approaches to its utilization. One of these is conversion of sewage sludge into adsorbents. Because biochemical sludges contain more carbon than cheap adsorbents produced through the chemistry path,

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many researches focused on making use of sludges to prepare the carbon-bearing adsorbents by various activating methods [3–5] and on application of the adsorbents to the removal of organics and inorganics [6] in wastewater. As sewage sludge is rich in carbonaceous material, several investigations about possibility of the conversion of sewage sludge into activated carbon by physical and chemical activation processes, have been carried out with respect to feasibility and preparation process optimisation [7]. Although many investigations were conducted in the removal of contaminants with activated carbon prepared from sewage sludge, there is not a detailed study in the utility of digested and dewatered sewage sludge in this area.

In this study, physical, chemical, morphological properties and sorption characteristics of anaerobically digested dewatered municipal sewage sludge were investigated. The purpose is to analyze the characteristics and adsorption capacity of sewage sludge in landfills as disposed with solid wastes.

2. EXPERIMENTAL

Physical and chemical characterization. Physical properties of the anaerobically digestered and dewatered municipal sewage sludge which originates from domestic wastewater treated by advanced biological treatment were characterized. Total solids (*TS*) were determined by drying a measured mass of sludge to a constant weight at 103–105 °C for 24 h whereas total volatile solids (*TVS*) were determined by igniting the dry solids at 550 °C for 2 h in a furnace. Both *TS* and *TVS* are widely used parameters in sludge treatment and management practices as masures of dry matter and organic matter in sludge. The metal contents of dewaterd anaerobically digested municipal sludge were analyzed using atomic absorption spectrophotometry after digesting sludge sample in a microwave digestion system, following the Standard Method 3030 [8]. The measurement of the total Kjeldahl-N and total phosphorus were conducted according to standard methods [8]. Results of physical and chemical characterization of the sewage sludge are presented as the average values for two replicates of the five samples obtained from the treatment plant at various times.

Mineralogical characterization. The mesopore and micropore size distributions were estimated based on the Barrett–Joyner–Halenda (BJH) [11] and Horwath –Kawazoe (HK) theory [12], respectively. The Brunauer–Emmet–Teller (BET) surface areas and BJH pore distributions were determined using the Quantachrome Ins. Quadrasorb SI model instrument by the nitrogen adsorption at 77 K. The specific surface area was calculated based on the BET equation [9]. The micropore surface area and volume were calculated by the t-method [10]. The scanning electron microscope

(SEM) images were obtained using a Zeiss Marka EVO LS 10 model scanning electron microscope. X-ray diffraction (XRD) measurements were performed on a X-ray diffractometer using CuK_α radiation. Qualitative estimation of the surface functional groups was performed by the Fourier transform infra-red spectroscopy (Perkin Elmer Spectrum 100 Model) by the potassium bromide (KBr) pellet method.

Cation exchange capacity. The copper bisethylenediamine complex method [13] was used to determine the cation exchange capacity (*CEC*) of the clays. 50 cm^3 of 1 M $CuCl_2$ solution was mixed with 102 cm^3 of 1 M ethylenediamine solution to allow the formation of the $[Cu(en)_2]^{2+}$ complex. A slight excess of the amine ensures complete formation of the complex. The solution was diluted with water to 1 dm^3 to obtain 0.05 M solution of the complex. 0.5 g of dry clay sample was mixed with 5 cm^3 of the complex solution in an Erlenmeyer flask, diluted with distilled water to 25 cm^3 and the mixture was shaken for 30 min in a thermostatic water bath and centrifuged. The concentration of the complex remaining in the supernatant was determined by the iodometric method. 5 cm^3 of the supernatant was mixed with 5 cm^3 of 0.1 M HCl to decompose the $[Cu(en)_2]^{2+}$ complex and 0.5 g/cm^3 of KI salt was added. The mixture was titrated with 0.02 M $Na_2S_2O_3$ solution with starch as an indicator and the cation exchange capacity was calculated from the formula:

$$CEC\frac{meq}{100}=\frac{MSV\left(x-y\right)}{1000m} \tag{1}$$

where M is the molar weight of the complex, S is the concentration of the thio solution, V is the volume (cm^3) of the complex taken for iodometric titration, m is the weight of the adsorbent (g), x is the volume (cm^3) of thio required for blank titration (without the adsorbent) and y is the volume (cm^3) of thio required for the titration with the adsorbent.

Sorption experiments. The adsorption experiments were carried out in 100 cm^3 Erlenmeyer flasks by mixing a constant amount of sewage sludge with a constant volume of the aqueous solution of 4-CP and 2,4-DCP. 2,4-DCP and 4-CP have been selected as adsorbates since these pollutants are important toxic organic components of leachate. The contents in the flasks were agitated by placing them at constant temperature water bath for a known time interval. The mixture was then filtered and 4-CP and 2,4-DCP remaining unadsorbed in the supernatant liquid was determined with a UV spectrophotometer (Varian Cary 50 UV/VIS spektrophotometer). Sorption experiments were performed with aqueous solutions of 4-CP and 2,4-DCP, one by one.

3. RESULTS AND DISCUSSION

3.1. PHYSICAL AND CHEMICAL CHARACTERIZATION

Physical and chemical properties of sewage sludge are given in Table 1. pH of the sludge material was found to be 7.05 indicating that strong biological digestion of the sewage sludge occured at the wastewater treatment plant. Strong digestion have typically yielded the pH value in the range of 6.6–7.4. The electrical conductivity (*EC*) of the sludge material was determined to be 14.05 mS/cm. Total Kjeldahl nitrogen (*TKN*) and total phosphorus (*TP*) of anaerobically digested and dewatered sewage sludge were found to be consistent with the values given by Metcalf and Eddy [14]. The specific gravity (G_s) of sewage sludge was determined to be in the range of 2.5–2.7 g/cm^3 which is lower than that of inert soils but consistent with the values obtained by other authors investigating sewage sludge materials [15].

Table 1

Physical and chemical properties of the sewage sludge

Parameter	pH	*EC* [mS/cm]	*TVS* [%]	*TS* [%]	*TKN* [mg/kg dry mass]	*TP* [mg/kg]	G_s [g/cm^3]
Value	7.05	14.05	45	95.8	396	220	2.67

The *CEC* is the number of equivalents of exchangeable charge per mass of clay, which is equivalent with the layer charge. The *CEC* value of sewage sludge was found to be 30.28 meq/100 g that indicates moderate sorption capacity.

Table 2

CEC [meq/100 g] and heavy metal content [mg/dm^3] of sewage sludge

Parameter	CEC	Ni	Cu	Zn	Cr	Pb
Value	30.28	192.5	480	991	280	31

A major concern of utilization of sewage sludge is the possible release of heavy metals. Table 2 reveals heavy metal content of the sewage sludge. As sewage sludge is rich in carbonaceous material, metals bound up with the carbon structure or carbon had some affinity for metals adsorption. As a matter of fact, the expected level of metal leaching to wastewater from sewage sludge during adsorption process will be low. Otherwise, this process is not encouraged to use of sewage sludge into drinking water treatment [16].

3.2. MINERALOGICAL CHARACTERIZATION

XRD and XRF analysis gives chemical and minerological composition of the sewage sludge, respectively. Sewage sludge minerologically contains calcite ($CaCO_3$), quartz (SiO_2) gismondine ($CaAl_2Si_2O_8{\cdot}H_2O$). Silica was found to be the dominant component of the sewage sludge. Chemical characteristic of the sewage sludge is given in Table 3.

Table 3

Chemical composition of sewage sludge

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Content [%]	31.67	4.68	2.94	17.67	1.55	4.13	1.31

SEM techniques were employed to examine the surface physical morphology of the sludge.

The pores are classifed in the following classes, depending on their size:
- micropores (size < 2 nm), ultramicropores (size < 0.7 nm),
- mesopores (2 nm < size < 50 nm),
- macropores (size > 50 nm).

Pores can have a regular or, more commonly, an irregular shape. The most similar geometric form is used to represent pore shape: cylinders (in some oxides like alumina and magnesia), slits (in activated carbons and clays) and voids between connected solid spheres (in silica and many solids obtained from gels). Cylinders (size.diameter) and slits (size.distance between walls) are the most widely used models being simple to handle. Morphological characteristics of interest are surface area, pore volume, area and pore size distributions [17].

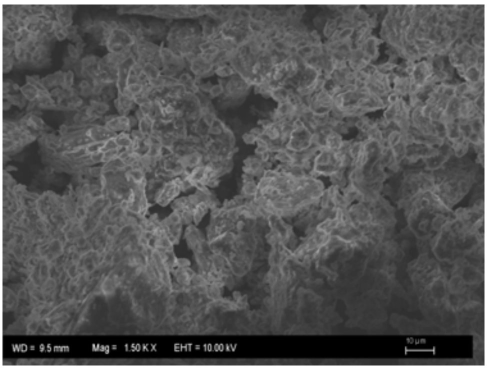

Fig. 1. SEM photograph of the sewage sludge (magnification 1000×)

Figure 1 shows the SEM photographs of the sludge. Pores of various sizes and shapes could be observed in the figure. In general, the pores of the sludge have irregular shapes in a geometric form of slits as activated carbons and clays.

Although the information obtained from FT-IR scanning was limited as the concentrations of the functional groups on the sample surface were in fact very low, the absorption spectra provide the evidence of the presence of some surface functional groups. In the FT-IR spectrum of sewage sludge peaks at 2923–2853 cm^{-1} representing an aliphatic methyl group indicate lipids on the surface of sewage sludge. The peak observed at 1424 cm^{-1} corresponds to cellulose on the surface. The broad and flat band at 3282 cm^{-1} could be assigned to hydroxyl groups probably attributed to adsorbed water. The main band in the FT-IR spectra of sewage sludge in the region 1200–900 cm^{-1} and centreed at 1007 cm^{-1} was assigned to Si–O–Si structures associated with pronounced concentration of silicon in the sample. The band in the region 1550–1750 cm^{-1} and centred at 1638 cm^{-1} was assigned to carboxyl groups (COO^-) on the surface which is possibly in enolic form. C–H structures originating from aromatic compounds manifesting with 650–900 cm^{-1} bands can also be observed at sewage sludge surface. Summing up, it can be concluded from the FT-IR spectra that Si–O–C, Si–O–Si, Al–O–(OH)–Al structures, carboxyl and hydroxyl groups, polysaccharides, lipides and cellulose were found on the surface of anaerobically digested dewatered sewage sludge. These results are consistent with the study investigating FT-IR spectrum of sewage sludge [16].

The BET surface area (S_B), external surface area (including mesopores and macropores area, S_e) and micropores surface area (S_m) were determined to be 2.193, 1.688 and 0.505 m^2/g, respectively. The results of the BET analysis show that the sewage sludge has mesoporous and macroporous structure. The total pore volume (V_t), average pore diameter (D_p) and pore width were found to be 0.306 cm^3/g 163.529 nm and 77.7 nm, respectively. It can be concluded from these results that the surface area of the sewage sludge was found to be lower but the pore diameter (D_p) and pore width of the sample were determined to be higher as compared with inorganic materials.

3.3. SORPTION EXPERIMENTS

Stock solutions of 4-CP and 2,4-DCP were prepared by dissolving 1 g of analytical reagent grade (Merck, Gemany) in 1 dm^3 of distilled water without pH adjustment. Some of the properties of 4-CP and 2,4-DCP are given in Table 4. Batch adsorption experiments were carried out by allowing an accurately weighed amount of dried and sieved sewage sludge sample to reach equilibrium with 4-CP and 2,4-DCP solutions of various initial concentrations at 298, 308 and 318 K. Samples of known weights of sewage sludge were added to 250 dm^3 stoppered conical flasks, each containing 100 dm^3 of solution. The bottles were shaken in a temperature-controlled shaker (Gallenkamp orbital incubator) at a constant speed of 180 rpm. Preliminary experiments at 298 K showed that adsorption equilibrium was reached within 240 min. At the end of this period, the contents of the bottles were filtered and the supernatant was subsequently analyzed for residual concentration of 4-CP and 2,4-DCP by UV-Vis spectrophotometry (Varian Cary 50) at the wavelength of 225 nm and 285 nm, respectively.

Table 4

Physical and chemical properties of 4-C and 2,4-DCP

Property	4-Chlorophenol	2,4-Dichlorophenol
Formula	ClC_6H_4OH	$C_6H_3Cl_2OH$
Molecular weight	128.56 g/mol	163.01 g/mol
Solubility in water (293 K)	27 g/dm^3	4.5 g/dm^3
pK_a	9.41	7.85

In adsorption isotherm studies, solutions with various initial concentrations were added, pH was not adjusted and the equilibrium time was set at 240 min, which was enough according to the preliminary experiments. Each experiment was duplicated under identical conditions. The amount of sorbate in the solid phase q_e (mg/g) was calculated from the equation;

$$q_e = \frac{V\left(C_0 - C_e\right)}{m} \tag{2}$$

where C_0 and C_e are concentrations of initial and retained 4-CP and 2,4-DCP in the solution (mg/dm^3), respectively, V is the volume of the solution (dm^3) and m is the weight of the adsorbent (g).

Kinetic studies were performed following a similar procedure at 298, 308, and 318 K, pH was not adjusted, and the initial concentration were 25 mg/ dm^3 for 4-CP and 2,4-DCP. The uptake of the adsorbate q_t (mg/g) at time t, was calculated from:

$$q_t = \frac{V\left(C_0 - C_t\right)}{m} \tag{3}$$

whereC_t is theconcentration of the adsorbate (mg/dm^3) in solution after time t.

The effect of the adsorbent dosage on the adsorption of 4-CP and 2,4-DCP on sewage sludge is shown in Fig. 2. Sorbent dosage was varied between 0.1 and 10 g/dm^3 for 4-CP and 2,4-DCP and equilibrated after 240 min. The removal of 4-CP and 2.4-DCP increases with the increase of sorbent dosage. The increase may be explained by an increase in the surface area of the adsorbent samples [18] . However, increase in removal efficiency is not linear. These results are consistent with the results obtained by

Kuleyin [18]. Optimum sorbent dosage is considered to be 7 g/dm^3 and 6 g/dm^3 for 4-CP and 2,4-DCP removal, respectively.

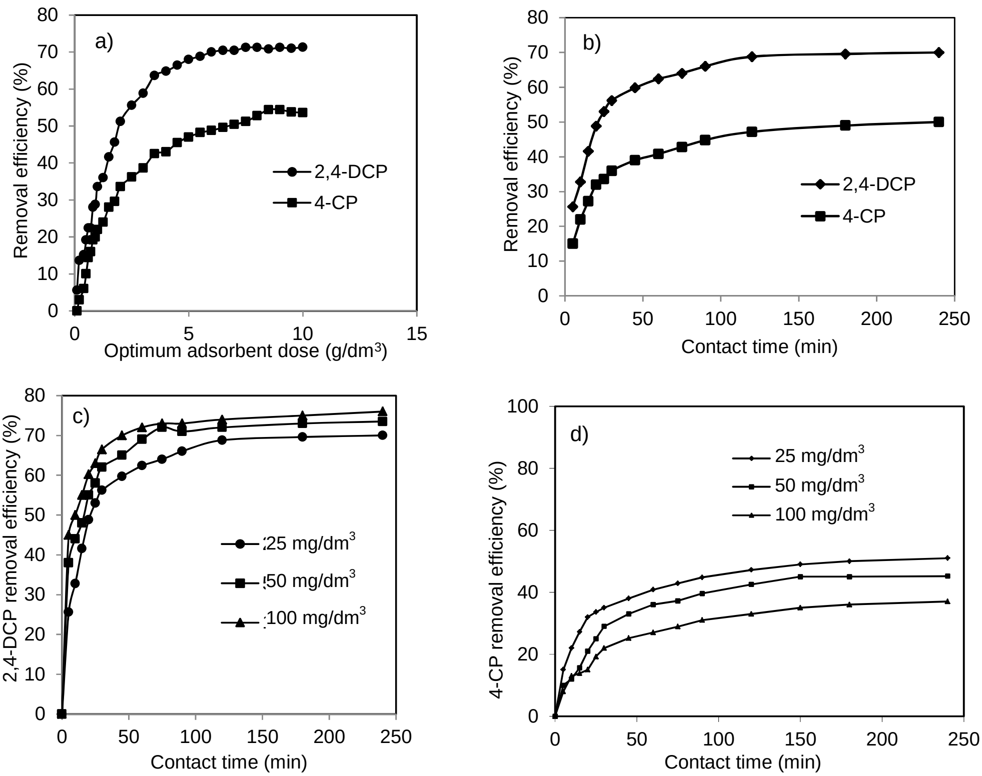

Fig. 2. Effect of adsorbent dosage, contact time and initial concentration on 4-CP and 2,4-DCP removal using sewage sludge

Figure 2 presents the plot of 4-CP and 2,4-DCP removal versus contact time for anaerobically digested dewatered sludge at initial concentrations between 25 and 100 mg/dm^3 at 298 K with the contact time of 120 min. Increase in contact time increased the removal efficiency of 4-CP and 2,4-DCP. Rapid removal was noticed initially which decreased gradually and reached equilibrium at around 240 min. The initial rapid decrease may be due to availability of more adsorption/vacant sites at the initial stage. As a result, there exists an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent. This can be explained by strong attractive forces between 4-CP or 2,4-DCP particles and the sorbent and fast diffusion into the intraparticle matrix to attain rapid equilibrium [19]. The amount of 4-CP and 2,4-DCP adsorbed (mg/g) increased with increase in contact time. 4-CP and 2,4-DCP removal versus time curves are single, smooth and continuous leading to saturation, suggesting the possibility of monolayer coverage of 4-CP and 2,4-DCP on the outer surface of the adsorbent.

Adsorption isotherms describe the relationship between the amount of the adsorbed substance and the concentration of dissolved adsorbate in the liquid at equilibrium. The Langmuir, Freundlich, Temkin and Sips isotherm models were examined to describe the adsorption equilibrium of 4-CP and 2,4-DCP onto sewage sludge. The studies were conducted at the effective initial pH of 6.8, agitation rate of 180 rpm and equilibration time of 240 min. The batch isothermal data fitted to the four models used in this study solved by using the curve fitting toolbox of MATLAB program. The residual degrees of freedom (R^2) of the obtained models are calculated so as to evaluate the goodness of fit. Isotherm model equations, the correlation coefficients and the constants of adsorption isotherm models are given in Tables 5 and 6.

The Langmuir isotherm defines the equilibrium parameters of homogenous surfaces, monolayer adsorption and distribution of adsorption sites [20]. Binding to the surface is primarily by physical forces and implict in its derivation is the assumption that all adsorption sites have equal affinities for adsorbate molecules and that the presence of adsorbed molecules at one site do not affect the adsorption of molecules at an adjacent site [19, 20].

Table 5

Isotherm parameters for 2,4-DCP adsorption on sewage sludge at various temperatures

Model	Equation	Parameters	Temperature [K]		
			298	318	338
Langmuir	$q_e = \dfrac{Q_0 k_L C_e}{1 + k_L C_e}$	Q_o	1.751	1.483	2.119
		k_L	0.026	0.019	0.007
		R^2	1	0.998	1
Freundlich	$q_e = k_F C_e^{1/n}$	k_F	0.07	0.04	0.03
		n	1.39	1.37	1.35
		R^2	0.999	0.998	0.986
Temkin	$q_e = \dfrac{RT \ln\left(a_T C_e\right)}{b_T}$	a_T	0.31	0.22	0.15
		b_T	71.95	92.11	106.5
		R^2	0.995	0.997	0.991
Sips	$q_e = \dfrac{k_S C_e^{b_s}}{1 + a_s C_e^{b_s}}$	k_S	0.045	0.021	0.015
		b_S	1.029	1.15	1.004
		a_S	0.027	0.018	0.007
		R^2	1	1	1

As can be seen from Tables 5 and 6, the Langmuir model effectively described the adsorption data with all R^2 values higher than 0.99 for 2,4-DCP adsorption and greater than 0.95 for 4-CP adsorption, which indicates a monolayer adsorption. The maximum monomolecular capacities were found to be 0.026 dm^3/g for 2,4-DCP at 298 K and 0.031 dm^3/g for 4-CP at 318 K.

Table 6

Isotherm parameters for 4-CP adsorption on sewage sludge at various temperatures

Model	Equation	Parameters	Temperature [K]		
			298	318	338
Langmuir	$q_e = \frac{Q_0 k_L C_e}{1 + k_L C_e}$	Q_0	9.91	9.28	12.16
		k_L	0.018	0.031	0.017
		R^2	0.998	0.986	0.959
Freundlich	$q_e = k_F C_e^{1/n}$	k_F	0.389	0.647	0.396
		n	1.586	1.823	1.477
		R^2	0.998	1	0.999
Temkin	$q_e = \frac{RT \ln(a_T C_e)}{b_T}$	a_T	0.1837	0.2837	0.1939
		b_T	11.52	12.48	11.26
		R^2	0.994	0.982	0.967
Sips	$q_e = \frac{k_S C_e^{b_s}}{1 + a_s C_e^{b_s}}$	k_S	0.2321	0.6171	0.4935
		b_S	0.883	0.581	0.546
		a_S	0.018	0.0083	0.029
		R^2	1	1	1

The Freundlich isotherm is originally empirical in nature but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. This assumed that the stronger binding sites are occupied first and the binding strength decreases with the increasing degree of site occupation. High k_f and $1/n$ values implies that the binding capacity reaches the highest value, and affinity between the adsorbent and adsorbate is also higher. The value of the exponent n gives an indication on the favorability of adsorption. The values of n in the range of 2–10 represent good adsorption, 1–2 – moderately difficult, and lower than 1 – poor [21]. It can be concluded from Tables 5 and 6 that adsorption of 2,4-DCP and 4-CP on anaerobically digested and dewatered sewage sludge is moderate ($1.35 < n < 1.39$ for 2,4-DCP and $1.477 < n < 1.823$ for 4-CP).

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The heat of sorption of all molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions [19]. The parameters of the Temkin model as well as the correlation coefficients t (>0.99 for 2,4-DCP and >0.96 for 4-CP) indicate a good linearity. The variation of adsorption energy is positive for all the studied temperatures which indicates that the adsorption reaction is exothermic. The experimental equilibrium curves are very close to those predicted by the Temkin model. Consequently, the Temkin isotherm can describe adequately the adsorption isotherms of 2,4-DCP and 4-CP onto anaerobically digested dewatered sewage sludge. If just the two-parameter models used in this study are compared, the Langmuir model seems to be more suitable for 2,4-DCP and the Freundlich model – for 4-CP.

The Sips isotherm is also expressed as Langmuir–Freundlich isotherm. At low adsorbate concentrations, it effectively reduces to the Freundlich isotherm and thus it does not obey the Henry's law. At high adsorbate concentrations, it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm [19]. The Sips equation fits adequately the experimental results. Based on the maximum adsorption capacity values, the results for 2,4-DCP adsorption are identical to those obtained using the Langmuir isotherm. The parameter k_S changes in the same manner as k_L of the Langmuir equation.

In order to investigate the adsorption mechanism and potential rate controlling steps such as mass transport and chemical reaction processes, two kinetic models (Lagergren's pseudo-first order and Ho and McKay's pseudo-second order) were chosen to test the experimental data. Kinetic model equations used in this study and the calculated kinetic parameters are given in Table 7.

Table 7

Kinetic parameters for the adsorption of 2,4-DCP and 4-CP onto sewage sludge at 298 K

Kinetic model	Kinetic parameters	Sewage sludge	
		2,4-DCP	4-CP
Pseudo-first order	k_1	0.0265	0.0188
	q_e	5.5718	4.8831
	R^2	0.9821	0.9837
Pseudo-second order	k_2	0.0093	0.0077
	q_e	10.482	8.8028
	R^2	0.9995	0.9995

The pseudo-first order equation or the so called Lagergren equation can be expressed as follows

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{4}$$

where k_1 is the adsorption rate constant, q_t is the amount of 2,4-DCP and 4-CP adsorbed at time t (mg/g) and q_e is the amount of 2,4-DCP and 4-CP adsorbed at saturation. After integration of Eq. (4) we have

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

The plots of $\log(q_e - q_t)$ in function of t give a linear relationship. k_1 and q_e values can be determined from the slope and the intercept of the equation. Figure 3 shows the plots of linearized form of the pseudo-first order equation. Kinetic parameters along with the correlation coefficients of the kinetic models are shown in Table 7. As can be seen from Fig. 3 and Table 7, the correlation coefficients of the first order kinetic model obtained at 298 are quite high (>0.98). Also, the calculated q_e values give reasonable results, thus the adsorption data of 2,4-DCP and 4-CP on anaerobically digested dewatered sewage sludge fits well to Lagergren's pseudo-first order equation.

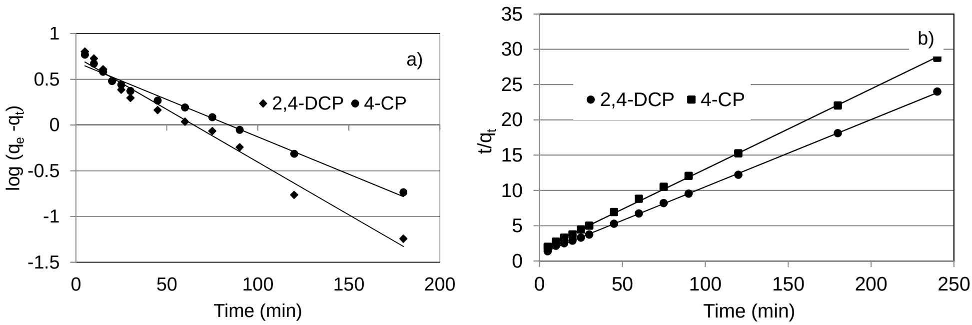

Fig. 3. Adsorption kinetics of 2,4-DCP and 4-CP at 298 K;
models of: a) pseudo-first order, (b) pseudo-second order

The pseudo-second order kinetic equation was first proposed by Blanchard et al. [22] and since then it has been frequently employed to analyze sorption data obtained from various experiments as reviewed by Ho et al. [23]:

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t\right)^2 \tag{6}$$

After integration we have:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where q_e is the amount of the solute adsorbed at the equilibrium (mg/g), k_2 is the equilibrium rate constant of pseudo-second order model (g/mg·min). q_e and k_2 values can be determined from the slope and the intercept of the plots of t/q in function of t, respectively (Fig. 3). The calculated q_e values fit better the experimental data than the calculated values of the pseudo-first order model. Therefore, the adsorption of 2,4-DCP and 4-CP can be better approximated by the pseudo-second order model. Correlation coefficients as shown in Table 7 are also considerably high for pseudo-second order kinetic model.

Although Lagergren's pseudo-first order equation provided a good fitting ($R^2 > 0.98$) to the experimental data, Ho and McKay's pseudo-second order kinetic model ($R^2 > 0.99$) described the kinetic data better than the Lagergren's model. This may be attributed the fact that the adsorption rate of 2,4-DCP and 4-CP onto sewage sludge depends on the behavior over a whole range of concentrations. Therefore, the adsorption reaction can be approximated more favourably by the pseudo-second order kinetic model.

4. CONCLUSION

Physical, chemical, morphological properties and sorption characteristics of anaerobically digested dewatered municipal sewage sludge were investigated. Adsorption isotherms and kinetics of 2,4-DCP and 4-CP adsorption onto sewage sludge were also studied at the temperature range of 298–338 K.

Sewage sludge mineralogically contains calcite ($CaCO_3$), quartz (SiO_2), gismondine ($CaAl_2Si_2O_8 \cdot H_2O$) and silica was found to be the dominant component of sewage sludge. SEM photographs of the sludge show that pores of different sizes and different shapes could be observed. BET analyses of the sewage sludge show that sewage sludge has mesoporous and macroporous structure. Its surface area was found to be lower but pore diameters and pore widths of the samples were determined to be higher as compared with inorganic materials. From the FT-IR spectra, Si–O–C, Si–O–Si, Al–O–(OH)–Al structures, carboxyl and hydroxyl groups, polysaccharides, lipids and cellulose were identified on the surface of anaerobically digested dewatered sewage sludge.

Optimum conditions for 2,4-DCP and 4-CP removal by sewage sludge were found to be pH = 7.0, adsorbent dose = 6 g/dm^3 for 2,4-DCP and 7 g/dm^3 for 4-CP. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved after about 240 min. The adsorption performances were strongly affected by parameters such as initial concentration of 2,4-DCP and 4-CP ions and temperature. Increasing the initial 2,4-DCP and 4-CP concentration in the adsorbent suspension resulted in an increase of its uptake.

Among the two- and three-parameter isotherms, the experimental data showed good fits with Langmuir, Freundlich, Temkin and Sips isotherm equations. Considering two-parameter models examined in this study, the Langmuir model is more suitable for the description of adsorption of 4-CP, while and the Freundlich model better describes adsorption of 2,4-DCP onto sewage sludge.

Adsorption kinetics was found to follow second-order rate expression with initial adsorption rates (h_0) being the highest for adsorption of 4-CP and 2,4-DCP onto sewage sludge. The adsorption of 4-CP and 2,4-DCP ions was rapid during the first 20 min and the equilibrium was attained within 2 h.

Anaerobically digested dewatered sewage sludge showed better adsorptive characteristics for the removal of 2,4-DCP. Although sewage sludge is a moderately effective adsorbent for both 4-CP and 2,4-DCP solutions, high amounts of sewage sludge were required. Since sewage sludge contains heavy metals, this feature may be a disadvantage for the practical use of high mass sludge in the investigation of adsorption from the aqueous solutions. But it can be concluded from the results of this work that anaerobically digested, dewatered sewage sludge enables removal of chlorophenol from leachates disposed with solid wastes in landfills, and partially avoid contamination of groundwater by xenobiotic organic compounds such as phenols.

SYMBOLS

C_0 – initial 4-CP and 2,4-DCPconcentration, mg/dm^3
C_e – equilibrium concentration at liquid phase, mg/dm^3
q_e – equilibrium concentration at solid phase, mg/g
q_t – concentration at solid phase at time t, mg/g
T – temperature, K
R – universal gas constant, 8.314 J/(mol·K)
t – time, min
k_F – Freundlich isotherm constant, adsorption capacity, dm^3/g
n – Freundlich isotherm constant, adsprption intensity, mg/g
Q_0 – Langmuir isotherm constant, maximum pollutant uptake, mg/g
k_L – Langmuir isotherm equilibrium constant, dm^3/mg
a_t – Temkin isotherm constant, dm^3/g
b_t – Temkin isotherm constant related to heat of sorption, J/mol
k_s – Sips model isotherm constant, dm^3/g
b_s – Sips model, exponent
a_s – Sips model constant, dm^3/mg
k_1 – rate constant of pseudo-first order kinetic model, 1/min
k_2 – rate constant of pseudo-second order kinetic model, g/(mg·min)
m – adsorbent mass per 1 dm^3 of solution, g/dm^3
V – volume of solution, dm^3
R^2 – regression correlation coefficient

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