



Removal of Octyl Phenol Ethoxylate (OPE) Using Processed and Unprocessed Industrial Biological Waste Sludge

Ali Rıza Dinçer*, İbrahim Feda Aral

Namık Kemal University, Çorlu, Tekirdağ-Turkey

*Corresponding author's e-mail: adincer@nku.edu.tr

Keywords: Waste Sludge, Adsorption, Octyl Phenol Ethoxylate, Pyrolyzed sludge

Abstract: This study investigated the Octyl Phenol Ethoxylate (OPE) removal potentials of raw and treated industrial treatment sludges (ITS) at different pH. Experiments were conducted in a set of 500 ml Erlenmeyer flasks, into which OPE solutions of 300 ml with different initial concentrations (50–300 µg/l) were added into. Adsorption of Octyl Phenol Ethoxylate from an aqueous solution into ITS105 (T=105°C), ITS300 (T=300°C), ITS600 (T=600°C) and ITS450 (pyrolyzed, T=450°C) was carried out at a room temperature. The OPE adsorption rate increase in the treatment sludge processed at 600°C. As opposed to the sludge treated at 105°C, the adsorption rate decreased as the concentration increased. The reason for this was that the porous structure was degraded at 600°C, and the surface charge balance was disrupted. ITS300 had a lower adsorption capacity for Octyl Phenol Ethoxylate removal than ITS105, ITS600 and ITS450 (pyrolyzed). The treatment sludge pyrolyzed at 450°C conformed with the Freundlich isotherm at pH 4 ($R^2=0.94$) and pH 7 ($R^2=0.89$). The treatment sludge heat-treated at 600°C conformed with the Freundlich isotherm at pH 4 ($R^2=0.97$), pH 7 ($R^2=0.98$) and pH 10 ($R^2=0.99$). Additionally, for ITS600, the Brunauer, Emmett and Teller (BET) isotherm was valid at neutral pH. The OPE adsorption coefficient for ITS600 at pH 4 and pH 7 was calculated as 1.05 L/µg and 1.083 L/µg, respectively. According to the BET isotherm (for ITS600) the q_m values at pH 4 and pH 7 were respectively 8.21 µg/g and 2.92 µg/g. The temperature of the adsorption value obtained with the Temkin isotherm showed that the interaction between the OPE and the adsorbent substances was not a chemical or ionic interaction but probably a physical interaction.

Introduction

Activated carbon has been used as an adsorbent material for many years. Considering its sustainable life cycle, activated carbon obtained from waste constitutes a serious alternative to activated carbon not produced from waste material (Moreira et al. 2017; Ravenni et al. 2020). Several studies have recently been published to investigate production of adsorbents from different types of waste. Some of these waste materials are: Agricultural wastes (Adegoke et al. 2015; Sewu et al. 2017), waste sludges (Khoshbouy et al. 2019; Choi et al. 2019; Vera et al. 2019; Zhang et al. 2019; Li et al. 2020; Gu et al. 2021), sawdust (Gupta et al. 2009), biochar (Wang et al. 2021) and clay (Auta et al. 2012).

Biological sewage sludge contains many hazardous substances such as pathogenic organisms, toxic organic pollutants and heavy metals (Seo et al. 2020). Metals that are prevalently found in industrial wastewaters are lead, mercury, chromium, arsenic, cadmium, zinc, copper and nickel (Araujo et al. 2018). Joshi et al. (2004) stated that ion exchange is the basis in adsorption with biomass. In general, the dead form of biomass is utilized for biosorption studies (Kulkarni

2015). Sirianuntapiboon et al. found that the adsorption ability of biosludge increased with an increase in sludge age. Autoclaved biosludge showed the highest adsorption ability under acidic conditions (pH 3), while resting biosludge showed the highest adsorption ability under neutral or weak alkaline conditions (Sirianuntapiboon et al. 2004). Sewage sludge is carbonaceous in nature and rich in organic materials. So, it can be converted into activated carbon after chemical treatment (Fan et al. 2008).

Endocrine disrupting compounds, such as Octyl Phenol Ethoxylate (OPE), are chemicals that act as hormones, creating negative effects on living creatures (Dinçer et al. 2018; Cirja et al. 2008). Effective treatment of endocrine disrupting compounds with this complex structure is an important issue. Extensive studies are available to completely treat endocrine disrupting compounds, turn them into harmless products or remove their endocrine activities. In recent years, the discovery of the estrogen-like activity of the metabolites of some alkylphenols and APEOs, including 4-nonylphenol and 4-tert octyl phenol, has caused concerns about the endocrine disrupting effects observed in aquatic biota. Due to the hydrophobic and non-ionic structures of these compounds, their biological treatment

is poor, and the remaining products may have toxic effects in receiving bodies (Nimrod et al., 1996; Ferguson et al. 2000). Due to their high consumption rates, Bisphenol A (BPA) and Octyl Phenol Ethoxylate (OPE) are two of the xenobiotics that have attracted academic interest. BPA and OPE have been reported to be common everywhere in the environment (Umar et al. 2013).

In this study, the adsorption properties and adsorption capacity of heat-treated sewage sludge were studied. The Langmuir, Freundlich, Temkin and Brunauer-Emmett-Teller (BET) isotherm models were tested for their applicability.

Material and Methods

Octyl phenol ethoxylate (OPEO) is a member of the nonionic surfactant family of alkylphenol polyethoxylates. OPEO (Triton™-X45; CAS 9002-93-1; purity: 98%) was purchased from Sigma-Aldrich (USA) and Merck (Germany) and used without further purification. Triton™-X45 is a mixture of OPEOs with an average ethoxylate chain length of 4.5. All other reagents and solvents were of at least analytical grade and obtained from Merck (Germany), Fluka (USA) or Sigma-Aldrich (USA).

OPEO analysis was performed on an HPLC device (Agilent 1100 Series, Agilent Technologies, USA) equipped with a diode array detector (G1315A, Agilent Series) and a Novapak C18 (3.9mm × 150 mm, Waters, USA) reversed phase column. The detection wavelength and column temperature were set at 225 nm and 25°C, respectively. The mobile phase consisted of acetonitrile-0.01% phosphoric acid in water (65/35, v/v) used at a flow rate of 1.0 mL/min. The instrument detection limit and quantification limit of the OPEO for an injection volume of 100 µL were calculated as 78 µg/L and 234 µg/L, respectively (Dinçer et al., 2018).

Waste activated sludge was obtained from the Çerkezköy Organized Industrial Zone full scale wastewater treatment plant in Çerkezköy, Tekirdağ. The sludge sample was first dried at 105°C for 7 days in an oven, crushed and sieved (diameter < 2 mm). Adsorption experiments were carried out at room temperature (25±2°C) under the batch mode. The pH of the solutions was adjusted to the initial pH throughout the experiments. A similar procedure was followed for another set of experiments with different Octyl Phenol Ethoxylate concentrations and pH values. To determine the optimum pH

for the adsorption of Octyl Phenol Ethoxylate, the effect of pH was observed over the pH range of 4–10. The pH of the adsorbents for all adsorption experiments was adjusted using dilute solutions of HCl or NaOH accordingly. The quantity of adsorption at equilibrium, q_e (µg/g) ($q_e = (C_0 - C_e)V/M$) was calculated, where C_0 and C_e (µg/l) were the liquid phase concentration of the Octyl Phenol Ethoxylate at the initial point and equilibrium, respectively. V (L) was the volume of the solution, and M (g) was the mass of the dry adsorbents used. OPE removal efficiencies were calculated by using the equation $E = (C_0 - C_e)/C_0$. The experimental data were analyzed by using the Langmuir, Freundlich, Temkin and Brunauer-Emmett-Teller (BET) isotherm models, and the constants of these equations were determined.

The treatment sludges taken from the biological wastewater treatment plant of the Organized Industrial Zone were subjected to heat treatment at 105°C, 300°C, 450°C (pyrolyzed), and 600°C. A total of 20 g of biological sewage sludge was used in the pyrolysis activation process. Each sample was heated to the activation temperature (450°C) in the presence of an inert gas (N₂). The dried sludges were broken into pieces, separated into certain particle sizes (≤2mm) by a sieve and used for the adsorption experiments. The adsorption experiments were carried out for 120 min to determine the effects of time on adsorption. The surface areas of the treated sludges were measured by a Quantachrome Autosorb-1 surface area analyzer. The pore structures of the samples were determined using N₂ adsorption-desorption isotherms at 77 K. Before measurements, the samples were degassed under vacuum at 105°C (ITS105) and 200°C for (ITS300, ITS450 and ITS600) 18 h to remove moisture and adsorbates adhered to their surfaces. The surface areas of the treated sludges were 2.9, 1.4, 1.9 and 3.1 m²/g for ITS105°C, ITS300°C, ITS450°C (pyrolyzed) and ITS600°C, respectively (Table 2). The chemical composition of the treated sludges was measured using ICP spectroscopy. The chemical analysis results of the sludge dried at 105°C are shown in Table 1.

Results and Discussion

The chemical and physical properties of the adsorbent materials are given in Tables 1 and 2. The structure of the sludge majorly consisted of C and O with ratios of 30.75% and 19.67%, respectively. The sludge contained Ca, Mg, Fe and Cl at high concentrations. When the sludge drying temperature was

Table 1. Elemental composition of raw treatment sludge (ITS105)

Parameters	%w	Parameters	%w
C	30.75	Mn	1.4
O	19.67	Ni	3.02
N	3.8	Cu	1.26
P	5.04	K	2.35
Ca	8.21	Fe	3.12
Mg	2.58	Si	6.9
Al	1.94	Ti	0.5
Na	0.7	S	2.2
Zn	1.77	Cl	4.81

increased from 105°C to 300°C, the treatment sludge surface area decreased from 2.9 m²/g to 1.4 m²/g. The sludge surface area treated at 450°C in the presence of nitrogen gas was found to be 1.9 m²/g. The treated sludge surface area at 600°C increased to 3.1 m²/g. It was understood from the adsorption efficiency and surface area change that the micro and macro pore structure changed depending on the process temperature of the sludge. The largest pore size was measured in the sludge dried at 105°C (pore size=8.12 nm). By increasing the sludge drying temperature from 300°C to 600°C, the pore size increased from 2.32 nm to 4.47 nm. In relation to the increase in the pore size, the pore volume also increased. It was thought that, as the surface area and pore volume of the sludge treated at 600°C increased, this inevitably increased the adsorption.

The Octyl Phenol Ethoxylate binding capacities of the adsorbents (ITS105°C and ITS300°C) are shown in Fig. 1 as a function of the initial pH and the initial OPE concentration. The effects of pH 4, pH 7 and pH 10 on the adsorption of Octyl Phenol Ethoxylate by ITS105 and ITS300 were analyzed at Octyl Phenol Ethoxylate concentrations of 45, 90, 135, 180 and 270 µg/l. When the initial pH of the Octyl Phenol Ethoxylate solutions was increased from 4 to 7, the amounts of Octyl Phenol Ethoxylate adsorbed at the equilibrium decreased from 11.94 to 5.342 µg/g for the 270 µg/l initial OPE concentration. Further increases in pH from 7 to 10 resulted in decreases in the adsorption capacity of ITS105. For low concentrations, there was a rapid uptake of Octyl Phenol Ethoxylate due to surface mass transfer. Carbonaceous adsorbents possessing

high surface area and porosity are materials that are preferred for the removal of organics (Jain et al. 2003). Based on the obtained data, the activated sludge dried at 105°C showed a better performance than the sludge treated at 300°C at pH 4 and pH 7. It is thought that the adsorption amount increased as a result of the negative charge of the bacteria surface constituting the treatment sludge and the positive charging of the OPE at low pH. The OPE adsorption amount in the sludge dried at 300°C was found to be very low. As seen in the values given in Table 2, the BET surface area, pore volume and pore diameter of the sludge dried at 300°C were much lower than those of the sludge dried at 105°C. The small pore diameter and pore volume of the sludge dried at 300°C caused a negative effect on OPE removal. It is an expected result that adsorption rates are low at low OPE concentrations. As the influent OPE concentration increases, the amount of substance adsorbed will naturally increase.

Fig. 2 shows the C₀ (µg/g) versus q_e (µg/g) change plot of the sludge treated at 105°C and 450°C. The adsorption capacity of the pyrolyzed treatment sludge at pH 7 was higher than those at pH 4 and pH 10. When the adsorption values of both adsorbent materials were compared at pH 10, the adsorption value of the treatment sludge pyrolyzed at 450°C was found higher. It was considered that the low adsorption value of the sludge dried at 105°C was associated with that the surface charge of this sludge was negative, and the OPE was also charged negatively at high pH. The low pore diameter and pore volume of the treatment sludge pyrolyzed at 450°C caused a low adsorption

Table 2. BET surface area (m²/g), pore size (nm) and pore volume (cm³/g) of the studied samples (ITS105, ITS300, ITS450, ITS600)

	BET (m ² /g)	V (cm ³ /g)	Pore Size (nm)
Treatment Sludge (105°C)	2.9	0.0236	8.12
Treatment Sludge (300°C)	1.4	0.0132	2.32
Treatment Sludge(450°C Pyrolyzed)	1.9	0.0169	2.83
Treatment Sludge (600°C)	3.1	0.027	4.47

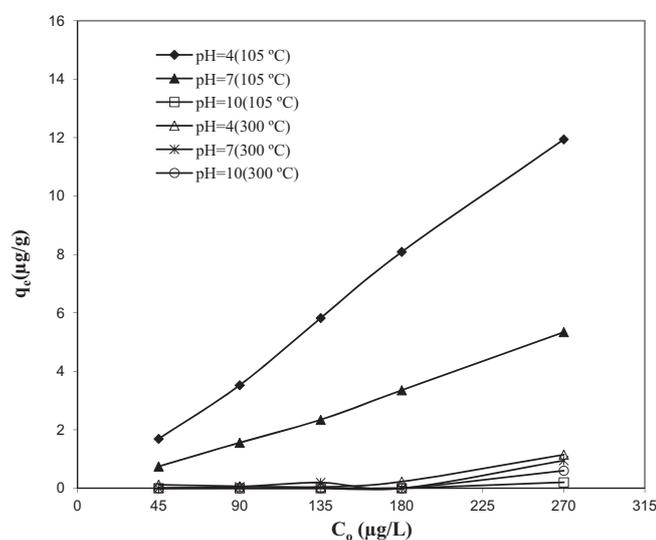


Fig. 1. Variation of equilibrium adsorption capacity (q_e) of ITS105 and ITS300 adsorbents depending on pH and influent OPE concentrations (C_0) ($\Theta_H = 2$ h)

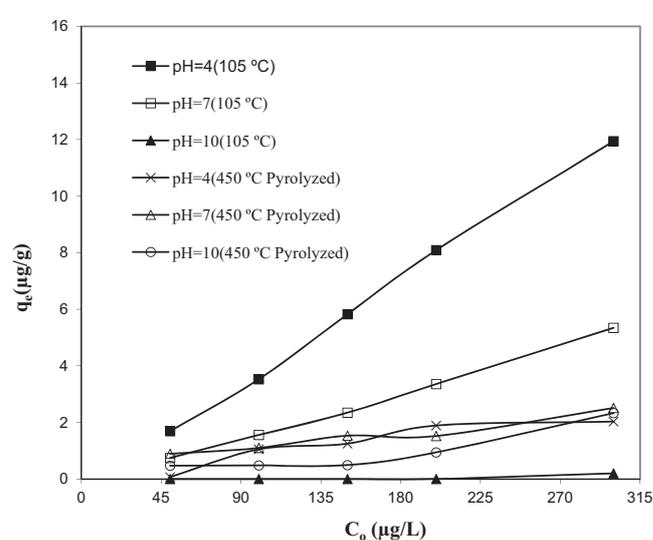


Fig. 2. Variation of equilibrium adsorption capacity (q_e) of ITS105 and ITS450 (pyrolyzed) adsorbents depending on pH and influent OPE concentrations (C_0) ($\Theta_H = 2$ h)

efficiency. As the influent OPE concentration increased, the OPE adsorption efficiency of both adsorbent substances also increased. The highest adsorption efficiency of the sludge processed at 105°C occurred at a low pH. On the other hand, the highest adsorption efficiency of the pyrolyzed sludge occurred at pH 7. In the case of the pyrolyzed sludge, biosorption was maximal at pH 7.0 and decreased thereafter. The equilibrium sorption capacity of the pyrolyzed sludge increased from 2.03 to 2.51 $\mu\text{g/g}$ when the solution pH was changed from 4.0 to 7.0. The equilibrium sorption capacities of the pyrolyzed sludge were 2.03, 2.51 and 2.33 at pH 4, pH 7 and pH 10, respectively, for the 270 $\mu\text{g/l}$ initial Octyl Phenol Ethoxylate concentration. An increase in the initial Octyl Phenol Ethoxylate concentration led to an increase in the adsorption capacity of the dye on ITS105, ITS300 and ITS450 (pyrolyzed). This was due to the increase in the driving force of the concentration gradient with an increase in the initial Octyl Phenol Ethoxylate concentration. The amount of Octyl Phenol Ethoxylate adsorbed onto the pyrolyzed sludge was lower in comparison to ITS105 at the equilibrium.

Fig. 3 shows the effects of the initial pH and concentrations on adsorption by heat-treated activated sludge (ITS600). When the initial pH of the Octyl Phenol Ethoxylate solutions was increased from 4 to 7, the amounts of the Octyl Phenol Ethoxylate adsorbed at the equilibrium increased from 5.23 to 5.47 $\mu\text{g/g}$ for the 270 $\mu\text{g/l}$ initial OPE concentration. Further increases in the pH from 7 to 10 resulted in decreases in the adsorption capacity of ITS600. The results indicated that the amount adsorbed per specified amount of adsorbent ($\mu\text{g/g}$) decreased when the firing temperature was increased from 105 to 600°C. The amount adsorbed per specified amount of adsorbent for ($\mu\text{g/g}$) pH 7 ranged from 1.605 to 5.47. The adsorption capacity of each biosorbent increased by increasing the initial Octyl Phenol Ethoxylate concentration. The equilibrium sorption capacities of ITS105 were 11.94, 5.342 and 0.2 $\mu\text{g/g}$ at pH 4, pH 7 and pH 10, respectively, for the 270 $\mu\text{g/l}$ initial Octyl Phenol Ethoxylate concentration. In the

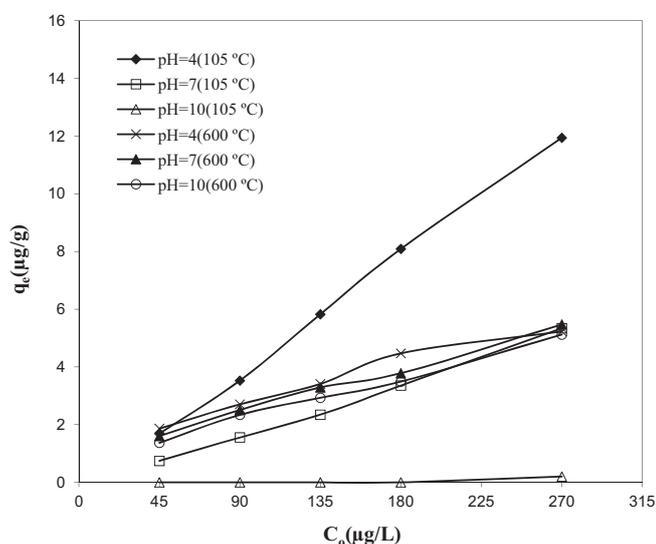


Fig. 3. Variation of equilibrium adsorption capacity (q_e) of ITS105 and ITS600 adsorbents depending on pH and influent OPE concentrations (C_0) ($\Theta_H = 2$ h)

sludge treated at 300°C, 450°C and 600°C, the OPE adsorption increased in the order of ITS600>ITS450>ITS300. This situation was determined to be associated with the surface area, pore diameter and pore volume of the adsorbent substances.

The OPE removal efficiencies of the adsorbents obtained as a result of the treatment of sewage sludge at different temperatures, depending on pH and concentration, are shown in Fig. 4. The OPE removal efficiency of the sewage sludge treated at 105°C was found to be the highest at pH 4. In the sludge treated at 105°C, the adsorption efficiency increased as the influent OPE concentration increased at all pH values. Adsorption took place at a minimum rate in the sludge treated at 300°C. A limited increase in adsorption was observed at the concentration of 270 $\mu\text{g/L}$ OPE. This was thought to be caused by deterioration of the activated sludge structure and insufficient carbonization at this temperature. The OPE adsorption rate increased in the sewage sludge treated at 600°C. Unlike the sludge treated at 105°C, the rate of adsorption decreased as the concentration increased. This was due to the deterioration of the porous structure at 600°C and disruption of the surface load balance. In the sewage sludge treated at 450°C, the adsorption rate decreased. It is thought that the decrease in the macro and microporous structure during the pyrolysis process was effective in reducing the adsorption efficiency. In the treatment sludge subjected to the pyrolysis process, the adsorption was higher at low concentrations and neutral pH. Pyrolysis temperature and the activator/dried sludge ratio greatly affect the surface area and pore properties of a sludge-based adsorbent (Yang et al. 2016).

Adsorption Model Parameters

Table 3 and Table 4 present the Langmuir, Freundlich, Temkin and BET isotherm parameters for Octyl Phenol Ethoxylate adsorption on ITS105, ITS300, ITS600 and Pyrolyzed (450°C) biological activated sludge. An adsorption isotherm is mainly important to describe how solutes interact with adsorbents.

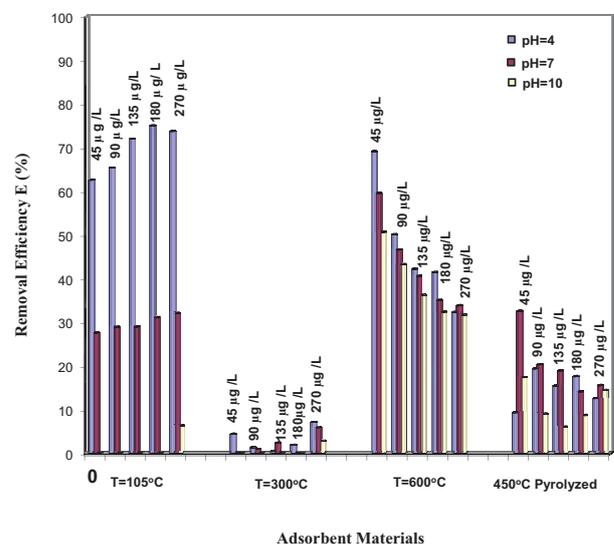


Fig. 4. Removal efficiency ($E\%$) of adsorbents depending on influent OPE concentrations and pH ($\Theta_H = 2$ h)

Adsorption isotherms are discussed here by modeling the Langmuir, Freundlich, Temkin and Brunauer Emmett Teller (BET) isotherms.

The Freundlich isotherm model assumed a heterogenous adsorption on the surface of the adsorbent. According to the Freundlich isotherm model, the stronger binding zones on the surface are infiltrated initially, the binding strength decreases with increasing site coverage degree, and this results in reduced adsorption in time (Tan et al. 2009; Lonappan et al. 2016). The Freundlich's isotherm (linear form) fits the following equation (Khoshbouy et al. 2019; Ravenni et al. 2020):

$$\ln q_e = \ln K_f + \frac{1}{n} C_e \quad (1)$$

where

q_e : the amount adsorbed per specified amount of adsorbent (mg/g)

K_f : a constant related to the adsorption capacity(L/g)

C_e : the concentration in solution(mg/L)

$1/n$: an empirical parameter related to the intensity of adsorption which varies with the heterogeneity of the adsorbent.

For values in the range of $0.1 < 1/n > 1$, adsorption is favorable (Namasivayam et al., 1992). From the slope and intercept of the best fit lines, the following Freundlich isotherm constants were found: $k_f=0.032 \mu\text{g/g}$, $1/n=1.41$, for ITS105°C. The result that the $1/n$ value was higher than 1 showed that the adsorption did not fit this isotherm. In the sludge treated at 450°C, for pH 4, the $1/n$ and k_f values were found as 0.57 and 0.097 ($R^2=0.94$), while these were found as 0.49 and 0.163 ($R^2=0.89$) at pH 7. For the sludge treated at 600°C, all coefficients conformed with the Freundlich isotherm. The constant related to the adsorption capacity, K_p gave the maximum value at pH 4.

The Langmuir isotherm model was formed based on the assumption of a homogenous, single-layer adsorption onto the surface without re-adsorption of the adsorbate on the surface (Tan et al. 2009; Lonappan et al. 2016). The Langmuir isotherm (linear form) is represented by the following equation (Khoshbouy et al. 2019; Ravenni et al. 2020):

$$\frac{C_e}{q_e} = \frac{1}{(q_m \cdot K_L)} + \frac{1}{q_m \cdot C_e} \quad (2)$$

Here, q_e is the amount of adsorbed substance per unit adsorbent weight at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), C_e is the concentration of solute staying in the solution without being adsorbed at equilibrium (mg/L), and K_L is a value related to the adsorption temperature (L/mg).

In the C_e versus C_e/q_e linear plot, the $1/q_m$ and $1/(q_m \cdot K_L)$ values were found based on the slope and the intercept, respectively. As seen from the values given in Table 3, calculation could not be made due to the negative results in the sludges treated at 105 and 300°C. In light of these data, it was determined that the R^2 value was 0.95, and the maximum adsorption rate was $7.29 \mu\text{g/g}$ in the sludge that was treated at 600°C at pH 4. Due to its lower R^2 values in comparison to the other isotherm models, the adsorption was not explained by the Langmuir isotherm.

The linear form of the Temkin isotherm model is given below (Vijayaraghavan et al. 2006). The Temkin isotherm model accounts for the effects of indirect adsorbate/adsorbent interactions on the adsorption process. It is assumed that the adsorption temperature of all molecules in the layer linearly decreases as a result of the increased surface coating (Ringot et al. 2007). From the plot of q_e versus $\ln C_e$, RT/b_T can be calculated from the slope, and $RT/b_T \cdot \ln A_T$ can be calculated from the intercept.

$$q_e = \frac{R \cdot T}{b_T} \ln A_T + \frac{R \cdot T}{b_T} \ln C_e \quad (3)$$

b_T refers to the Temkin constant related to the temperature of adsorption (J/mol), and A_T is a constant related to the adsorption capacity (L/g). R is the gas constant (8.314 J/mol K), and T is the temperature (K) (Nunes et al. 2009). A higher value of the adsorption capacity (A_T) ($0.234 \text{ L}/\mu\text{g}$) was obtained at pH 4 in the sludge treated at 600°C. The positive b_T value shows that the adsorption was exothermic. In general, it was found that, as the adsorption capacity increased, the adsorption temperature constant also increased. As the b_T values of the sludges treated at 105°C, 450°C and 600°C were $< 8 \text{ kJ/mol}$ (Araujo et al. 2018), it may be stated that the adsorption was physical adsorption.

The linear mathematical expression of the Brunauer-Emmett-Teller (BET) isotherm related to adsorption from a solution is given in equation 4. The Brunauer-Emmett-Teller theory is valid for multi-layer adsorption systems. The Brunauer-Emmett-Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface. From the plot of C_e/C_o versus $C_e/[(C_o - C_e) \cdot q_e]$, $(k-1)/k \cdot q_m$ from the slope and $1/k \cdot q_m$ from the intercept can be obtained.

$$\frac{C_e}{[C_o - C_e]q_e} = \frac{1}{k q_m} + \frac{k-1}{k q_m} \cdot \left(\frac{C_e}{C_o} \right) \quad (4)$$

In this equation, k is a constant explaining the energy of interaction with the surface (L/mg), and q_m is the theoretical saturation capacity (mg/g) (Tsai et al. 2006).

Looking at Table 4, it is seen that the R^2 correlation coefficients at values other than pH 7 were not as large as needed to explain the adsorption with the BET isotherm. The BET isotherm coefficients for the sludge treated at 600°C (at pH 7) were found as $q_m = 2.92 \mu\text{g/g}$, $k = 1.083 \text{ L}/\mu\text{g}$ and $R^2 = 0.99$. For the same adsorbent, the BET isotherm coefficients at pH 4 were $q_m = 8.21 \mu\text{g/g}$, $k = 1.05 \text{ L}/\mu\text{g}$ and $R^2 = 0.88$.

Conclusions

ITS105, ITS300, ITS600 and Pyrolyzed 450 were used to remove Octyl Phenol Ethoxylate at different pH values, and a comparative experiment was conducted among the adsorbents. When the treatment temperature applied on the sludge was increased from 105°C to 300°C, 450°C and 600°C, the surface area changes were found respectively as $2.9 \text{ m}^2/\text{g}$, $1.4 \text{ m}^2/\text{g}$, $1.9 \text{ m}^2/\text{g}$, and $3.1 \text{ m}^2/\text{g}$. The highest OPE removal efficiency was found in the sludge treated at 105°C and 600°C. In the sludge treated at 300°C, the BET surface area decreased by more than 50%, and consequently, the pore volume and pore diameter of

Table 3. Freundlich and Langmuir Models adsorption parameters

Freundlich Equation ($q_e = k_f \cdot C_e^{1/n}$)									
	pH=4			pH=7			pH=10		
	1/n	K_f ($\mu\text{g/g}$)	R^2 –	1/n	K_f ($\mu\text{g/g}$)	R^2 –	1/n	K_f ($\mu\text{g/g}$)	R^2 –
105°C	1.41	0.032	0.978	–	–	–	–	–	–
300°C	–	–	–	–	–	–	–	–	–
450°C	0.57	0.097	0.94	0.49	0.163	0.89	–	–	–
600°C	0.41	0.641	0.97	0.52	0.37	0.98	0.595	0.23	0.99
Langmuir Equation ($C_e/q_e = 1/(q_m \cdot K_L) + 1/q_m \cdot C_e$)									
	pH=4			pH=7			pH=10		
	q_m ($\mu\text{g/g}$)	K_L ($\text{L}/\mu\text{g}$)	R^2 –	q_m ($\mu\text{g/g}$)	K_L ($\text{L}/\mu\text{g}$)	R^2 –	q_m ($\mu\text{g/g}$)	K_L ($\text{L}/\mu\text{g}$)	R^2 –
105°C	–	–	–	–	–	–	–	–	–
300°C	–	–	–	–	–	–	–	–	–
450°C	4.2	0.0047	0.79	3.85	0.0068	0.73	8.84	0.0071	0.88
600°C	7.29	0.0168	0.95	8.42	0.0099	0.89	8.84	0.0071	0.88

Table 4. Temkin and Brunauer Emmett Teller(BET) Models adsorption parameters

Temkin Equation ($q_e = (R \cdot T/b_T) \cdot \ln A_T + (R \cdot T/b_T) \cdot \ln C_e$)									
	pH=4			pH=7			pH=10		
	b_T (J/mol)	A_T $\text{L}/\mu\text{g}$	R^2 –	b_T (J/mol)	A_T $\text{L}/\mu\text{g}$	R^2 –	b_T (J/mol)	A_T $\text{L}/\mu\text{g}$	R^2 –
105°C	40	0.0644	0.93	117	0.0334	0.88	–	–	0.37
300°C	–	–	0.39	–	–	0.45	–	–	0.41
450°C	257	0.0281	0.93	423	0.0883	0.78	–	–	0.52
600°C	226	0.234	0.92	191	0.123	0.90	184	0.0885	0.91
Brunauer, Emmett and Teller(BET) Equation ($C_e/[C_e - C_o] \cdot q_e] = 1/k \cdot q_m + (k-1/k \cdot q_m) \cdot (C_e/C_o)$)									
	pH=4			pH=7			pH=10		
	q_m ($\mu\text{g/g}$)	k ($\text{L}/\mu\text{g}$)	R^2 –	q_m ($\mu\text{g/g}$)	k ($\text{L}/\mu\text{g}$)	R^2 –	q_m ($\mu\text{g/g}$)	k ($\text{L}/\mu\text{g}$)	R^2 –
105°C	5.208	-0.334	0.86	–	–	0.63	–	–	0.22
300°C	–	–	0.34	–	–	0.20	–	–	–
450°C	–	–	0.10	–	–	0.20	–	–	0.54
600°C	8.21	1.05	0.88	2.92	1.083	0.99	–	–	0.49

the adsorbent material decreased. The surface area of the sludge treated at 450°C in the presence of nitrogen gas was 1.9 m²/g, its pore volume was 0.0169 cm³/g, and its pore diameter was 2.83 nm. The OPE removal efficiency in this sludge was lower than in the sludges treated at 105°C and higher than 300°C. The highest surface area in the sewage sludge treated at 600°C was found to be 3.1 m²/g. In this sludge, the pore diameter was lower than that of the sludge treated at 105°C. In comparison to the sludge treated at 105°C, the pore volume of the sludge treated at 600°C was found to be higher, although the pore diameter was lower. In light of the experimental data, the sludge treated at 600°C was associated best with the Freundlich adsorption isotherm at pH 4 ($k_f = 0.641$, $R^2 = 0.97$). For the same sludge, from the Langmuir isotherm equation, the value of $q_m = 7.29 \mu\text{g/g}$ was

found ($R^2 = 0.95$). In the neutral conditions (pH 7), the result was associated with the BET isotherm ($q_m = 2.92 \mu\text{g/g}$, $R^2 = 0.99$). As an accessible and obtainable raw material, sewage sludge may be subjected to different thermal treatments and used in the removal of OPE which cannot be removed in wastewater treatment systems.

References

- Adegoke, K.A. & Bello, O.S. (2015). Dye sequestration using agricultural wastes as adsorbents, *Water Resources and Industry*, 12, pp. 8–24, <https://doi.org/10.1016/j.wri.2015.09.002>.
- Araujo, C.S.T., Almeida, I.L.S., Rezende, H.C. & Marcionilo, S.M.L.O. (2018). Elucidation of mechanism involved in adsorption of

- Pb(II) onto lobeira fruit (*Solanum lycocarpum*) using Langmuir, Freundlich and Temkin isotherms, *Microchemical Journal*, 137, pp. 348–354, <https://doi.org/10.1016/j.microc.2017.11.009>.
- Auta, M. & Hameed, B.H. (2012). Modified mesoporous clay adsorbent for adsorption isotherm and kinetics of methylene blue, *Chemical Engineering Journal*, 198–199, pp. 219–227, <https://doi.org/10.1016/j.cej.2012.05.075>.
- Choi, H.J. & Yu, S.W. (2019). Biosorption of methylene blue from aqueous solution by agricultural bioadsorbent corncob, *Environmental Engineering Research*, 24, 1, pp. 99–106, <https://doi.org/10.4491/eer.2018.107>.
- Cirja, M., Ivashechkin, P., Schäffer, A., & Corvini, P.F. (2008). Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR), *Reviews in Environmental Science and Biotechnology*, 7, 1, pp. 61–78, DOI: 10.1007/s11157-007-9121-8.
- Kulkarni, S.J. (2015). A short review on arsenic removal from water, *International Journal of Innovative Research in Science Engineering and Technology*, 1, 1, pp. 253–256.
- Dinçer, A.R., Güneş, Y., Hancı, T.Ö., Güneş, E. & Khoei, S. (2018). Effects of Endocrine Disrupting compounds (Bisphenol A and Octyl Phenol Ethoxylate) on COD removal efficiency, *SAR Journal*, 1, 2, pp. 35–4, DOI: 10.18421/SAR12-01.
- Fan, X. & Zhang, X. (2008). Adsorption properties of activated carbon from sewage sludge to alkaline-black, *Materials Letters*, 62, 10–11, pp. 1704–1706, doi.org/10.1016/j.matlet.2007.09.085.
- Ferguson, P.L., Iden, C.R. & Brownawell, B.J. (2000). Analysis of alkylphenol ethoxylate metabolites in the aquatic environment using liquid chromatography electrospray mass spectrometry, *Analytical Chemistry*, 72, 18, pp. 4322–4330, <https://doi.org/10.1021/ac000342n>.
- Gu, H., Lin, W., Sun, S., Wu, C., Yang, F., Ziwei, Y., Chen, N., Ren, J. & Zheng, S. (2021). Calcium oxide modification and application in Cd(II) removal, *Ecotoxicology and Environmental Safety*, 209, 111760, <https://doi.org/10.1016/j.ecoenv.2020.111760>.
- Gupta, S. & Babu, B.V. (2009). Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies, *Chemical Engineering Journal*, 150, 2–3, pp. 352–365, <https://doi.org/10.1016/j.cej.2009.01.013>.
- Jain, A.K., Gupta, V.K., Bhatnagar & A., Suhas. (2003). Utilization of industrial wasteproducts as adsorbent for the removal of dyes, *Journal of Hazardous Materials*, 101, 1, pp. 31–42, [https://doi.org/10.1016/S0304-3894\(03\)00146-8](https://doi.org/10.1016/S0304-3894(03)00146-8).
- Joshi, M., Bansal, R. & Purwar, R. (2004). Colour removal from textile effluents, *Indian Journal of Fibre and Textile Research*, 29, 2, pp. 239–259.
- Khoshbouy, R., Takahashi, F. & Yoshikawa, K. (2019). Preparation of high surface area sludge based activated hydrochar via hydrothermal carbonization and application in the removal of basic dye, *Environmental Research*, 175, pp. 457–467, doi.org/10.1016/j.envres.2019.04.002.
- Li, Y., Chang, F., Huang, B., Song, Y., Zhao, H. & Wang, K. (2020). Activated carbon preparation from pyrolysis char of sewage sludge and its adsorption performance for organic compounds in sewage, *Fuel*, 266, 117053, <https://doi.org/10.1016/j.fuel.2020.117053>.
- Lonappan, L., Rouissi, T., Das, R.K., Brar, S.K., Ramirez, A.V., Verma, M., Surampalli, R.Y. & Valero, J.R. (2016). Adsorption of methylene blue on biochar microparticles derived from different waste materials, *Waste Management*, 49, pp. 537–544, doi.org/10.1016/j.wasman.2016.01.015.
- Moreira, M.T., Noya, I. & Feijoo, G. (2017). The prospective use of biochar as adsorption matrix – a review from a lifecycle perspective, *Biorescience Technology*, 246, pp. 135–141, <https://doi.org/10.1016/j.biortech.2017.08.041>.
- Namasivayam, C. & Yamuna, R.T. (1992). Removal of congo red from aqueous solutions by biogas waste slurry, *Journal of Chemical Technology and Biotechnology*, 53, 2, pp. 153–157, <https://doi.org/10.1002/jctb.280530208>.
- Nidheesh, P.V., Gandhimathi, R., Ramesh, S.T. & Singh, T.S.A. (2012). Kinetic analysis of crystal violet adsorption on to bottom ash, *Turkish Journal of Engineering and Environmental Sciences*, 36, pp. 249–262, DOI: 10.3906/muh-1110-3.
- Nimrod, A.C. & Benson, W.H. (1996). Environmental estrogenic effects of Alkylphenol ethoxylates, *Critical Reviews in Toxicology*, 26, 3, pp. 335–364, doi.org/10.3109/10408449609012527.
- Nunes A., Franca S.A. & Olievera L.S. (2009). Activated carbon from waste biomass: An alternative use for biodiesel production solid residues, *Biorescience Technology*, 100, 5, pp. 1786–1792, <https://doi.org/10.1016/j.biortech.2008.09.032>.
- Perez, M., Torrades, F., Domenech, X. & Peral, J.F. (2002). Oxidation of Textile Effluents, *Water Research*, 36, 11, pp. 2703–2710, [https://doi.org/10.1016/S0043-1354\(01\)00506-1](https://doi.org/10.1016/S0043-1354(01)00506-1).
- Ravenni, G., Gafaggi, G., Sarossy, Z., Nielsen, K.T.R., Ahrenfeldt, J. & Henriksen, U.B. (2020). Waste chars from wood gasification and wastewater sludge pyrolysis compared to commercial activated carbon for the removal of cationic and anionic dyes from aqueous solution, *Biorescience Technology Reports*, 10, 100421, doi.org/10.1016/j.biteb.2020.100421.
- Ringot, D., Lerzy, B., Chaplain, K., Bonhoure, J.P., Auclair, E. & Larondelle, Y. (2007). In vitro biosorption of ochratoxin A on the yeast industry by-products: comparison of isotherm models, *Biorescience Technology*, 98, 9, pp. 1812–1821, doi.org/10.1016/j.biortech.2006.06.015.
- Seo, J.H., Kim, N., Park, M., Lee, S., Yeon, S. & Park, D. (2020). Evaluation of metal removal performance of rod-type biosorbent prepared from sewage-sludge, *Environmental Engineering Research*, 25, 5, pp. 700–706, DOI: <https://doi.org/10.4491/eer.2019.201>.
- Sewu, D.D., Boakye, P. & Woo, S.H. (2017). Highly efficient adsorption of cationic dye by biochar produced with Korean cabbage waste, *Biorescience Technology*, 224, pp. 206–213, <https://doi.org/10.1016/j.biortech.2016.11.009>.
- Sirianuntapiboon, S. & Saengow, W. (2004). Removal of Vat Dyes from Textile Wastewater Using Biosludge, *Water Quality Research Journal*, 39, 3, pp. 276–284, doi.org/10.2166/wqrj.2004.038.
- Tan, I.A.W., Ahmad, A.L. & Hameed, B.H. (2009). Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon, *Journal of Hazardous Materials*, 164, 2–3, pp. 473–482, <https://doi.org/10.1016/j.jhazmat.2008.08.025>.
- Tsai, W.T., Lai, C.W., Su, T.Y. (2006). Adsorption of Bisphenol-A from Aqueous Solution onto Minerals and Carbon Adsorbents, *Journal of Hazardous Materials*, 134, 1–3, pp. 169–175, <https://doi.org/10.1016/j.jhazmat.2005.10.055>.
- Umar, M., Roddick, F., L.Fan. & Aziz, H.A. (2013). Application of ozone for the removal of bisphenol A from water and wastewater-A review, *Chemosphere*, 90, 8, pp. 2197–2207, <https://doi.org/10.1016/j.chemosphere.2012.09.090>.
- Vera, L.M., Bermejo, D., Uguna, M.F., Garcia, N., Flores & M., Gonzalez, E. (2019). Fixed bed column modeling of lead(II) and cadmium(II) ions biosorption on sugarcane bagasse, *Environmental Engineering Research*, 24, 1, pp. 33–37, <https://doi.org/10.4491/eer.2018.042>.
- Vijayaraghavan, K., Padmesh, T.V.N., Palanivelu, K. & Velan, M. (2006). Biosorption of nickel (II) ions onto Sargassum wightii: Application of two-parameter and three-parameter isotherm models, *Journal of Hazardous Materials*, 133, 1–3, pp. 304–308, <https://doi.org/10.1016/j.jhazmat.2005.10.016>.

- Wang, H., Lou, X., Hu, Q. & Sun, T. (2021). Adsorption of antibiotics from water by using Chinese herbal medicine residues derived biochar: Preparation and properties studies, *Journal of Molecular Liquids*, 325, 114967, <https://doi.org/10.1016/j.molliq.2020.114967>.
- Yang, X., Xu, G., Yu, H. & Zhang, Z. (2016). Preparation of ferric activated sludge based adsorbent from biological sludge for tetracycline removal, *Bioresource Technology*, 211, pp. 566–573, <https://doi.org/10.1016/j.biortech.2016.03.140>.
- Zhang, L., Pan, J., Liu, L., Song, K. & Wang, Q. (2019). Combined physical and chemical activation of sludge-based adsorbent enhances Cr(VI) removal from wastewater, *Journal of Cleaner Production*, 238, 117904, <https://doi.org/10.1016/j.jclepro.2019.117904>.