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HEAVY METAL ADSORPTION BY DEWATERED IRON-CONTAINING WASTE SLUDGE

ADSORPCJA METALI CIĘŻKICH PRZEZ ODWODNIONY OSAD ŚCIEKOWY ZAWIERAJĄCY ŻELAZO

Abstract: Drinking water treatment plants produce significant amounts of waste sludge. In this study, removal of Nickel ion by use of wastewater sludge was aimed. The adsorption capability of waste sludge was optimized with varying physical parameters such as pH, adsorbent dosage, adsorbate concentration, contact time, shaking speed and temperature. Initial concentration was set as 25 mg/dm³, adsorbent dose was set as 0.3 g/cm³, and temperature was set as 25 °C. Compliance of balance data with Langmuir, Freundlich, Temkin and D-R isotherm models was investigated. The highest R^2 values were obtained with Freundlich isotherm ($R^2 = 0.92-0.95$). Adsorption kinetics was analysed using pseudo-first order, pseudo-second order, Weber and Morris intraparticle diffusion and Elovich kinetic models, and the system was found to be in a better compliance with pseudo-second order kinetic model. Iron sludge was used as sorbent, and accordingly total iron ion measurements were carried out to determine its possible effects on water. Additionally, SEM, EDX, FTIR spectroscopy, XRD spectrum and atomic force microscope (AFM) measurements were conducted to determine the interaction between the sorbent and metal ions, in addition to characterization of the sorbent. As indicated by research results, drinking water treatment sludge proved to be a potential adsorbent for removal of nickel(II) ions from the solution.

Keywords: waste sludge, isotherm study, iron, Ni(II) ions

Introduction

Heavy metals are nonbiodegradable wastes commonly detected in industrial wastes, therefore they should be removed from water before discharge [1]. Nickel and iron are toxic heavy metals which pose serious threats for human health. Primary sources of nickel are; electroplating, iron, steel industries, electrical engineering and electronic production, chemical industry, plastic production and coal combustion. This element belongs to second grade toxicity class and it is characterized with low mutagenic and carcinogenic attributes. Main sources of this element are metallurgy, chemical, dye industry, fabric painting and textile printing [2].

Water supply systems usually comprise a water intake, purification facilities, transit pipelines, pumping stations and storage facilities [3]. Various drinking water treatment

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processes generate a vast amount of waste sludge around the worlds, which requires economically sustainable and environment-friendly ways of sludge removal methods [4]. Coagulation and flocculation are basic pre-treatment methods used for waste removal in wastewater treatment, and aluminum and iron salts are conventionally used for this purpose, for a long period [5]. Drinking water treatment sludge (DWTS) is referred to as aluminum, iron or polymeric sludge depending on the type of coagulant used in the treatment plant.

Sludge amount and composition is generally dependent on water quality, removal efficiency, as well as the type and dose of coagulant. Sludge amount is within the interval of 1-5 % of the total amount of untreated water [6]. Sludge typically consists of the suspension of inorganic and organic materials such as silica, hydrated aluminum oxide and iron oxide [7]. Water content of wet sludge is generally higher than 80 % by weight. Organic material content of dewatered sludge is around 25 % and its particle size distribution is under 100 μm [8].

Pollutant or hazardous substance content of DWTP sludge is relatively low, which allows the use of DWTP sludge as adsorbent material. Additionally, there is still limited number of studies on DWTP sludge as adsorbent material for removal of heavy metal ions [9].

Waste sludge has been subject of various studies for degradation and reuse of sludge discharge. These studies involve the recycling and reuse of coagulants [10], the use of waste sludge as coagulant in waste water treatment [11], its use as adsorbent for removal of phosphorus [12, 13], manganese [14], fluoride [15], arsenic [16, 17], boron [18], ammonium [19], Pb(II), Cr(III), Cr(VI) [20] from aqueous solutions; its use for dewatering with waste sludge [21], in brick [22] and ceramic production [23], its use in soil amendment [24, 25] and cement production [26]. Reuse of sludge can be beneficial for production of a cost-efficient adsorbent for removal of heavy metal ions, in addition to reduction of solid waste amounts generated by DWTPs.

The aim of this research is to evaluate the adsorption capacity of iron-based waterworks sludge, produced by drinking water treatment plants, during the removal of Ni(II) ion from water. During the research, various experimental parameters such as the pH of aqueous solution, contact time, initial concentration and temperature and their effect on adsorption process were analyzed. Additionally, kinetic models (pseudo first order, pseudo second order, Elovich and intraparticle diffusion models) were evaluated in terms of their effectiveness and isotherm models (Langmuir, Freundlich, Temkin and Dubinin Radushkevich) were examined to determine their applicability. Thermodynamic feasibility of adsorption process was evaluated on the basis of thermodynamic parameters (Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS)). As waste sludge with iron content was used as sorbent, total Fe ion measurements were performed to determine its effect on water.

Scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) spectrum and atomic force microscopy (AFM) analyses were applied to determine the interaction of DWTP sludge with metal ions. Sorption experiments were performed for three times and mean values of the samples were presented. The presented data are the mean values obtained from experiments, standard error ($\leq 6\%$) and error bars are shown in the figures.

Material and methods

Preparation of adsorbent

The adsorbent material was developed using the sludge generated by the sludge dewatering unit (belt press) of the drinking water treatment plant in Sivas province. In this plant, FeCl_3 is used as coagulant (800 kg/d) to remove flocculation and colloidal substances. Sludge is mainly composed of iron, iron hydroxide, clay and colloidal substances [27]. Sludge was washed with distilled water and left to drying at 105 °C for 24 hours. After cooling down at room temperature, sludge was pulverized and sieved with 1 mm mesh sieve. During the preparation stage, only analytical grade reagents of the highest quality were used in addition to deionized water.

Reagents

4.050 g nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) was used so as to obtain 1000 mg/dm³ in 1 dm³ volume, to prepare the Ni solution. Solutions with different concentrations were prepared by dilution of stock solution.

Characterization of adsorbent

FTIR spectrum was used to determine the frequency variations of functional groups in the adsorbent. The region of most interest for chemical analysis is the mid-infrared region with the wavenumber range of 4000 to 400 cm⁻¹ [28]. The spectra, measured in 400-4000 cm⁻¹ interval, are given in Figure 1. FTIR peaks represent various chemical bonds in the sample that are likely to be effective in sorption activity. The peak at 3364.61 cm⁻¹ is assigned to -OH polar groups. The bands 1416.80 cm⁻¹ are assigned to aliphatic -CH₂ units. The sorption peaks at 1633.78 cm⁻¹ are assigned to aromatic C=O and C=C vibration indicating presence of hard carbon components. The peaks around 985.96 cm⁻¹ correspond to aliphatic C-O-C and alcohol -OH representing oxygenated functional groups of cellulosic and ligneous components [29]. The band at 509.00 cm⁻¹ may correspond to SiO-H vibration [30]. The oxygen containing functional groups have been reported to have an important role related to the capacity of organic sorbents in heavy metal absorption [29]. Accordingly, it can be inferred that, the physical sorption of Ni²⁺ by DWTP sludge is related to the coulombic forces which represent the electrostatic energy arising from the interaction between the metal ions and oxygenated functional groups of the adsorbent [31].

EDX (Energy dispersive X-ray) analyses were performed for elemental analyses before and after adsorption (Fig. 2). No nickel ions were detected in EDX analyses performed prior to biosorption. Also, Ni(II) ions were detected to be adsorbed by waste sludge, after adsorption process.

SEM and AFM micrographs provide quantitative analyses. Morphological characteristics of adsorbents are commonly investigated with SEM analysis [32]. SEM micrographs of the samples are given in Figure 3. The change in the surface morphology before and after sorption can be clearly seen in the image. Prior to adsorption, sorbent surface has a rougher structure, whereas after sorption these voids are filled and the surface took on a smoother appearance. Surface roughness decreases with ion adsorption. Metal removal can be characterized with the reduced volume of specific regions and total pores after Ni(II) adsorption.

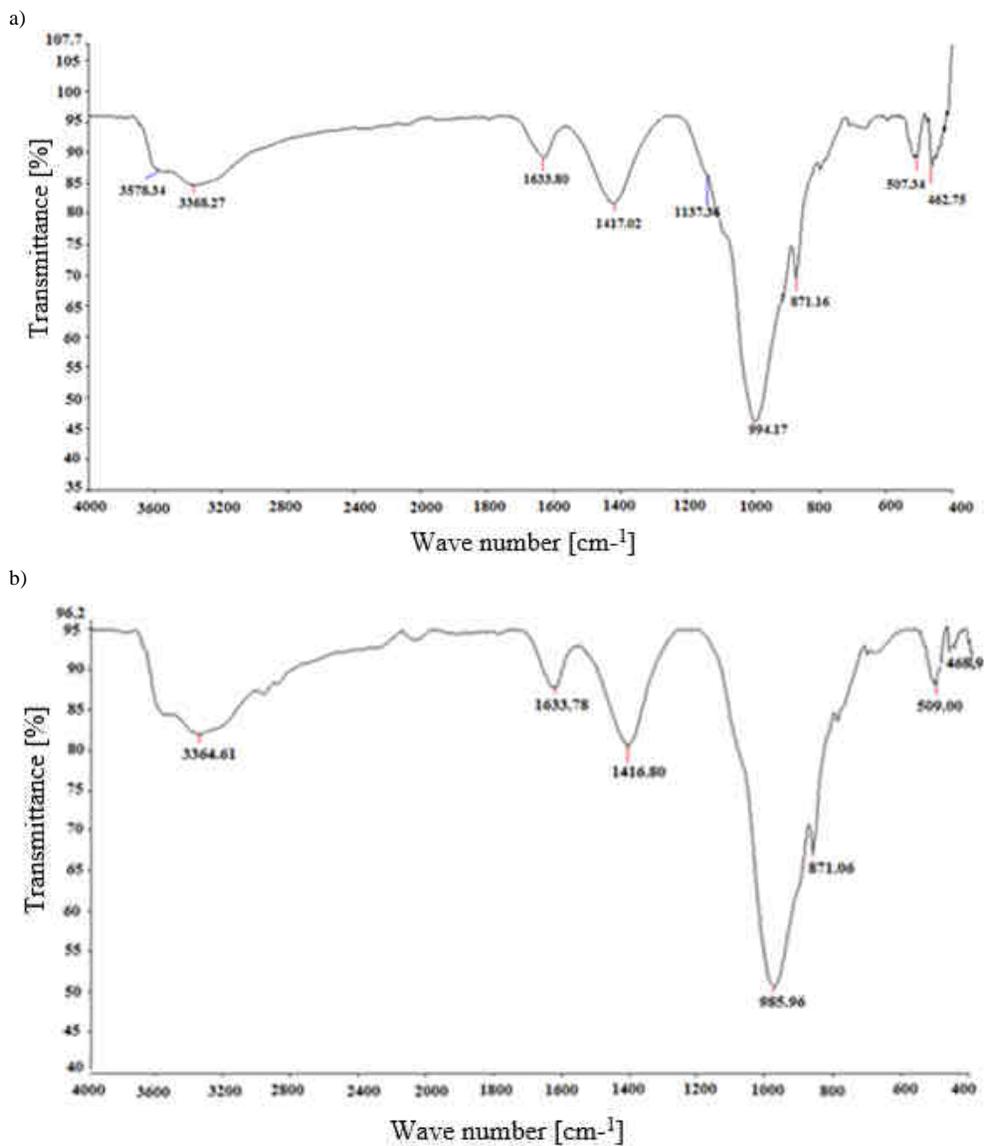
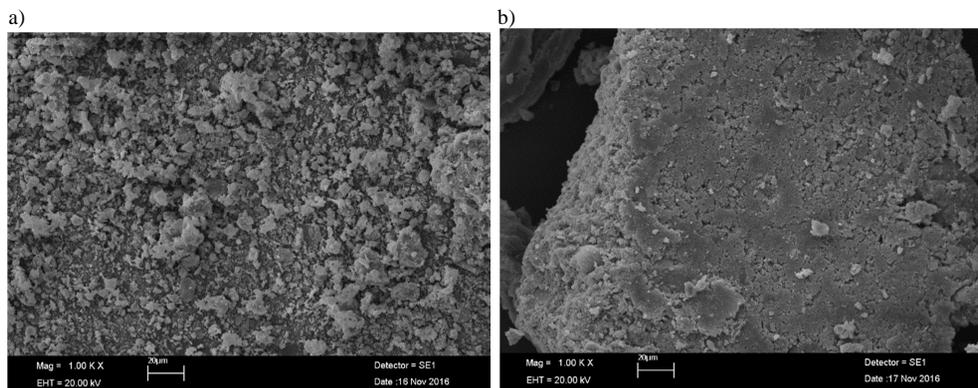
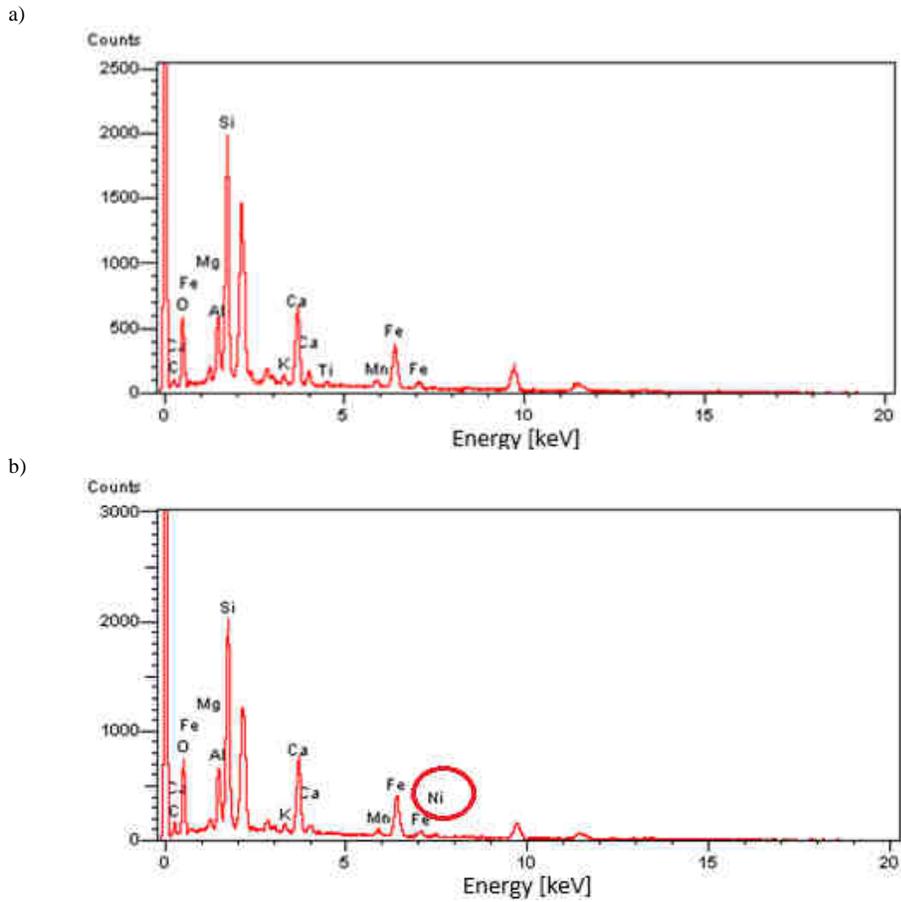


Fig. 1. FTIR spectrum: a) before and b) after adsorption



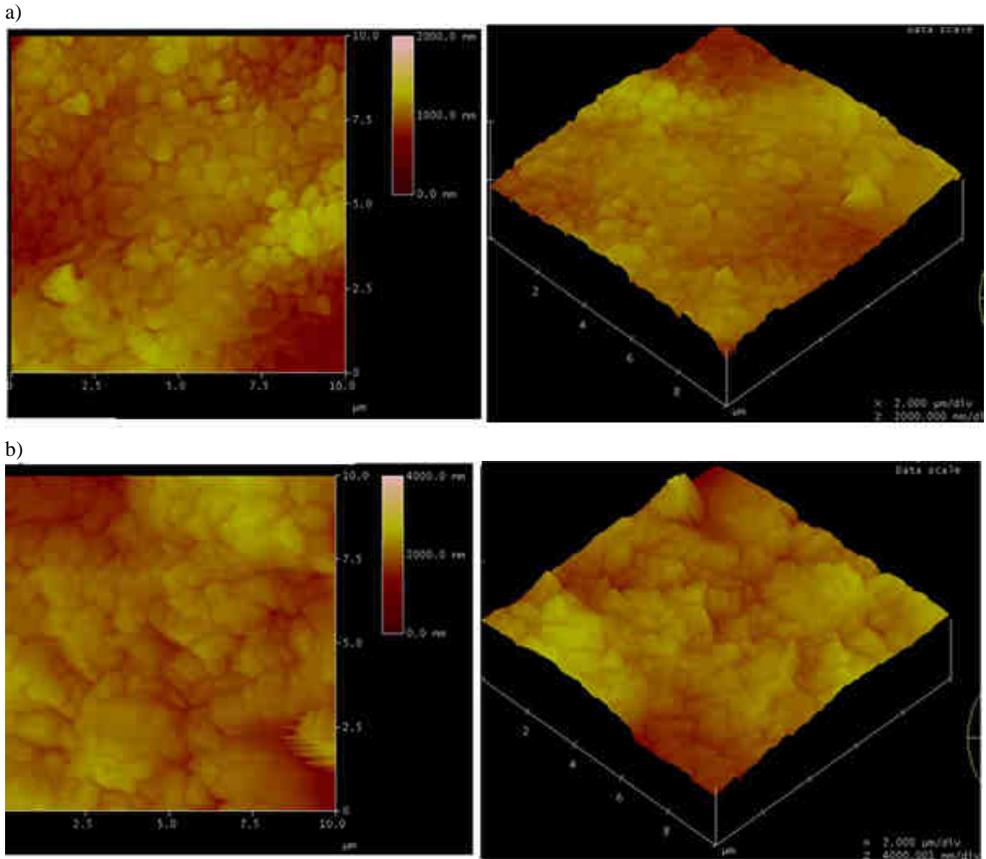


Fig. 4. AFM image of sorbent: a) before and b) after adsorption

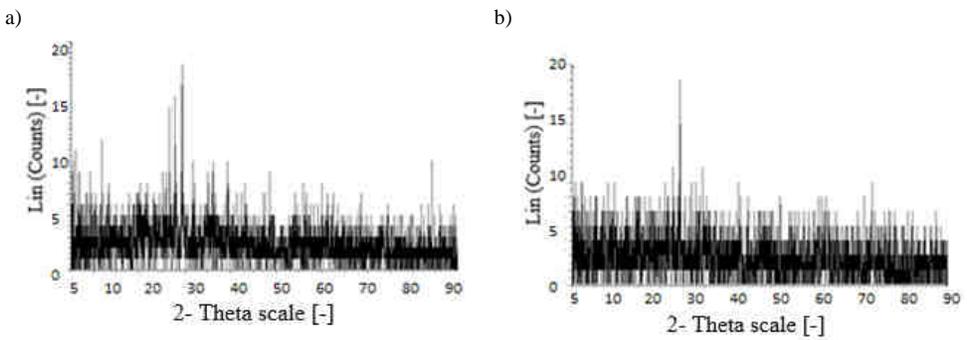


Fig. 5. XRD: a) before and b) after adsorption

Surface and cross section images of the adsorbents were taken by using AFM to determine morphological properties such as surface porosity, roughness and texture [33]. Surface characterization involves micro-porosity, roughness and macro-pores size distribution measurements using atomic force microscopy before and after adsorption (Fig. 4). In Figure 5, XRD spectrum shows the sharp peaks of DWTP sludge. Similar peaks were present before and after adsorption, which indicates sorbent underwent no structural degradation during adsorption.

Batch adsorption experiments

Batch equilibrium technique was used to remove Ni(II) ions from aqueous solution of DWTP sludge. Initial concentration of the solutions in the pH study was prepared using diluted HCl or NaOH. 100 cm³ nickel solutions were put in 250 cm³ capped vials and then adsorbents were added. The tests were carried out with a temperature-controlled rotating shaker (Wise Shake, SHO-2D) within the specified period. Afterwards samples were subjected to centrifuge and free metal ions in the samples were analyzed with Merck NOVA60 UV spectrophotometer. Measurements were made by making appropriate dilutions (measurement range 0.02-5.00 mg Ni/dm³). All pH readings were performed with Thermo Orion - STARA2145 brand pH meter.

The tests were performed at pH (3.0-7.0), with initial metal concentration (5.0-50 mg/dm³), contact time (0-24 hours) and sorbent amount (0.1-1.0 g/dm³), temperature (20-50 °C), and shaking speed (50-200 rpm). Isotherms were examined for initial concentration and the used sorbent amounts. Also, removal kinetics of Ni(II) ions was investigated for varying pH values (3-7).

Adsorption capacity q_e and removal efficiency, E [%], were calculated using equations:

$$q_e = \frac{V \cdot (C_o - C_e)}{x} \quad (1)$$

$$E = \frac{(C_o - C_e)}{C_o} \cdot 100 \% \quad (2)$$

where q_e is the bound substance concentration [mg/g]; x is the adsorbent amount [g]; V is the solution's volume [cm³]; C_o is the initial concentration [mg/dm³]; and C_e is the final concentration of the solution [mg/dm³].

Results and discussion

Contact time

Under specified conditions ($T = 25$ °C, $C_o = 25$ mg/dm³, $x = 0.3$ g, pH = 5), nickel adsorption by DWTP sludge was investigated within 0-24 hours interval. Removal efficiency by percentage and q_e are given in Figure 6. Adsorption capacity was increased with increasing contact time. Adsorption rate was initially high afterwards it slowed down and reached equilibrium after 20 hours. After equilibrium, adsorbed ion amount did not display a time-dependent change. This is mainly due to the presence of free active regions

at the beginning of adsorption process which after a while will be occupied by adsorbate that slows down the adsorption process [34].

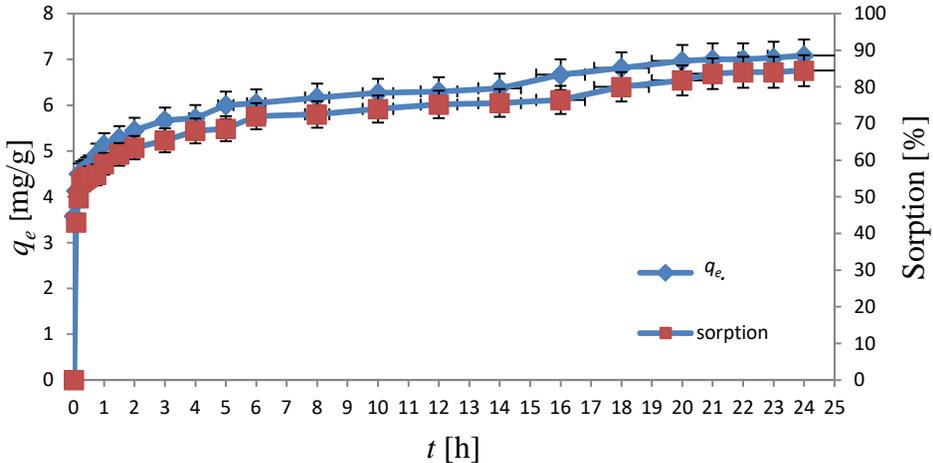


Fig. 6. Contact time

Effect of solution pH on Ni(II) adsorption

The tests were performed at pH 3-3.5-4-4.5-5-5.5-6-7 (Fig. 7a). Low pH value at the beginning of the process triggers the increase in the number of cationic adsorbent regions and results in a decrease in the number of anionic adsorption regions. This leads to an increase in the hydrogen ion concentration of the solution, thus leading to an increased rate of electrostatic repulsion.

As the pH value increases, the number of anionic adsorption regions on DWTP sludge surface which in turn results in an increase in OH^- ion concentration. Increasing electrostatic attraction force has a positive effect on the adsorption rate of nickel ions [35]. Evidently, lower pH facilitates the adsorption of ions by surface due to the presence of H^+ ions, whereas, higher pH results in a more active surface for adsorption of cations as a result of deposition of OH^- ions [36]. In this research q_e was found as 6.12 mg/g, and efficiency as 73.4 % at pH 3, whereas q_e was found as 7.22 mg/g and efficiency was found as 86.6 % at pH 7. Increasing pH resulted in increased adsorption capacity and efficiency as also supported by other studies [37-39].

Following the adsorption process, total Fe ($\text{Fe}^{2+} + \text{Fe}^{3+}$) measurements were performed to detect the iron sludge's possible effects on water. An increase in the released amount of Fe was observed with increasing pH. Total Fe amount was found as 0.4 mg/dm^3 at pH 3, whereas it was found as 0.9 mg/dm^3 at pH 7 (Fig. 7b).

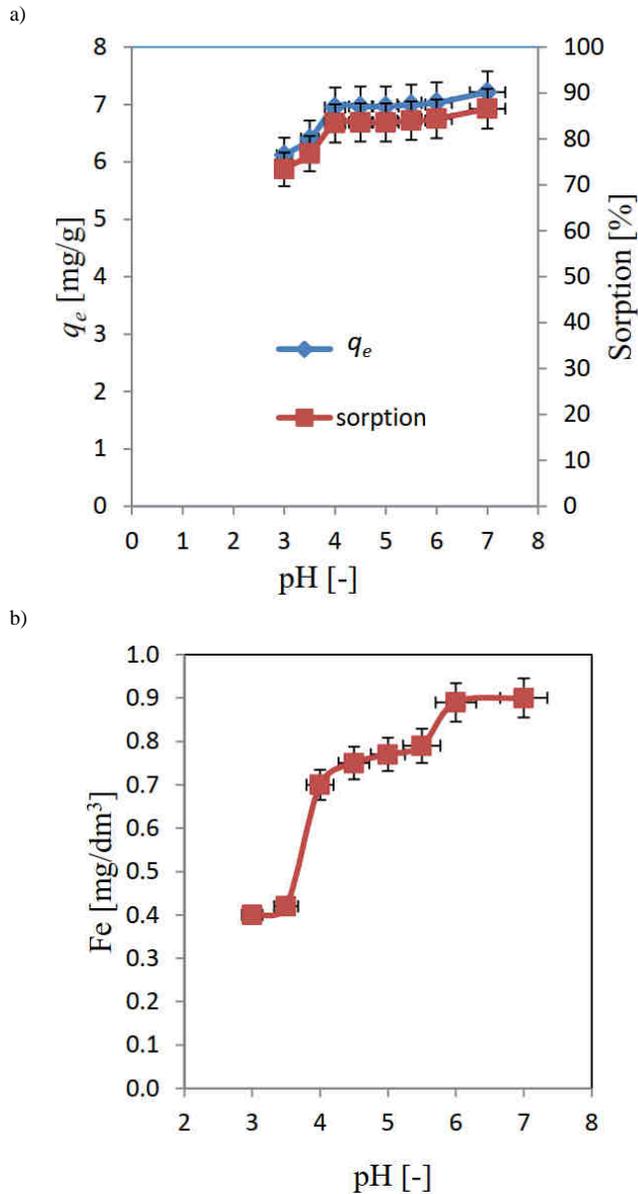


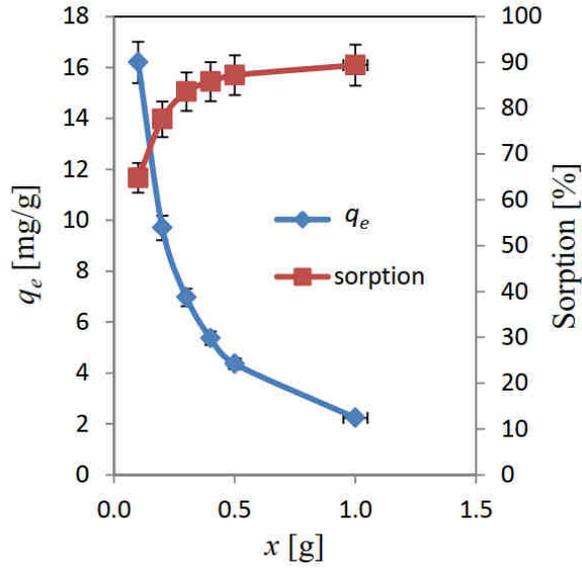
Fig. 7. Dependence: a) q_e , b) Fe amount on pH

Effect of adsorbent dose on Ni(II) adsorption

Analyses were performed within 0.1-1 g/cm³ interval to examine the change in adsorption efficiency depending on sorbent amount (Fig. 8a). The highest q_e value (16.20 mg/g) was obtained with use of 0.1 g sorbent resulting with 64.8 % efficiency. The highest efficiency was found as 89.4 % for 1 g sorbent and q_e was 2.24 mg/g, which is

consistent with previous studies [40, 41]. The reduction in adsorption capacity with increasing adsorbent dosage is mainly ascribed to the increase in unsaturated adsorption sites throughout the adsorption reaction. This also attributable to particle interactions such accumulation arising from high sorbent concentration. Such accumulations lead to lead to a decrease in total active surface regions of the adsorbent [34].

a)



b)

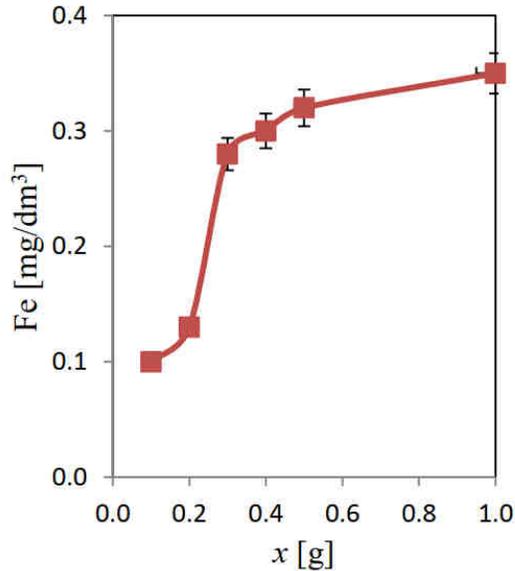
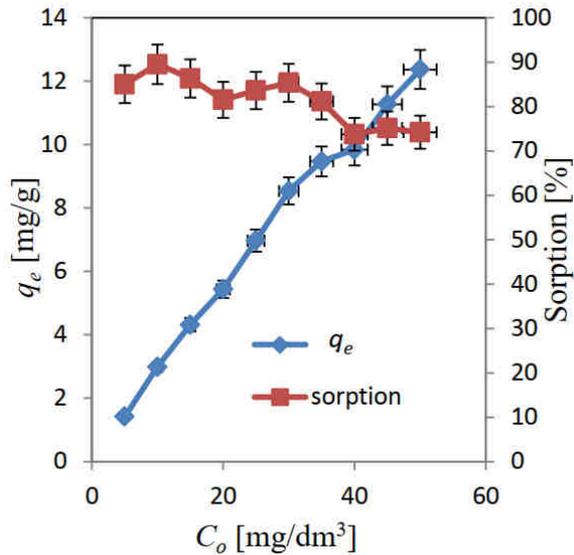


Fig. 8. Dependence: a) q_e , b) Fe amount on sorbent amount

The increase in the amount of used sorbent and the change in Fe amount are shown in Figure 8b. An increase was observed in Fe amount depending on the sorbent amount. 0.1 mg Fe/dm³ was measured when 0.1 g sorbent was used, and 0.35 mg Fe/dm³ was measured when 1 g sorbent was used.

Effect of initial concentration on Ni(II) adsorption

a)



b)

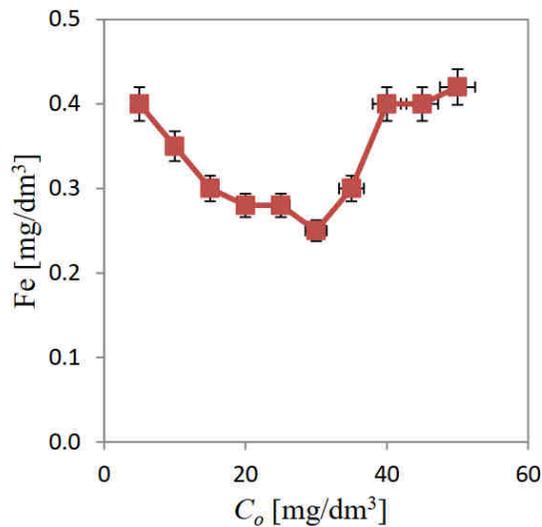


Fig. 9. Dependence: a) q_e , b) Fe amount on concentration of Ni(II)

Initial concentration varied between 5-50 mg/dm³ during the study (Fig. 9). Higher initial concentrations increase the availability of nickel molecules, thus increasing the possibility to collide with sorbent surfaces [42]. Accordingly, efficiency increases increasing concentration [43, 44]. The highest q_e value was measured as 12.37 mg/g for 50 mg/dm³ Ni(II) concentration, whereas the lowest value was measured as 1.42 mg/g for 5 mg/dm³ Ni(II) concentration. Initial concentration was observed to have no significant effect on the released amount of Fe ions (Fig. 9b).

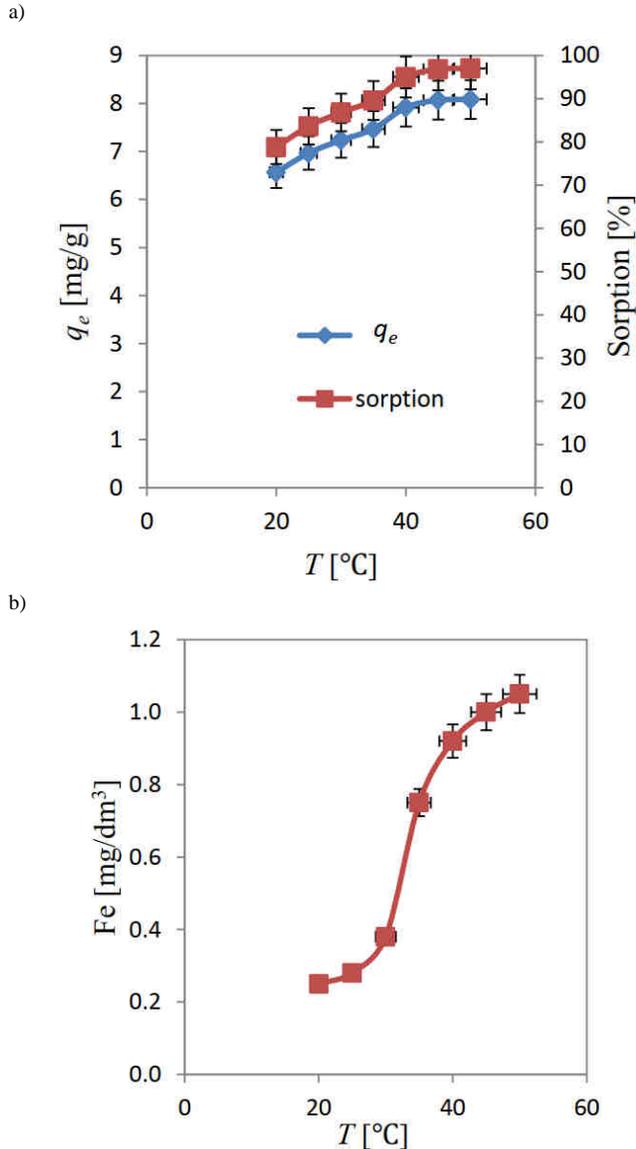


Fig. 10. Dependence: a) q_e , b) Fe amount on temperature of ambient

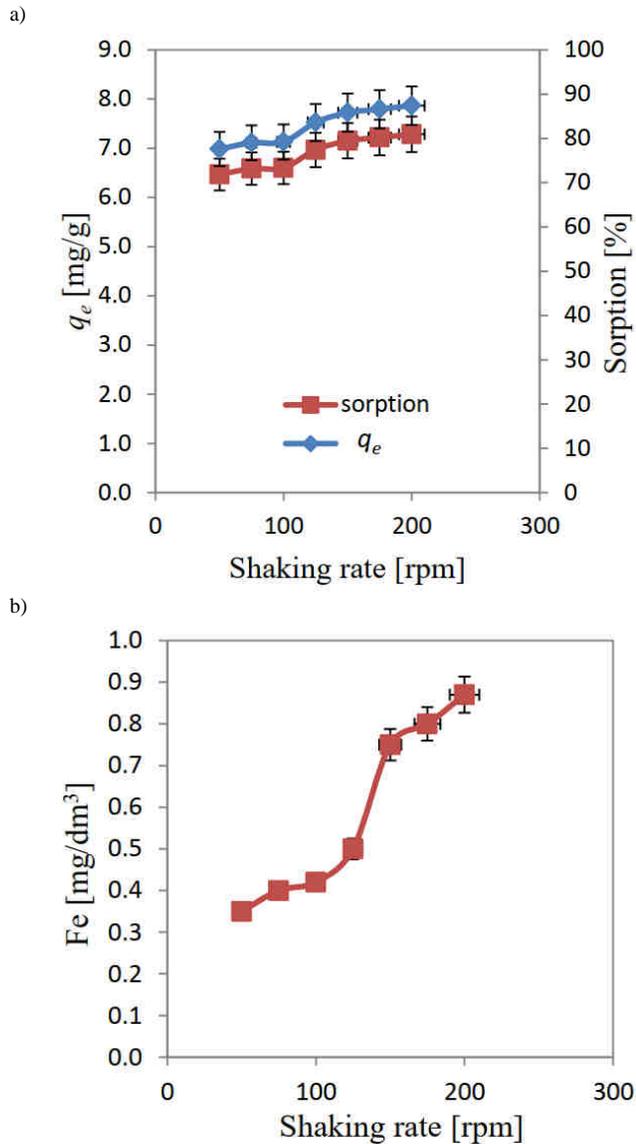


Fig. 11. Dependence: a) q_e , b) Fe amount on shaking rate

Effect of temperature on Ni(II) adsorption

The effect of temperature on adsorption was examined at 20-50 °C and the results are shown in Figure 10. As indicated in the Figure, adsorption capacity increased with increasing temperature. The process is considered to be exothermic. An increase in Fe amount is also observed with increasing temperature (Fig. 10b). The increase in sorbent

amount at higher temperatures occurs as a result of increased impact frequency between sorbent and solute, which results in an increase sorption rate on sludge surface [45].

To adsorb a cation on sorbent surface; cation must be released by the surrounding water molecules. System requires additional energy for removal of these water molecules. If this energy exceeds the amount released after the binding of cation onto the sorbent, then overall sorption process is endothermic [46].

Effect of shaking rate on Ni(II) adsorption

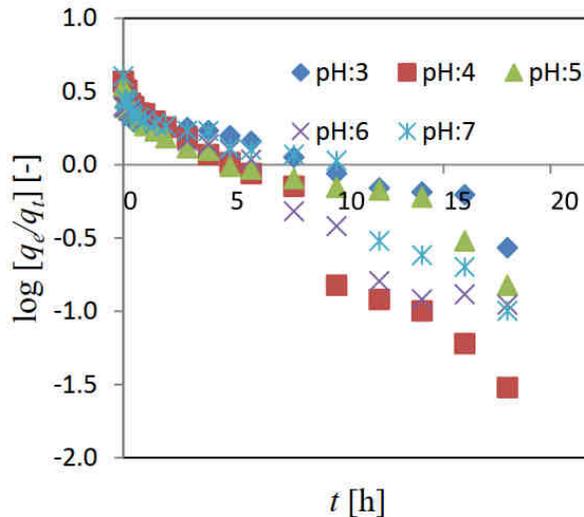
Determination of the optimum shaking speed in wastewater treatment is crucial due to the energy consumption of this process and its effect on adsorption efficiency. The change in sorption efficiency related to the shaking speed is given in Figure 11a, and the change in Fe amount is given in Figure 11b. q_e is 6.47 mg/dm^3 and efficiency is 77.6 % at 50 rpm, whereas, q_e is 7.28 mg/dm^3 and efficiency is 87.4 % at 200 rpm. Fe amount is 0.35 mg/dm^3 at 50 rpm and 0.87 at 200 rpm. Such effect is attributable to the decrease in boundary layer thickness surrounding adsorbent particles as a result of increased shaking speed. External mass transfer rate of metals increases as a result of increasing heavy metal diffusion into the boundary layer between adsorbent particles and surrounding solution arising from increased shaking speed [47].

Models

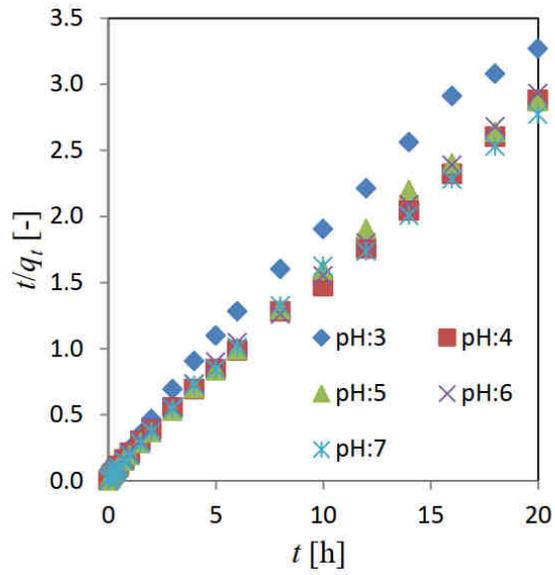
Kinetic modeling

Kinetic tests were carried out at pH 3-4-5-6-7 for 0-20 hours. Pseudo-first order (Fig. 12a), pseudo-second order kinetic models (Fig. 12b), Weber and Morris model (Fig. 12c) and Elovich model (Fig. 12d) were applied on the obtained kinetic modeling results. The calculated kinetic constants are given in Table 1.

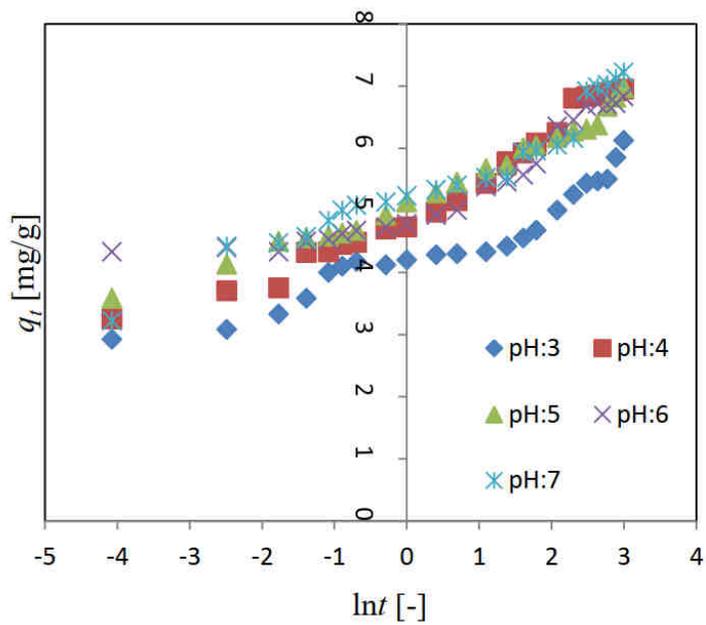
a)



b)



c)



d)

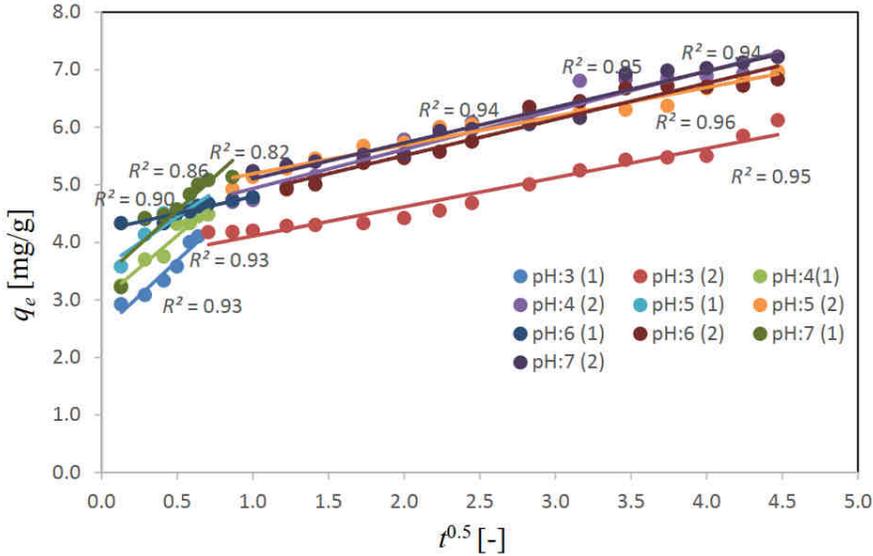


Fig. 12. Graphs of: a) pseudo-first order, b) pseudo-second order, c) Elovich and d) Weber-Morris kinetic models

Table 1

Kinetic constant for adsorption

pH	q_{exp} [mg/g]	Pseudo-first order			Pseudo-second order			Weber-Morris					
		k_f	q_e	R^2	k_s	q_e	R^2	- I -			-II-		
							k_{id}	C	R^2	k_{id}	C	R^2	
3	6.12	0.014	1.30	0.90	0.305	5.83	0.99	2.434	2.465	0.93	0.507	3.605	0.95
4	6.95	0.008	1.00	0.97	0.315	7.02	0.99	0.243	2.994	0.93	0.680	4.255	0.94
5	6.97	0.014	1.74	0.99	0.340	6.78	0.99	0.792	3.541	0.86	0.498	4.494	0.95
6	7.03	0.015	3.15	0.96	0.283	6.99	0.99	0.585	4.21	0.90	0.629	4.250	0.94
7	7.22	0.025	3.02	0.97	0.284	7.14	0.99	2.739	4.362	0.82	0.621	4.483	0.95
		Elovich											
		β	a	R^2									
3	6.12	2.387	181	0.90									
4	6.95	1.685	48.6	0.95									
5	6.97	2.110	476	0.97									
6	7.03	1.297	1071	0.84									
7	7.22	1.967	290	0.93									

Pseudo-first order model

Lagergren [48] reported that the adsorption of pollutants on the adsorbent complies to a pseudo-first order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \tag{3}$$

where q_e and q_t are the sorption capacity [mg/g] of adsorbent at equilibrium, and time t [min], respectively, and k_f is the pseudo-first-order sorption rate constant [s^{-1}].

Pseudo-second order model

Ho and McKay [49] introduced the pseudo-second order kinetic model for sorption as given below:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_s is the pseudo-second order sorption rate constant [$g/(mg\ s)$]; at $t = 0$, $k_s q_e^2$ is adsorption rate which is thus termed as initial sorption rate, h [$mg/(g\ s)$].

As indicated in Table 1, the highest R^2 values (0.99) are obtained with pseudo-second order model. Also, when compared with pseudo-first order model, the theoretical q_e models yielded by this model were found to be closer to experimental q_e values. Consequently, adsorption process was found to be in compliance with pseudo-second order kinetic model. Similar kinetic behaviours were also reported in previous studies [33, 34, 50].

Weber and Morris model (Intraparticle diffusion)

Intraparticle diffusion model was tested to determine the diffusion mechanisms and rate limiting steps in adsorption process. The theory of the model was introduced by Weber and Morris (Eq. (5)) [51]:

$$q = k_{id} t^{0.5} + C \quad (5)$$

In this model, k_{id} [$mg\ g^{-1}\ min^{1/2}$] denotes the intraparticle diffusion rate constant which is affected by temperature and particle diameter, while C is the intercept value that gives an estimated thickness of the boundary layer, i.e. the larger is the intercept, the greater is the boundary effect.

As shown in Figure 12d, nickel adsorption does not intercept with origin for all pH values and it occurs in two steps. The rate constants for the two resulting steps were $k_{id1} > k_{id2}$ for pH 3-5-7 and $k_{id2} > k_{id1}$ for pH 4-6 and C values for each step increase with increasing pH value. This is indicative of the increase in boundary layer thickness with increasing pH, and the consequent decrease in diffusion rate [52].

Elovich model

Elovich's equation has been widely applied to define adsorption of gases on solid materials. This equation is also used to define heavy metal adsorption in aqueous solutions. The model defines the kinetics of chemical adsorption process using the following equation [53]:

$$q_t = \frac{1}{\beta_e} \ln(\alpha\beta_e) + \frac{1}{\beta_e} \ln t \quad (6)$$

where α is the initial rate [mg/g min] as (d_{qt}/d_t) converges to β_e when q_t converges to zero, and the parameter β_e relates to extent of activation energy and surface coverage for chemisorptions [g/mg].

High correlation coefficients were obtained for all pH values in Elovich kinetic model (Table 1). Similar results were also reported in previous studies [54, 55]. This is indicative of the higher significance of limited diffusion rate in Ni(II) adsorption with DWTP sludge. According to the results, the rate can be increased but increasing the adsorption temperature. This tendency regarding β_e is consistent with those in conventionally activated chemical adsorption systems that indicates that β_e relates to the regions available for absorption.

Reportedly, Ni(II) adsorption on DWTP sludge may involve valance forces through electron share or exchange between adsorbent and adsorbate [56]. This may correspond to exchangeable H⁺ ions and OH groups available in DWTP sludge. Accordingly, ion exchange mechanism plays a major role in the adsorption process. The literature reports countless studies on heavy metal removal from waters and effluents, including chemical precipitation, such as ion exchange and adsorption. Studies of many authors indicate that the ion exchange process is one of the main mechanisms of sorption of heavy metals [57-61].

Equilibrium modeling

Adsorption isotherm gives an estimation of how adsorption molecules are distributed among liquid and solid phases when adsorption process reaches equilibrium. The data obtained from the tests performed with different Ni(II) concentrations (C_o) and sorbent dosages (x) were used in Langmuir, Freundlich, Temkin and D-R (Dubinin-Radushkevich) models. Isotherm parameters for adsorption process are given in Table 2.

Table 2

Adsorption isotherm parameters

Model	Isotherm parameters		
		C_o [mg/dm ³]	x [g]
Langmuir	R^2	0.90	0.92
	K_a [dm ³ /mg]	6.90	2.62
	Q_{max} [mg/g]	2.63	0.22
	R_L	0.005	0.015
Freundlich	R^2	0.92	0.95
	K_F [dm ³ /g]	2.41	9.95
	n	1.48	3.72
Temkin	R^2	0.86	0.93
	A [dm ³ /g]	1.07	0.05
	B	3.81	-1.33
D-R	R^2	0.89	0.63
	β [mol ² /J ²]	-0.40	1.61
	q_{max} [mg/g]	9.19	0.99
	E_{ads} [kJ/mol]	1.107	0.39

Langmuir isotherm

Langmuir model assumes that adsorbates are present on specific homogeneous regions on adsorbents and this model is successfully used in various monolayer adsorption processes [62]. The nonlinear form of Langmuir isotherm model is defined with the following equation [63]:

$$q_e = \frac{Q_{max} \cdot K_a \cdot C_e}{1 + K_a \cdot C_e} \quad (7)$$

where Q_{max} denotes the maximum adsorbate uptake at equilibrium state, C_e is the adsorbate concentration at equilibrium and K_a is the coefficient for the affinity between the adsorbate and adsorbant.

The main characteristic of Langmuir isotherm is its provability with the dimensionless equilibrium constant termed R_L :

$$R_L = \frac{1}{1 + K_a \cdot C_o} \quad (8)$$

where C_o is the initial Ni(II) concentration. R_L values indicate whether the isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [64]. In this study, R_L values were found between zero and one, which indicates that, Langmuir isotherm is suitable for use in Ni(II) adsorption with DWTP sludge.

Freundlich isotherm

Freundlich isotherm applies for both monolayer (chemical adsorption) and multilayer adsorption (physical adsorption) and it is based on the assumption that adsorbent adsorbate is adsorbed on the heterogeneous surface of the adsorbent [65]. Freundlich equation is given:

$$q_e = k \cdot C_e^{\frac{1}{n}} \quad (9)$$

where k is the adsorption capacity and “ n ” is the Freundlich constant related to the intensity of adsorption. There is a positive correlation between the magnitude of “ n ” and adsorption intensity. In general “ n ” values in 2-10 interval indicate good adsorption, values between 1-2 indicate limited adsorption and values lower than 1 indicate weak adsorption characteristic [66]. In this study “ n ” was found as 1.48 for C_o and as 3.723 for x . Also the highest R^2 values were found at Freundlich isotherm. It is reported in various other researches that Freundlich is the best isotherm for adsorption process [67, 68].

Dubinin-Radushkevich (D-R) isotherm

The D-R isotherm was developed to explain the effect of the porous structure of a sorbent on adsorption [69]. The model can also be applied to define whether a Ni(II) adsorption process is physical or chemical in nature. The linearised D-R isotherm is defined as below:

$$\ln q_e = \ln q_{max} - \beta \cdot \varepsilon^2 \quad (10)$$

where β is the constant related with adsorption average free energy per 1 mole of adsorbed material [mol^2/J^2], q_e is the adsorbed amount at equilibrium [mol/g], q_{max} is the theoretical

saturation capacity [mol/g] and ε is Polanyi potential [kJ/mol] calculated with the following equation:

$$\varepsilon = R \cdot T \cdot \ln \left(1 + \frac{1}{C_e} \right) \quad (11)$$

In the equation; R denotes the universal gas constant $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ and T is the absolute temperature [K]. The graph of $\ln q_e$ values versus ε^2 values yields a line with slope $-\beta$ and intercept $\ln q_{max}$. β gives an estimation of the average free energy of adsorption per one molecule of adsorbed material. The relationship between these values is defined in equation [70]:

$$E_{ads} = \frac{1}{\sqrt{2\beta}} \quad (12)$$

This parameter gives an idea as to which of the chemical ion or physical adsorption mechanisms is effective. Average adsorption energy, E_{ads} , values between 8-16 kJ/mol indicate chemical ion exchange, and values lower than 8 kJ/mol indicate physical adsorption mechanism [71]. In this study, sorption mechanism can be associated with physical interactions as E values are found to be lower than 8 kJ/mol.

Temkin isotherm

Temkin isotherm assumes that, the heat from adsorption of all molecules in the layer displays a linear decrease with the coverage of molecules, and the adsorption process is uniformly distributed due to the adsorbate - adsorbate repulsions. Temkin isotherm is defined by equation [72]:

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (13)$$

where B_T relates to the adsorption heat and A_T is the equilibrium binding constant. B_T and A_T can be estimated via a plot of q_e versus $\ln C_e$. In this research, high R^2 values were obtained particularly for varying C_o value (0.93).

Thermodynamic parameters

Thermodynamic parameters for adsorption such as Gibbs free energy change (ΔG^0 , [J/mol]), enthalpy change (ΔH^0 , [J/mol]) and entropy change (ΔS^0 , [J/mol K]) can be estimated using the following equations [73]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (14)$$

$$\ln K_c = \frac{\Delta G^0}{R} + \frac{\Delta H^0}{RT} \quad (15)$$

where R is the universal gas constant, K_c is adsorption equilibrium constant and T is absolute temperature [K]. The Gibbs free energy value of an adsorption process at a given temperature can be calculated with K_c via the equation: $\Delta G^0 = -RT \ln K_c$.

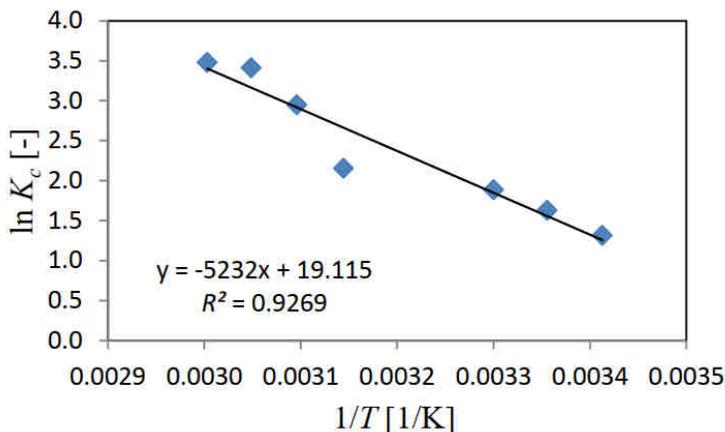


Fig. 13. Van t'Hoff graph

$\ln K_c - 1/T$ (Van t'Hoff) graph obtained for varying temperatures is given in Figure 13 and the thermodynamic parameters are given in Table 3. According to the results, ΔG^0 value is negative at varying temperature intervals. Negative Gibbs free energy values for all temperatures verify the spontaneous nature and applicability of biosorption process [74]. Also the decrease in the negative value of ΔG^0 with increasing temperature indicates that, adsorption process is facilitated at higher temperatures. The result is consistent with the temperature effect on the dynamics.

Table 3

Thermodynamic parameters

T [K]	b [dm ³ /g]	ΔG^0 [kJ/(K·mol)]	ΔH^0 [kJ/(K·mol)]	ΔS^0 [kJ/(K·mol)]
293	1.24	-3.20		
298	1.70	-4.04		
303	2.19	-4.74	-43.49	158.92
308	2.87	-5.51		
313	6.33	-7.66		
318	10.08	-9.01		
323	10.78	-9.33		

Negative ΔH^0 values are indicative of an exothermic adsorption process, and positive values indicate an endothermic process. Negative ΔG^0 and ΔH^0 values were also reported in other studies [41, 75].

The positive value of ΔS^0 indicates some changes in the adsorbent and adsorbate structures, and increased adsorption rates also lead to increased disorder or randomness of the entire system. The obtained thermodynamic parameters show that, DWTP sludge can be used as an efficient adsorbent for Ni(II) removal from aqueous solution.

The studies in the literature on adsorption related with Ni(II) ions were examined and compared with the values obtained in the present study (Table 4).

Table 4

Comparison of adsorption capacity of the present system with other studies

Adsorbent	Adsorption capacity [mg/g]	Reference
Bamboo powder	32.57	[76]
Coconut shells	83.16	[77]
Rice hull	5.02	[78]
Modified mangrove barks	4.78	[79]
Sargassum ilicifolium	1.85-1.425	[80]
Zeolite	1.98	[81]
Bentonite	19.92	[55]
Montmorillonite	28.4	[82]
Montmorillonite	21.1	[83]
Vermiculite	0.229	[84]
Coal fly ash prepared zeolite	8.96	[85]
DWTP sludge	6.97	This study

Conclusions

The adsorption by DWTP sludge proved to be effective in removal of nickel ions from water. Comprehensive researches have been performed to evaluate the effect of different parameters on adsorption. Adsorbate amount, solution's pH, metal concentration and temperature are among these parameters which are reported to be effective on adsorption. In various studies, pseudo first order and pseudo second order kinetics have been used to model adsorption kinetics. In these studies, pseudo second order kinetic model was found to yield more accurate results as in the case of this research. The rate constants in the intra-particle diffusion model varied as $k_{id1} > k_{id2}$, and C values at each step increased with increasing pH. In terms of equilibrium, Langmuir isotherm proved to be suitable for Ni(II) adsorption with DWTP sludge, whereas the results from Freundlich model were also consistent with experimental data in several situations. Isotherms other than Temkin and DR models were also successfully applied in other researches to estimate the adsorption equilibrium. In this research, the E values lower than 8 kJ/mol in DR model led to the assumption that sorption mechanism is based on physical interactions. Also, the conducted thermodynamic study yielded a negative ΔG^0 value, which verifies the spontaneity and applicability of the biosorption process. The obtained thermodynamic parameters showed that DWTP sludge can be used as an efficient adsorbent in removal of Ni(II).

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