



Removal of Fe⁺⁺ from Wastewater Using Sludge-polymer Hybrid Adsorbents

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1. Introduction

There are many problems related to existing of heavy metals in wastewater due to their high toxicity and impact on human and aquatic life, even after treatment by conventional methods. Several techniques have been developed and used to remove and/or recover a wide range of micropollutants from water and a variety of industrial effluents (Fu and Wang 2011, Gros et al. 2008, Abdel-Aziz et al. 2014). The success of a treatment method depends mainly on its efficiency and economic point of view.

Being produced in a large volume and facing problems in finding accepted disposal routes, sewage sludge has received great attention recently (Cieřlik et al., 2015). Several researches were conducted on re-use of sewage sludge include but not limited to land applications, filtration material, light concrete, brick, pavement applications, fertilizers, etc. (Smol et al. 2015, Bourrioug et al. 2015, Wu et al. 2015, Lucena et al. 2014, Chen et al. 2013).

Rapid increasing in sewage sludge production in recent decades should be taken into consideration for more efficient utilization and environmental impact sustainability. One of the important utilizations is gen-

erating adsorbents from sewage sludge where variant activation methods of sludge were investigated by many researchers to obtain carbon-bearing adsorbents (Yu and Zhong 2006, Andrey et al. 2001, Xiaoge et al. 2002, Smith et al. 2009). High carbon contents in sewage sludge and low cost production of adsorbents based on sludge make it promising adsorbents in heavy metals and organics removal and also the applicability of obtaining carbon high surface area gives the sludge materials superior properties as adsorbents used to remove pollutants from waste water (Smith et al. 2009, Martin et al. 2004). The ash of sewage sludge can be used in field of heavy metals removal from wastewater because it has nearly same chemical composition as fly ash (Otero et al. 2003, Huasong and Zhongyan 1999).

Various techniques have been used to produce sewage sludge based adsorbents, the methods such as (i) pyrolysis of dried sewage sludge; (ii) chemical activation of dried sewage sludge with ZnCl₂ followed by pyrolysis (Rozada et al. 2008); (iii) microwave heating technology as a cost effective alternative way to produce carbonaceous adsorbents from sewage sludge (Lin et al. 2012). The surface area and pore volume of the adsorbent were highly depends on the method of preparation.

The sludge based adsorbent can find several applications in waste water treatment such as removal of toxic metals ions (Seredych and Badosz 2006, Pan et al. 2003, Zhai et al. 2004, Sprynsky 2009), removal of organic pollutants (Pan et al. 2011, Anfruns et al. 2011), removal of dyes (Wang et al. 2008, Kargi and Ozmihc 2005, Crini 2006), etc. The aim of the present work is to study the removal of Fe⁺⁺ from industrial wastewater by using sludge-polymer hybrid adsorbents as low cost and more efficient adsorbent material. To this end PVDF nonreactive polymer (Polyvinylidene fluoride) as an auxiliary adsorbent was mixed with the sludge in different mass ratios. Polyvinylidene fluoride (PVDF) is a polymer with increasing scientific attention and industrial importance because of its durability and biocompatibility and high chemical resistance to many acids and alkalis (Xu et al. 2005, Yeow et al. 2005). The study was conducted by using synthetic wastewater samples containing Fe⁺⁺ in the form of FeSO₄ with different initial concentrations. Presence of Fe⁺⁺ in wastewater is an important issue for some industries such as steel production, galvanization of steel, metal finishing, and mining processes. The adsorbent performance was evaluated by measuring the

change in Fe^{++} concentration in the solution at different time intervals. Experimental data were modeled by using the linear form of Freundlich isotherm equation. The model is important for operational design and applicable practice of the adsorption systems.

2. Experimental section

2.1. Materials

Raw sewage sludge has been collected from the final disposal area. Sludge was ground and thermally treated at three different temperatures, 200, 400, and 600°C. Following previous studies the maximum temperature was limited at 600°C because a higher temperature (above 600°C) gave rise to a detrimental impact on the quality of sludge-based adsorbents, in terms of specific surface area, total pore volume and iodine value.

PVDF polymer (M.wt = 400000) was mixed with the treated sludge at different mass ratios to study the removal efficiency of Fe^{++} . All chemical reagents such as FeSO_4 , HCl, NaOH were in analytical grade. Stock solution was prepared by dissolving FeSO_4 in distilled water. Three different initial concentrations of Fe^{++} were prepared by dilution of the stock solution namely; 50, 100 and 150 ppm. Initial pH of the solution was fixed at 5 by adding either HCl or NaOH. All experiments were conducted at a temperature $25 \pm 1^\circ\text{C}$.

2.2. Apparatus and analysis

A lab scale standard jar test apparatus (Fig. 1) was used to conduct the experiments. It consists mainly of six impellers mounted on stainless steel shafts, variable speed motor and six graduated cylinders of 1 L capacity. The impeller is two 90° turbine blades of 5 cm diameter and 2 cm height. The impeller rotation speed was ranged from 0 to 200 rpm. During all experiments the rotational speed was maintained at 200 rpm.

Surface morphology of thermally treated sludge particles was carried out using JEOL JSM 6490A scanning electron microscope. Images were obtained by secondary electrons at 20 kV, to study micro-structure of treated sludge particles at 200, 400 and 600°C. Samples were sputter coated with monolayers of gold to enhance the electrical conductivity of sludge particles. Chemical structure was investigated using Fourier Transform Infrared (FT-IR). This analysis was performed using Brukers

Alpha FT-IR (Platinum ATR module). HACH DR/3900 spectrophotometer was used for quantitative determination of Fe^{++} using Phenanthroline method.

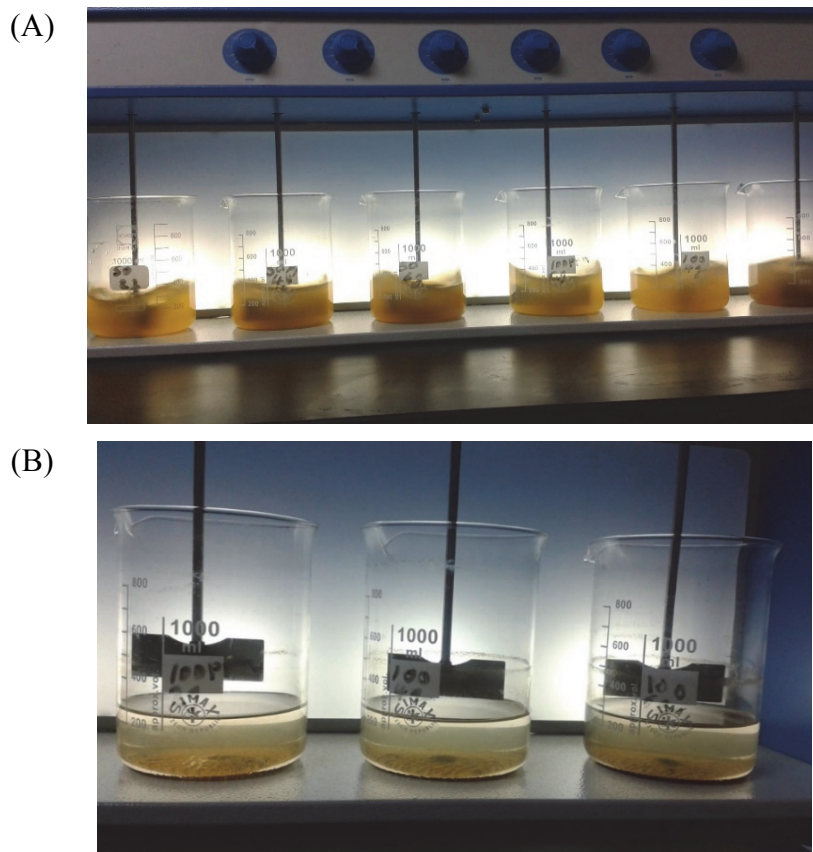


Fig. 1. Experimental apparatus (A: before treatment; B: after treatment)

Rys. 1. Urządzenie doświadczalne (A: przed procesem; B: po procesie)

Figure 2 shows different sequence of steps involved in carrying out the present work including sludge treatment, operating conditions and effluent analysis

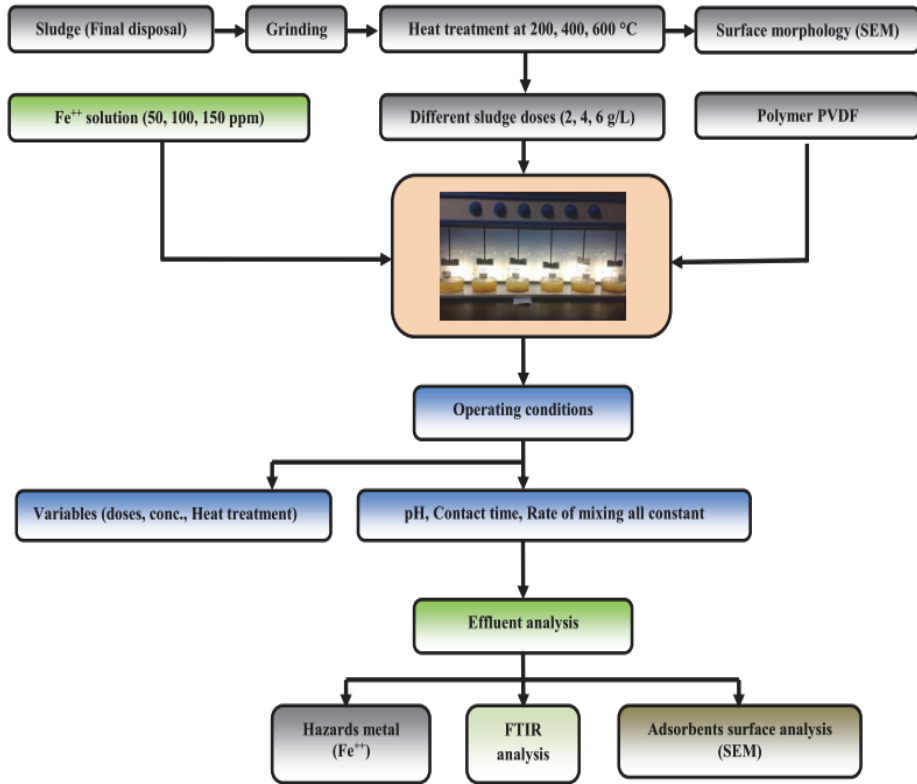


Fig. 2. Flow diagram outlining the different steps of the experimental work
Rys. 2. Schemat przedstawiający poszczególne etapy prac doświadczalnych

3. Results and discussion

Removal of Fe^{++} from aqueous solution was studied under different conditions such as contact time, initial concentration of Fe^{++} , adsorbent dose, sludge heat treatment, and polymer/sludge ratio.

The % removal of Cu^{+2} was calculated by using the equation:

$$\% \text{ removal} = \left(\frac{C_o - C}{C_o} \right) \times 100 \quad (1)$$

where C_o and C are initial and final concentrations of Fe^{++} respectively.

To study the effect of contact time on the removal efficacy of Fe^{++} at different initial concentrations, samples of the solutions were analyzed at different time intervals. The experimental results showed that the

rate of removal was rapid at initial stages where all active sites on the adsorbent surface were vacant and solute concentration gradient was high. On increasing contact time the rate of removal decreased gradually. This can be ascribed to the decrease in the driving force between the bulk of the solution and the liquid-adsorbent interface. The optimum contact time was 30 minutes.

Figure 3 shows the effect of initial concentration of Fe^{++} on the % removal at different adsorbent doses. The % removal of Fe^{++} increases with increasing initial concentration of Fe^{++} passes through maximum at 100 ppm and then decreases.

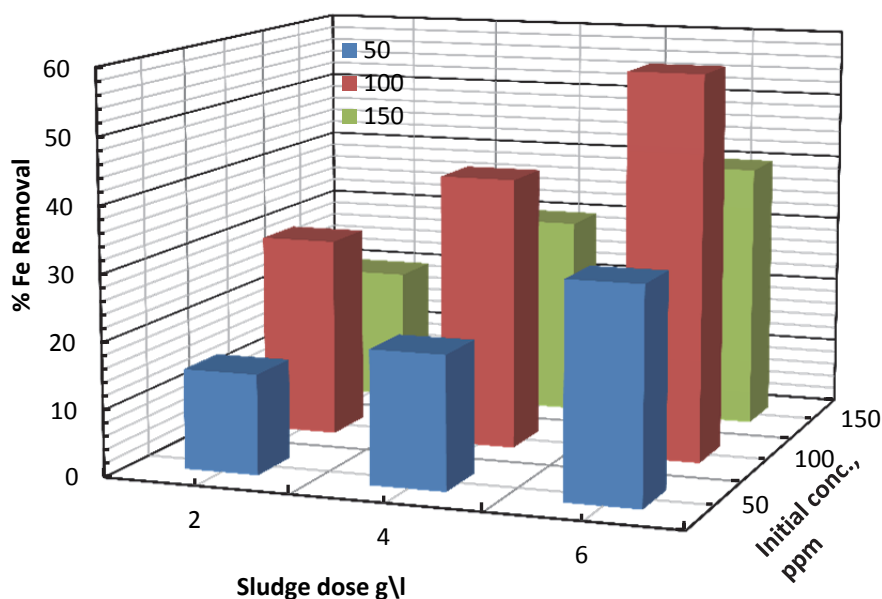


Fig. 3. Effect of initial concentration of Fe^{++} on the % removal at different adsorbent doses; sludge treated at $600^{\circ}C$

Rys. 3. Wpływ początkowego stężenia Fe^{++} na jego usunięcie przy różnych dawkach adsorbentu; osad przygotowany w temperaturze $600^{\circ}C$

Initial concentration of dissolved ions has two opposing effects namely (Abdel-Aziz 2013, Gutub et al. 2013, El-Ashtoukhy and Abdel-Aziz 2013); (i) increasing initial concentration leads to increasing the bulk concentration and increasing the concentration difference between the solution bulk and the interface with a consequent increase in the driv-

ing force for ions transfer and increasing the rate of removal. (ii) increasing initial concentration leads to increase the inter-ionic attraction and decreasing the diffusion of ions to the adsorbent surface with a consequent decrease in the rate of Fe^{++} transfer from the solution bulk to the adsorbent surface (Abdel-Aziz et al. 2013, Pang et al. 2014). As the concentration of metal ion increases, rapid saturation of the adsorbent and more surface sites are covered at a constant adsorbent dose consequently the adsorbent capacity gets exhausted due to non-availability of the surface sites (Namasivayam et al. 1996). Under the present range of operating parameters it seems that the first effect is predominant in the concentration range from 50-100 ppm and the second effect is predominant in the concentration range 100-150 ppm.

Figure 3 also shows the effect of adsorbent dose on Fe^{++} % removal at different initial concentrations. The data show that within the present range of parameters studied the % removal increases with increasing adsorbent dose, this may be attributed the fact that with increasing the adsorbent dose the surface area and the active adsorption sites for bonding the heavy metal ions will increase (Tekere et al. 1999, Abdel-Ghani et al. 2007).

To study the effect of heat treatment temperature the sludge after drying and grinding was treated at three different temperatures namely; 200, 400 and 600°C for 3 hours holding time. Mass losses of sludge increased with increasing temperature with a formation of little pores and structural changes. The weight losses are mainly due to dehydration, organic and inorganic materials decomposition (Chen and Jeyaseelan 2001).

Figure 4 shows that the maximum removal of Fe^{++} was achieved with sludge samples treated at 600°C at different sludge doses (2, 4, and 6 g/L). In order to explain the effect of sludge treatment temperature on the % removal, the sludge samples were analyzed by SEM analysis at the three temperatures 200, 400 and 600°C respectively.

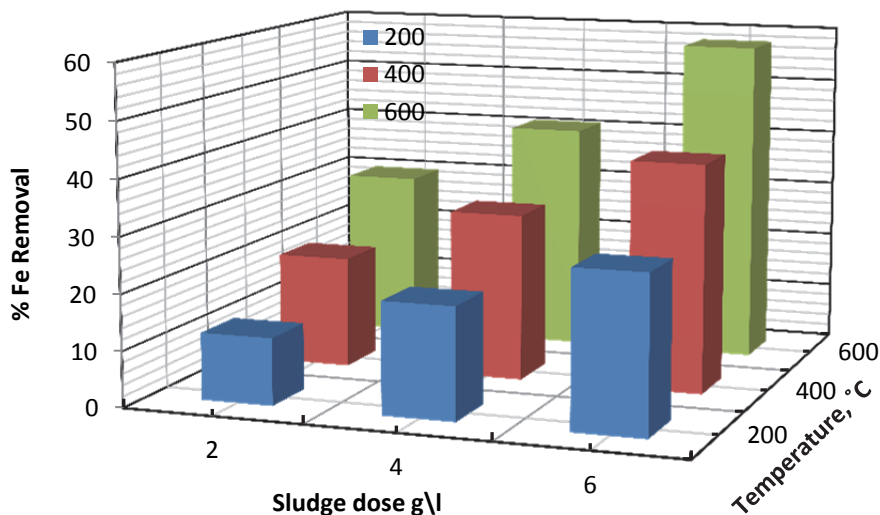


Fig. 4. Effect of sludge dose on Fe % removal at different heat treatment temperature; initial concentration = 100 ppm

Rys. 4. Wpływ dawki osadów na usunięciu Fe w zależności od temperatury przygotowywania osadów; początkowe stężenie = 100 ppm

Figure 5 Shows that the particle size decrease with increasing temperature and accordingly the surface area of the adsorbent and the % removal increase (Lu et al. 1995).

Also FTIR spectra shows visible changes during heating of sludge, which are related to surface structure. Figure 6 shows detailed spectra evolution with heating for selected wave number ranges. In general, organic functional groups found in sewage sludge tend to decrease with increasing temperature (Bandosz and Block 2006). Also some structural changes in the solid matrix can be discerned.

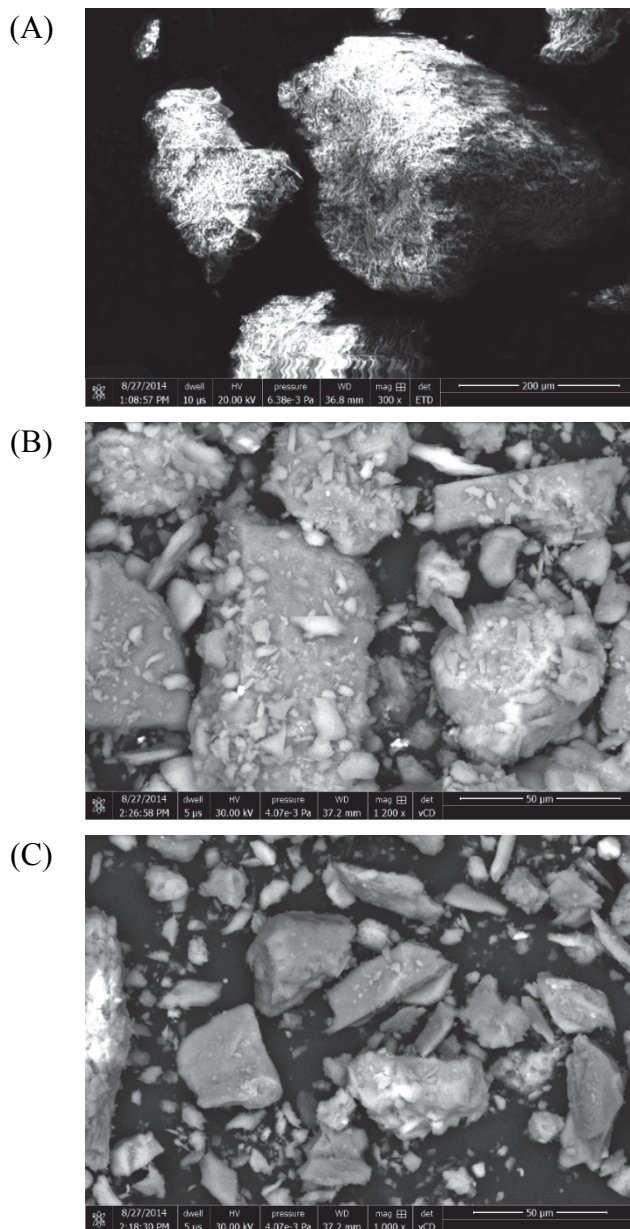


Fig. 5. SEM analysis of sludge samples at different temperatures (A: 200°C, B: 400°C, C: 600°C)

Rys. 5. Analiza SEM próbek osadu przygotowanych w różnych temperaturach (A: 200°C, B: 400°C, C: 600°C)

A broad band at 3630 cm⁻¹ corresponds to O–H stretching vibrations. These functional groups may represent compounds such as alcohols and carboxylic acids found in the sample. The peak at 1645 cm⁻¹ is due to the Amide I band. C=O stretching vibrations from other functionalities are found at the left of the 1692 cm⁻¹ peak. They refer to fatty acid carboxylic groups. The band at 1525 cm⁻¹ may be due to N–H bending, which is characteristic of the Amide II band. C=C aromatic skeletal vibrations can also be found between 1645 and 1500 cm⁻¹ and may exist in the sample due to lignin structures⁴¹. In the interval between 1400 and 1524 cm⁻¹, vibration of CH₂ groups and O–H bending vibrations for alcohols and carboxylic acids cause a variety of peaks. Consequently, a broad band around 1424 cm⁻¹ is detected. Band at 1027 cm⁻¹ has been assigned by several authors to polysaccharides. Peak at 874 cm⁻¹ can be assigned to inorganic carbonates, particularly calcium carbonate. Spectrum below 875 cm⁻¹ could be result of aromatic structures, amine and amide groups. In this study, an attempt has been made to detail the FTIR spectra of sewage sludge and chars regarding the changes experienced by the solid fraction through heat treatment within the entire temperature range (200-600°C), while being aware of its obvious limitations.

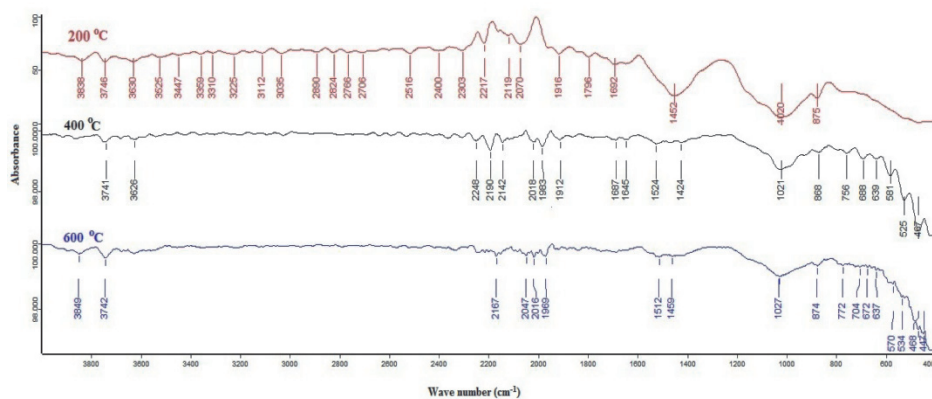


Fig. 6. FTIR spectra of sludge samples at different treatment temperatures

Rys. 6. Widma FTIR próbek osadu przygotowanych w różnych temperaturach

Table 1 shows the % removal of Fe⁺⁺ at different polymer/sludge ratio. Mixing of PVDF polymer with the sludge increased the % removal by a factor ranging from 4.62 to 15.63%. Despite the little effect of the

polymer on increasing the % removal of heavy metal ions, mixing of the polymer with the sludge has the advantage of reducing COD of the wastewater samples (JornWong and Phunchareon 1999, Chen and Zhao 2000, Mazzei et al. 2004, Betz et al. 2003).

Table 1. % removal of Fe⁺⁺ at different polymer/sludge ratio (sludge treatment temperature = 600°C)

Tabela 1. Usunięcie Fe⁺⁺ przy w różnym stosunku polimer/osad (temperatura obróbki osadu = 600°C)

% Sludge	% Polymer	Fe % removal
0	100	68.32
25	75	63.6
50	50	61.48
75	25	57.54
100	0	55

4. Data modeling

Data modeling and analysis is important to predict the adsorption performance of the sludge, express the capacity of and optimize the mechanism. The mathematical correlation obtained by the modeling analysis is important for operational design and applicable practice of the adsorption systems. The performance of an adsorbent can be studied by adsorption isotherm data, which can be obtained by a series of experimental tests. Several isotherm models are commonly used in modeling the adsorption data, such as Freundlich and Langmuir (Egashira et al. 2013, Foo and Hameed 2010, Langmuir 2012, Freundlich 1906).

The linear forms of the Freundlich and Langmuir isotherms are given in equations (2) and (3) respectively:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

$$\frac{C_e}{q_e} = \left[\frac{1}{q_m K_L} \right] + \frac{C_e}{q_m} \quad (3)$$

where,

q_e – equilibrium loading, mg/g, C_e – equilibrium concentration in mg/L,
 K_f – Freundlich constant, mg/g, n – Freundlich exponent,
 K_L – Langmuir constant, L/mg, q_m – maximum adsorption capacity, mg/g.

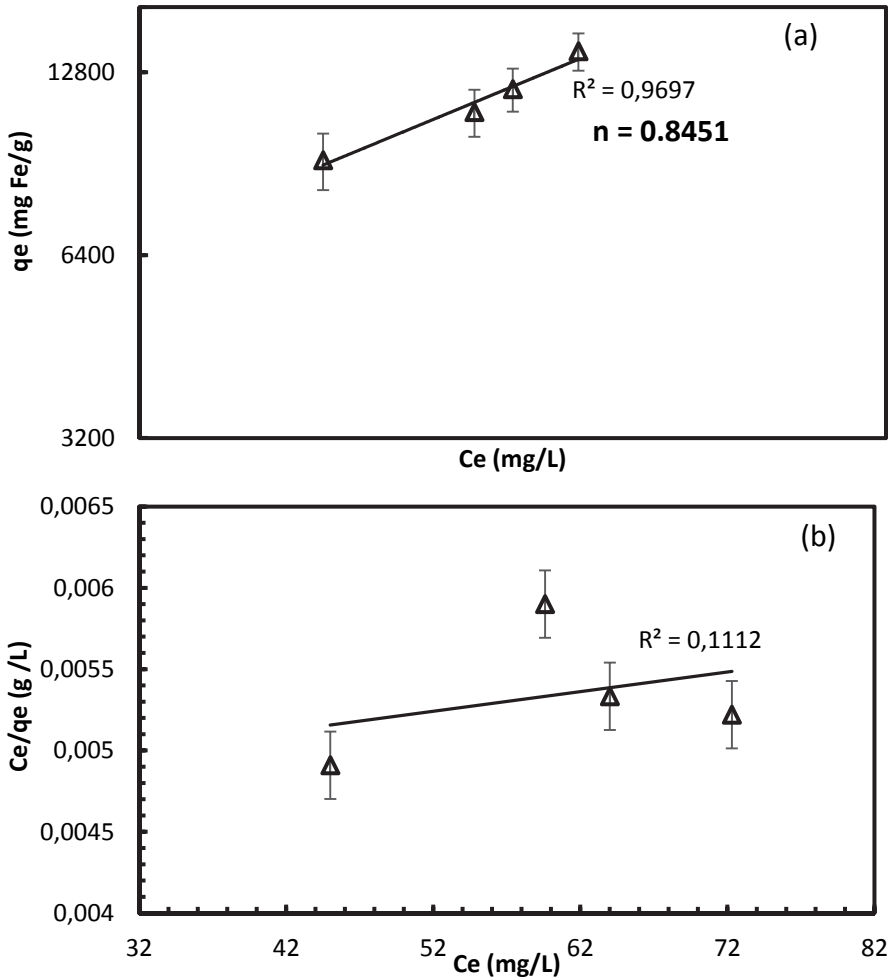


Fig. 7. Linear fitting plots of (a) Freundlich, (b) Langmuir
Rys. 7. Liniowe izotermy (a) Freundlicha, (b) Langmuira

Figure 7 shows linear fitting of Freundlich and Langmuir adsorption isotherms of the sewage sludge adsorbent by linear analysis. The data suggests that Freundlich isotherm model generates a satisfactory fit to the experimental data, while Langmuir isotherm model cannot. Langmuir isotherm assumes monolayer coverage on a homogeneous surface with identical adsorption sites. But these assumptions are valid for gas adsorption on solid surface. In solution-solid systems, with the hydration

forces, mass transport effects etc. the system is much more dynamic and complicated, and obeying the isotherm does not necessarily reflect the validity of the aforementioned assumptions. In such systems the isotherm adequacy can be seriously affected by the experimental conditions, in particular, the range of concentration of the solute/adsorbate. Previous studies reported that both of Langmuir and Freundlich isotherms might adequately describe the same set of liquid-solid adsorption data at certain concentration ranges, in particular if the concentration is small and the adsorption capacity of the solid is large enough to make both isotherm equations approach a linear form. Only one of the two isotherms correlates better with the data at high concentration.

In the field of water treatment it is usually aimed for very low equilibrium concentrations. In this case, the equilibrium concentration corresponds to the maximum permitted adsorbate concentration in the treated water. As such, in the case of Freundlich exponent $n < 1$ is a favorable isotherm curve. For the present experimental data n is 0.8451 which confirms a favorable isotherm.

5. Conclusions

Removal of Fe^{++} from dilute aqueous solutions has been studied experimentally by using sewage sludge-polymer hybrid adsorbent. Mixing the polymer with sludge increased the % removal by a factor ranging from 4.62 to 15.63%. SEM analysis confirmed that sludge treatment temperature 600°C produce smallest particle size and larger surface area while FTIR spectra showed that organic functional groups found in sewage sludge tend to decrease with increasing temperature.

The present experimental data fitted well Freundlich linear isotherm model with an exponent of 0.8451 which confirms a favorable isotherm. The model can be used for operational design of the present system.

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Usuwanie Fe^{++} ze ścieków przy użyciu hybrydowych adsorbentów osadowo-polimerowych

Streszczenie

W pracy badano usuwanie Fe^{++} za pomocą adsorpcji na osadowo-polimerowych adsorbentach hybrydowych. Osady pobrano z oczyszczalni ścieków komunalnych. Obróbkę termiczną osadu prowadzono w temperaturze 200, 400 i 600°C, w celu poprawy zdolności adsorpcyjnych. Fluorek poliwinylidenu (PVDF) – handlowy polimer – mieszano z osadami w różnych stosunkach masowych. Morfologia powierzchni i struktura chemiczna przetworzonego osadu była badana za pomocą SEM i FTIR. Badane parametry niezależne to: początkowe stężenie Fe^{++} , czas kontaktu, dawka osadu, obróbka termiczna osadu,

udział osadu/polimeru w mieszance. W badanych zakresach zmienności parametrów niezależnych, efektywność usuwania Fe⁺⁺ wzrasta wraz ze wzrostem dawki osadu. Zwiększenie początkowego stężenia Fe⁺⁺ z 50 do 100 ppm zwiększa skuteczność usuwania o współczynnik wynoszący maksymalnie 1,73. Dalsze zwiększanie stężenia od 100 do 150 ppm, prowadzi do zmniejszenia skuteczności usuwania do 43%. Hybrydowy adsorbent poprawił skuteczność usuwania aż do 63,6%. Dane doświadczalne odpowiadają liniowej izotermie Freundlicha. Adsorpcja Fe⁺⁺ przez adsorbent osadowy zachodzi poprzez monowarstwę i heterogeniczną powierzchnię.

Podkreślono możliwość zastosowania uzyskanych wyników do usuwania metali ciężkich ze ścieków przemysłowych.

Abstract

Removal of Fe⁺⁺ by adsorption on sludge-polymer hybrid adsorbents was studied. Sludge was collected from domestic disposal wastewater. Thermal treatment of sludge particles was carried out at 200, 400 and 600°C to improve adsorption capacity. Polyvinylidene fluoride (PVDF) commercial polymer was mixed with the sludge in different mass ratios. Surface morphology and chemical structure of treated sludge were investigated using SEM and FTIR. Parameters studied are initial concentration of Fe⁺⁺, contact time, sludge dose, heat treatment of the sludge, and sludge/polymer mixing ratio. Within the present range of studied parameters the removal efficiency of Fe⁺⁺ increases with increasing sludge dose. Increasing initial concentration of Fe⁺⁺ from 50 to 100 ppm increases the removal efficiency by a factor of maximum of 1.73. Further increasing in concentration from 100 to 150 ppm leads to decrease in removal efficiency up to 43%. Sludge-PVDF hybrid adsorbent improved removal efficiency up to 63.6%. Experimental data fits to Freundlich linear model. The mechanism of adsorption of Fe⁺⁺ by sludge adsorbent was found to take place through a monolayer and heterogeneous surface.

Potential applications of the present data in removing heavy metals from industrial waste solutions were highlighted.

Słowa kluczowe:

metale ciężkie, osady ściekowe, polimery, hybrydowe adsorbenty, izoterma adsorpcji

Keywords:

heavy metals, sewage sludge, polymers, hybrid adsorbents, adsorption isotherm