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# APPLICATION OF SD/MNP/PEI NANOCOMPOSITE FOR HEAVY METALS SORPTION

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**Abstract.** A magnetical nanocomposite based on sawdust, magnetic nanoparticles, and polyethylenimine was prepared to remove Pb(II), Cd(II) and Cu(II) ions from an aqueous solution. Adsorption on nanocomposite exhibited a maximum removal of 97 % for Pb(II). The adsorption capacity in the pseudo-second-order model for Pb(II) was studied and the value of 1.48 mg/g was obtained.

**Keywords:** sawdust, polyethylenimine, nanocomposite, heavy metals, Pb(II).

## 1. Introduction

There is an increasing worldwide concern for environmental protection and the conservation of nonrenewable natural resources. Along with the development of the global economy, clean water has been excessively consumed as a result of the growing problem of freshwater resources limitation especially facing increasing serious water pollution, in which the threat from heavy metal ions is one of the most urgent issues.[1] Heavy metal ions are serious threats to the environment. In recent years, with the rapid development of industry, more and more toxic heavy metals have entered the water body and soil. Heavy-metal pollution of aquatic environments is a long-term concern because of increasing discharges of heavy metals such as Pb (II), Cu (II), and Cd (II) into surface water.[2,3] These heavy metal ions are the most toxic water pollutants which cause major environmental health disorders. Because of the easy accumulation of these ions in the living systems, their perseverance and bioaccumulation in the food chain, they can cause serious and permanent damage to various organs even at very low concentrations.[4] In addition to the biological accumulation and enrichment of heavy metals, they cannot be degraded in nature, so they cause serious harm to the water system and can enter the human body through the food chain, thus posing a serious threat to human health. Lead is among important heavy metals that are well-known toxicants, used in metallurgy, tannery manufacturing, paper and pulp industries, metal products, paints and varnishes, battery manufacturing industries, galvanizing plants, *etc*.[5,6] Lead exists as Pb(II) in water that enters into food chains and accumulates in soft tissues of the body. It is a known metabolic poison and enzyme inhibitor that accumulates in bones, brain, kidneys, and muscles and causes a variety of health problems such as nervous system deterioration, failure of kidneys reduction infertility both in men and women, anemia, Alzheimer's disease and bone problems.[7,8] Cadmium is readily accumulated in living organisms, leading to multiple serious organ damage.[9] Due to the toxicities associated with Pb(II), Cu(II) and Cd(II), WHO has recommended the maximum permissible limit of lead, cadmium and copper in drinking water as 0.01, 0.005 and 1.5 $\frac{mg}{L}$ , respectively.[10-12] Therefore, the development of efficient heavy metal decontamination technologies is a matter of great significance to human life safety and quality of life. Using efficient and inexpensive adsorbents is one of the best ways to remove heavy metals from the environment.

Several methods have been applied for heavy metals removal in aqueous solution, including chemical precipitation,[13] oxidation,[14] adsorption,[15-17] electrochemical,[18] biosorption,[19] integration of phytogreen,[20] membrane filtration,[21-23] ion exchange,[24] ion flotation,[25] coagulation,[26] and electrolysis.[27] However, most of these methods could not be used in full scale application due to their high operation cost, low efficiency or potential secondary pollution.[28] Among these, adsorption is the most frequently studied method. The adsorption method is old and simple; it is really an efficient method for organic and metal ions removal and has been excessively studied and widely used in full-scale applications.[29] Adsorption has the advantages of easy operation, high efficiency, cost-effectiveness, easy regeneration and no second pollution. A variety of adsorbents have been used to remove heavy metals from

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waste water. Owing to the large industrial applications and toxicity associated with Pb(II), Cd(II) and Cu(II), these three ions were selected for the removal studies from water. Polyethyleneimine (PEI) with plenty of primary and secondary amine groups present in a macromolecular chain can partially reduce and simultaneously functionalize graphene oxide (GO). PEI-functionalized GO exhibits an interesting adsorption ability for toxic cations. In this regard, we used polyethyleneimine attached to magnetized sawdust (SD) to remove heavy metals.

The aim of this study is the synthesis of a new PEI functional magnetic sawdust nanocomposite and investigation of SD/MNP/PEI nanocomposite efficiency for the removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution and real media in a batch system. A systematic evaluation of the parameter involved such as contact time and investigation of the dynamics of the adsorption process with kinetic models has been performed. This study not only provides new perspectives for the cleanup of heavy metals but also reveals the application potential of the SD/MNP/PEI nanocomposite for pollution control.

## 2. Experimental

### 2.1. Material and Equipment

Sawdust was obtained from a Poplar tree, and washed with water, then dried, and sieved with 470-mesh. Polyethyleneimine (PEI, Mw = 2000 g/mol) was purchased from Sigma Aldrich. Other chemical reagents used in this work, including ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98 %), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ammonia solution (25 %), epichlorohydrin (EPC), sodium bicarbonate ($NaHCO_3$), sodium hydroxide (NaOH), $Pb(NO_3)_2$ (99 %), $Cd(NO_3)_2 \cdot 4H_2O$ (99 %) and $Cu(NO_3)_2 \cdot H_2O$ (99 %) were purchased from Merck. A stock solution of metal solutions with a concentration of 1000 mg/L was prepared by dissolving $Pb(NO_3)_2$, $Cd(NO_3)_2$ and $Cu(NO_3)_2$ in distilled water. Other solutions with different concentrations of metal ions were prepared by diluting the stock solution.

The analysis apparatus was Atomic Absorption Spectrophotometer (AAS) type AA-220 (Varian). However, there are other measurement methods for Pb(II)[30] – SEM MIRA3 (TESCAN). Fourier transform infrared spectrometry (FT-IR) analyses were carried out on BrukerVector 22 FT-IR Spectrometer in the range of 400–4000 $cm^{-1}$ employing the KBr pellet method. A vibrating sample magnetometer (VSM) was employed to determine magnetic properties of synthesized materials (Lake Shore 7037/9509-P, USA). Adjustment of pH was performed using 0.1M $HNO_3$ and 0.1M NaOH. The pH measurement was carried out using a Metrohm pH meter (model 744).

### 2.2. Synthesis of sawdust/ magnetic nanoparticles/ polyethylenimine (SD/MNP/PEI) nanocomposite

Sawdust was first washed with distilled water and then was sieved through a 470 µm standard sieve. Nanoparticles-loaded sawdust (SD-MNP) was prepared by modified co-precipitation method[31] (Fig 1).

The dried SD-MNP was steeped in epichlorohydrin (5 mL) and NaOH (1.4M, 10 mL) and stirred for 2 h at 60 °C. The obtained raw product was subsequently rinsed with NaOH (1.4M, 50 mL) and distilled water (50 mL). The epoxidized SD/MNP was added to a solution of $NaHCO_3$ (50 mM, pH 9, 50 mL) and PEI. The reaction system was incubated for 5 h with gentle stirring at 65 °C. The grafted nanocomposite was sequentially rinsed with $NaHCO_3$ and distilled water and dried in vacuum at 40 °C[32] (Fig 2).

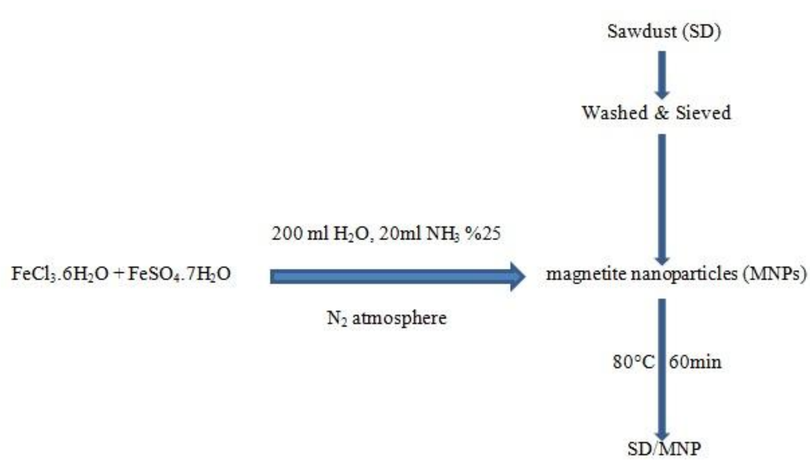


**Fig. 1.** Synthesis of SD/MNP

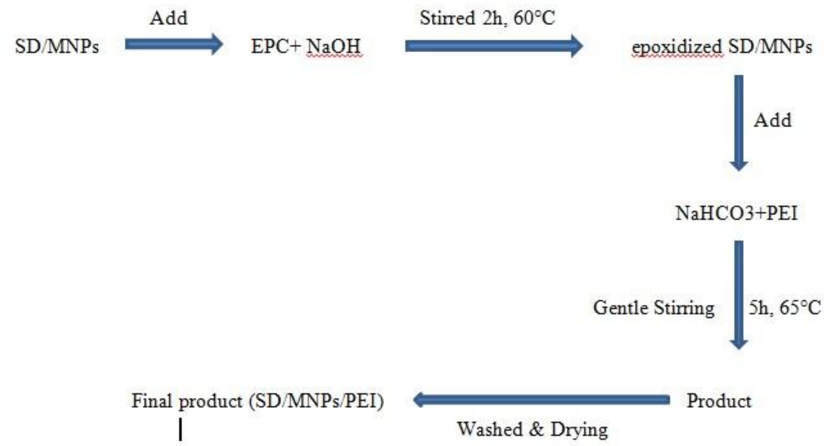


**Fig. 2.** Synthesis of SD/MNP/PEI

## 2.3. Batch sorption experiments

SD/MNP/PEI nanocomposite was used for the removal metal ions from aqueous solution. The stock solution (1000 mg/L) of metal ions, Pb(II), Cu(II) and Cd(II), were prepared from $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot H_2O$. A typical batch sorption experiment was carried out with 50 mL of aqueous solution of Pb (II), Cu (II) and Cd (II) with a known initial concentration at desirable pH in conical flasks at 25 °C.

0.2 g of SD/MNP/PEI were added to the above-mentioned solution. Then, the mixture was shaken for predetermined equilibrium time interval (80 min), and the samples were separated by a permanent magnet. The amount of Pb (II), Cu (II) and Cd (II) adsorbed onto SD/MNP/PEI was calculated from the mass balance between the initial ($C_o$) and equilibrium ($C_e$) concentrations (mg/L) of metal ions. Residual concentration of the heavy metal ions in the solution was determined by the use of an Atomic Absorption Spectrophotometer type AA-220. The metal uptake capacity ($q_e$ (mg/L)) of SD/MNP/PEI was calculated by the following equation:

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

$$Removal\ efficiency(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where $C_o$ and $C_e$ (mg/L) are the initial and equilibrium concentrations of contaminants, respectively. $q_e$ (mg/g) is the adsorbed amount of adsorbate per unit mass of the adsorbent at equilibrium. V (L) is the volume of adsorption solution, M (g) is the mass of adsorbent.[28, 33] All cation analysis was carried out by using Varian AA-220 atomic absorption spectrophotometer. Lamp current and wavelength of Pb (II), Cu (II) and Cd (II) were (5 mA, 217 nm), (4 mA, 327 nm) and (4 mA, 326 nm), respectively.

The effect of each influential parameter on the adsorption such as contact time was examined through varying the selected parameter in the above-mentioned procedure. All the reported data are the average of at least triplicate measurements.

## 2.4. The study of the kinetics of lead ions sorption on SD/MNP/PEI sorbent

50 mL of lead solution of 50 mg/L concentration was added to the 100 mL flask. 0.2 g/L of finely divided sorbent were added to this solution while switching on a stopwatch, then the mixture was shacked. The resulting solutions were studied at 25 °C. In an appropriate time interval, the muddy samples were taken which were filtered through a glass filter or with external magnetic field. Sampling was carried out at regular intervals up to 120 min.

# 3. Results and Discussion

## 3.1. SEM and EDX analysis

The surface morphologies of sawdust/$Fe_3O_4$/ polyethylenimine nanocomposite were obtained by a scanning electron microscopy. The SEM image of the synthesized SD/MNP/PEI nanocomposite is shown in Fig. 3. Image indicated a homogenous and smoother structure of the nanocomposite after PEI cross linking and no obvious pores were observed on the sawdust surface, the spherical morphology is related to the $Fe_3O_4$ NPs. The EDX analysis shows the existence of constituent elements C (28.34 %W), O (52.07 %W), Fe (12.55 %W) and N (7.03 %W). The presence of N in the resulting substance is due to the cross-linking PEI on SD/MNP. Therefore, it can be stated that the cross-linked PEI has successfully been attached to the SD/MNP. Presence of Fe indicated that a magnetic phase is created.

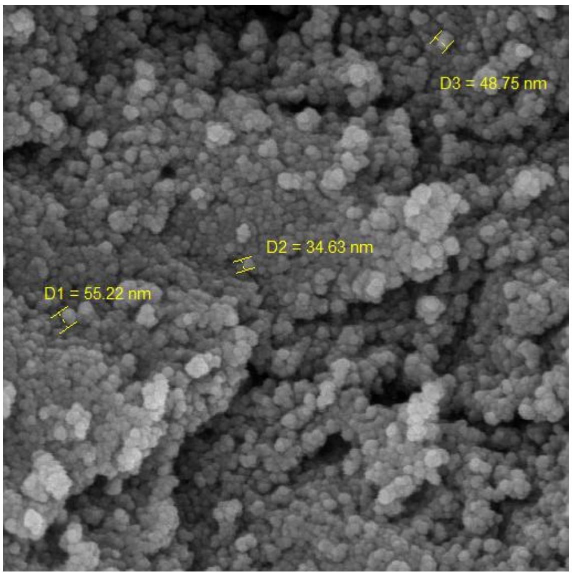


**Fig. 3.** SEM image of SD/MNP/PEI

## 3.2. FT-IR spectrum

The FT-IR spectrum of the SD/MNP/PEI nanocomposite is shown in Fig. 4; the functional groups are presented in Table 1. According to Fig. 4 and Table 1, the peak around 3300 cm$^{-1}$ occurs due to a stretching vibration of the O–H bond in the cellulose, which is part of the SD/MNP/PEI nanocomposition,[34] the peak at 1470-1590 cm$^{-1}$ occurs due to the bending of the N–H bond in the imine, attached on SD/MNP, the remaining peaks are identified in Table 1.

## 3.3. Vibrating sample magnetometer (VSM)

A vibrating sample magnetometer is a scientific instrument that measures magnetic properties based on Faraday's law of induction.[39] The hysteresis loop of the SD/MNP/PEI was also obtained using VSM by pertaining magnetic field from –15 to +15 KOe (Fig 5). The saturation magnetization (Ms) value at a temperature of 300 K was discovered to be 11.55 emu/g, which is useful for the repeated magnetic separation. This nanocomposite was synthesized according to the instructions of Ghasemi *et al.*,[36] which has shown good magnetic properties.

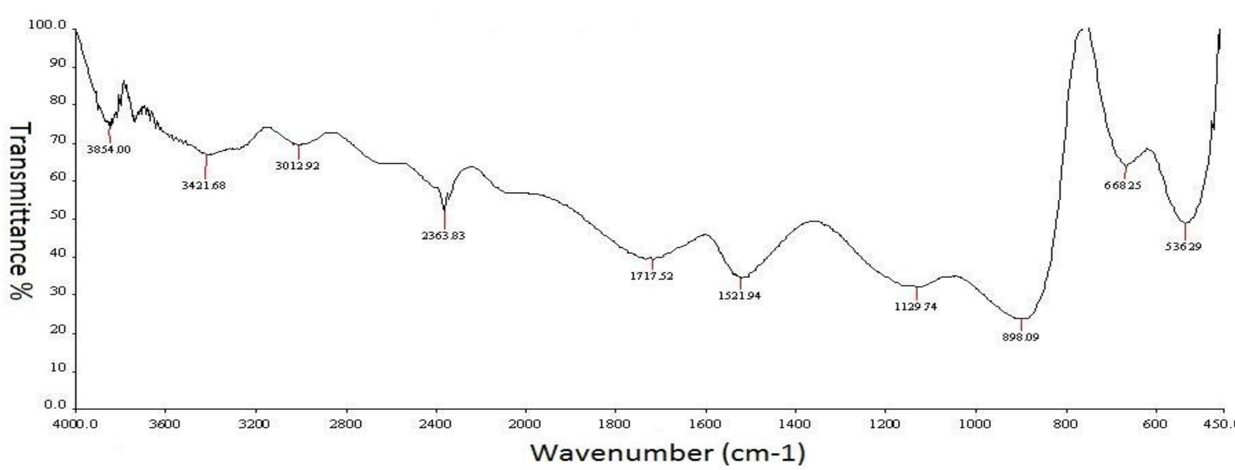


**Fig. 3.** FT-IR spectrum of SD/MNP/PEI

**Table 1.** The functional groups of SD/MNP/PEI

| Wavenumber, cm$^{-1}$ | Vibration | Probable groupings | Ref |
|---|---|---|---|
| 3300-3500 | symmetric stretches | O–H bond related to cellulose | [34] |
| 1129 | stretching | C–N bond related to PEI | [35] |
| 2850-3000 | asymmetric stretching | C–H bond presented in methyl group | [33] |
| 1737 | stretching | C=O bond | [33] [36] |
| 550-620 | stretching | Fe–O | [36] |
| 1470-1590 | bending | N–H | [37] |
| 2363 | symmetric bending stretching | O–H bond related to cellulose | [38] |

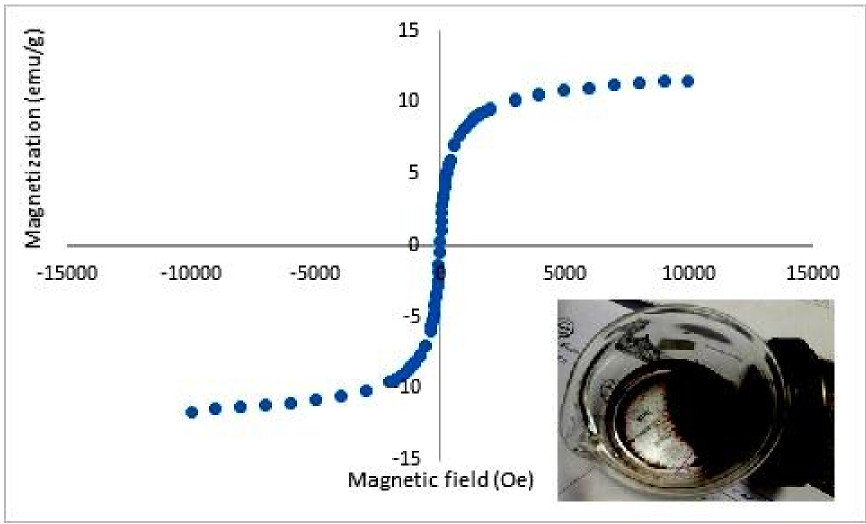


**Fig. 4.** M-H hysteresis loop/vibrating sample magnetometer (VSM) measurement of the SD/MNP/PEI

**Table 2.** Comparison of SD/MNP/PEI with other reported some magnetic composite sorbents in term of saturation magnetization (Ms)

| Magnetic sorbents | Ms (emu/g) | Ref |
|---|---|---|
| SD/MNP/PEI | 11.55 | This study |
| PVA-SA-embedded $Fe_3O_4$ magnetic nanoparticles (MNPs) | 5 | [40] |
| $Fe_3O_4$@mesoC | 5.5 | [41] |
| $Fe_3O_4$@$SiO_2$@CS-TETA-GO | 8.22 | [42] |
| Bio-magnetic membrane capsules (BMMCs) | 11.02 | [43] |

Overall, the prepared SD/MNP/PEI showed the higher saturation magnetization value to compare with most of the other documented composite materials, which is highly prerequisite for improving wastewater treatment processes and maintaining treatment systems economically feasible (Table 2).

## 3.4. Powers uptake

Using the aforementioned batch equilibrium method and the optimum conditions for the adsorption of each cation, the adsorption of Pb (II)' Cu (II) and Cd (II) on SD/MNP/PEI nanocomposite was studied at 25 °C.

Among these three heavy metals, lead has the maximum uptake on a nanocomposite. As illustrated below (Fig. 6), the amounts of removed Pb (II)' Cu (II) and Cd (II) on SD/MNP/PEI were 97, 52 and 47 percent, respectively. These results illustrated that the amine groups ($-NH_2$) can easily form coordination complexes with Pb (II), which were responsible for efficient adsorption. The ion solutions with concentrations 50 mg $L^{-1}$ were used in these experiments.

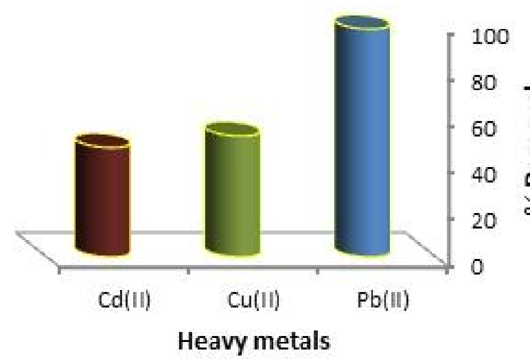


**Fig. 5.** Adsorption of $Pb^{2+}$, $Cu^{2+}$ and $Cd^{2+}$ onto an adsorbent. Conditions: Sorbent concentration 50 mg $L^{-1}$, Temp 25°C and 0.2 g of adsorbent

## 3.5. Effect of contact time

In order to reach maximum uptake, the effect of time on the removal of metal ions by nanocomposite was studied. The removal efficiency of three ions reached a maximum value after 80 min and then no further significant increase was observed for contact time of up to 2 h. The initial rapid uptake of metal ions may be ascribed to the presence of large number of vacant sites available for metal ions, and afterwards the remaining free metal ions are difficult to be occupied, because of repulsive forces between the free and adsorbed metal ions. According to the results, a contact time of 80 min was selected as an optimized time to a maximum uptake. The effect of contact time on the adsorption of Pb (II), Cu (II) and Cd (II) ions onto adsorbent can be seen in Fig. 7.

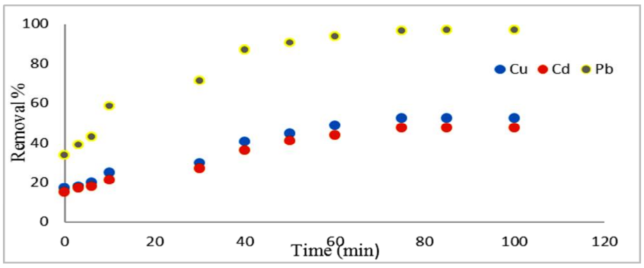


**Fig. 6.** Effect of contact time on adsorption of $Pb^{2+}$, $Cu^{2+}$ and $Cd^{2+}$ onto the adsorbent. Conditions: Sorbent concentration 50 mg $L^{-1}$, Temp 25°C and 0.2 g of adsorbent

## 3.6. Test on real sample

In order to evaluate the actual performance of the synthesized nanocomposite and applicability of the method to real sample, its performance was investigated for removal of lead from wastewater from the Takfam Company (Boukan, West Azerbijan, Iran). Determination of Pb(II) was performed by Atomic Absorption Spectrophotometer. The adsorbent amount of 0.2 g and 50 mL of wastewater with determined concentration were used to do this test. The real sample was diluted 2-fold, and after adsorption, the actual amount of lead metal was obtained using a calibration line graph. The results show good performance and 90 % of pollutant (Pb(II)) were removed with SD/MNP/PEI nanocomposite.

## 3.7. Kinetic study

The dynamics of the adsorption process in terms of the order and the rate constant can be evaluated using the kinetic adsorption data. In most works[44] in the current literature about liquid/solid adsorption kinetics, the respective applicability of pseudo-first order and pseudo-second kinetics for describing the data are compared. The process of Pb (II) removal from an aqueous phase by adsorbent can be explained by using the kinetic models and examining the rate-controlling mechanism of the adsorption process such as a chemical reaction, diffusion control and mass transfer. The kinetic parameters are useful in predicting the adsorption rate which can be used as the important information in designing and modeling of the adsorption operation.

The kinetics of Pb(II) removal is explicitly explained in the literature[45] using pseudo-first-order, pseudo-second-order and Intra-particle diffusion kinetic models.

### 3.7.1. Pseudo-first-order model

Pseudo-first order kinetics was first proposed at the end of the 19th century by Lagergren.[46] The sorption kinetics may be described by the pseudo-first-order Lagergren rate model. The equation is as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

Where $q_e$ and $q_t$ are the amounts of metals adsorbed on the sorbent (mg/g) at equilibrium and at time t, respectively, and $k_1$ is the rate constant of the first-order adsorption (1/min). The straight line plots of $\ln(q_e - q_t)$ against t were used to determine the rate constant, $k_1$ and correlation coefficient, $R^2$, values of the lead were calculated from this plot.[32, 44]

### 3.7.2. Pseudo-second-order model

Pseudo-second-order kinetics was introduced in the middle 80´s.[47, 48] However, it was not very popular until 1999 when Ho and McKay analyzed a number of experimental results taken from the literature.[49]

The pseudo-second-order rate equation shown as follows has been popularly applied to adsorption systems:

$$\frac{t}{q_t} = \frac{1}{k_2\left(q_2^2\right)} + \left(\frac{1}{q_2}\right)t \qquad (4)$$

where $k_2$ is the rate constant of adsorption (g/(mg min)), $q_2$ the amount adsorbed at equilibrium. The equilibrium adsorption amount ($q_2$) and the pseudo- second- order rate parameters ($k_1$) can be calculated from the slope and intercept of plot of $\frac{t}{q_t}$ versus t.[32]

### 3.7.3. Intra-particle diffusion model

The intra-particle diffusion model proposed by Weber and Morris[50, 51] has been widely applied for the analysis of adsorption kinetics. The intra-particle diffusion equation can be written as

$$q_t = C = k_{dif} t^{\frac{1}{2}} \qquad (5)$$

Where, $q_t$ is the amount of lead adsorbed onto the adsorbent at time. C is the intercept, and $k_{dif}$ is the intra-particle diffusion rate constant (mg/(g min$^{½}$)). These values can be calculated from the slope and intercept of plot of $q_t$ *versus* $t^{\frac{1}{2}}$.[32] According to the intra-particle diffusion model,[51] the plot of $q_t$ versus the square root of time ($t^{\frac{1}{2}}$) should be linear if the intra-particle diffusion is involved in the adsorption process.

All results and calculations are illustrated in Table 3 below. The correlation coefficients, $R^2$, showed that the pseudo-second-order model, an indication of an adsorptions mechanism, fits better the experimental data than the pseudo-first-order model. The studies on the adsorption of Pb (II) ions revealed that the process obeys the pseudo-second order kinetic model, the determining step might be a chemical sorption.

Table 3. Parameters of the kinetic models for Pb(II) adsorption onto SD/MNP/PEI ($c_o$ =50 mg $L^{-1}$, T=25 °C, pH=7, sorbent dosage=0.2 g $L^{-1}$, Time 0-120 min, 300 rpm)

| Kinetic Models | Parameters | Calculated |
|---|---|---|
| **Pseudo-first-order** | $q_1$<br>$k_1$<br>$R^2$ | 1.37<br>0.002<br>0.89 |
| **Pseudo-second-order** | $q_2$<br>$k_2$<br>$R^2$ | 1.48<br>0.031<br>0.99 |
| **Intra-particle diffusion** | $k_{dif}$<br>$C$<br>$R^2$ | .098<br>0.26<br>0.94 |

## 4. Conclusions

Throughout this paper the importance of removing heavy metal in general and lead in particular from industrial or domestic wastewater was highlighted. This important process was performed by adsorption. Adsorption has become one of the alternative treatments, in recent years; the search for low-cost adsorbents that have metal-binding capacities has been intensified.

Important achievements at the end of this article:

a) Successful synthesis of magnetic nanocomposites (SD/MNP/PEI).

b) Adsorption of the divalent cations on the SD/MNP/PEI nanocomposite exhibited the order of Pb (II) > Cu (II) > Cd (II), with a maximum removal of 97 % for Pb (II) ion on SD/MNP/PEI nanocomposite.

c) The results showed that the pseudo-second-order kinetic model could best illustrate the adsorption kinetics process of SD/MNP/PEI.

d) Low cost and recyclable synthesis of adsorbent.

e) Amino groups (in polyethlenimine) attached on a magnetite sawdust surface can easily be used to remove heavy metal ions from aqueous solutions and effectively for Pb (II) recycle without a significant loss of adsorption capacity.

f) The adsorption obeyed pseudo-second order kinetics, suggesting a chemisorption mechanism between heavy metal ions and SD/MNP/PEI nanocomposite.

g) The favorable adsorption time was selected by studying the contact time. A contact time of 80 min was selected as the optimized time to maximum uptake.

The obtained results clearly demonstrate the high efficiency of using new magnetic adsorbent, for water treatment from toxic heavy metals such as Lead, with a purification efficiency of up to 97 %.

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## ЗАСТОСУВАННЯ НАНОКОМПОЗИТУ SD/MNP/PEI ДЛЯ СОРБЦІЇ ВАЖКИХ МЕТАЛІВ

***Анотація.*** *Отримано магнітний нанокомпозит на основі тирси, магнітних наночастинок і поліетиленіміну для вилучення іонів Pb(II), Cd(II) і Cu(II) з водного розчину. Адсорбція на нанокомпозиті показала максимальне вилучення 97 % для Pb(II). Досліджено адсорбційну ємність у моделі псевдодругого порядку для Pb(II) і отримано значення 1,48 мг/г.*

***Ключові слова:*** *тирса, поліетиленімін, нанокомпозит, важкі метали, Pb(II).*