



Removal Of Dissolved Cadmium Ions from Contaminated Wastewater using Raw Scrap Zero-Valent Iron And Zero Valent Aluminum as Locally Available and Inexpensive Sorbent Wastes

Hayder M. Rashid and Ayad A.H. Faisal

University of Baghdad / Environmental Engineering Department

Abstract

The current study was to examine the reliability and effectiveness of using most abundant, inexpensive waste in the form of scrap raw zero valent aluminum ZVAI and zero valent iron ZVI for the capture, retard, and removal of one of the most serious and hazardous heavy metals cadmium dissolved in water. Batch tests were conducted to examine contact time (0-250) min, sorbent dose (0.25-1 g ZVAI/100 mL and 2-8 g ZVI/100 mL), initial pH (3-6), pollutant concentration of 50mg/L initially, and speed of agitation (0-250) rpm. Maximum contaminant removal efficiency corresponding to (90 %) for cadmium at 250 min contact time, 1g ZVAI/ 6g ZVI sorbent mass ratio, pH 5.5, pollutant concentration of 50 mg/L initially, and 250 rpm agitation speed were obtained. Langmuir and Freundlich isotherms were presumed to fit the batch kinetics data for the sorption of Cd(II) onto ZVAI and/or ZVI and found that Langmuir (I) was the most representative model type with coefficient of determination R^2 greater than 0.9115. Kinetics data for the sorption of Cd(II) onto ZVAI/ZVI mixture and due to the good agreement between the fitted and the experimental results; the data was found to obey the pseudo second order model. The scanning electron microscopy (SEM) for the ZVI and ZVAI was conducted before and after the sorbent-liquid reaction and revealed distinct morphological changes in the sorbent surface due to the contaminant saturation and pore channel blockages that ceased the sorption process.

Keywords: Cadmium, ZVI, ZVAI, Langmuir, SEM, Equilibrium

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1- Introduction

The echo system nowadays suffers in nature from the drastic and devastating impacts resulted from the direct/indirect disposal of the most toxic heavy metals that due to their higher relative density are capable of penetrating and percolating down the unsaturated soil towards the most vital water resource (groundwater) and contaminate it. Rather than the contamination resulted from the natural activities, the anthropogenic sources also contribute to such contamination. These sources comprise the illegal midnight dumping, UST leakages, improper disposal of drums of hazardous wastes, uncontrolled incineration, and discharging of heavy metal based liquid wastes into other territories of the most common problems encountering the ecosystem pollution is the widespread contamination of surface water and groundwater with heavy metals. These metals are defined as metallic elements that have a relatively high density compared with water. In addition to the arsenite, zinc, lead, mercury, cobalt, chromium heavy metals, cadmium is one of the most hazardous species that easily damage the human organs [5], this metal has had higher tendency

to accumulate kidney tissues when accidentally ingested [6].

During the 60's, the passive *in situ* remedial technique of pump and treat was used to remove the heavy metals from contaminated groundwater. Due to ongoing accumulation of contaminants and its effectiveness during the later stages of the remedial process; this technique was limited for the contaminant recovery only [10]. A promising *in situ* remedial technology such as PRB has recently emerged to use sequenced sorbent materials [11], [12] or mixed sorbents [13]. Different materials such as peat, coconut shells, corns, red mud, waste fillers, workshop scrapes of iron and aluminum, etc., have been proposed to construct the matrix of the PRB. Different ex-studies are analogous in principle to this study such as [14] for the investigation of silty-clay soils as reactive medium for the sorption of cadmium [15] conducted a batch study using zero valent iron as a reactive medium for the removal of high level cadmium from groundwater, [16] studied the biosorption of cadmium onto *Lechuguilla* biomass, [17] investigated the feasibility of using a mixture of activated sludge with ZVI for the removal of cadmium from contaminate groundwater.

investigated the removal of red dye and cadmium from wastewater using CKD, Error! Reference source not found. used a mixture of ZVI and ZVAI at optimum conditions for the removal of dissolved heavy metals.

The object of this study was to decontaminate cadmium based wastewater using other abundant and inexpensive wastes such as ZVI and ZVAI scrap wastes produced from certain workshops in Baghdad and other governorates; the sustainability aims to ease the overburden of such waste materials on the disposal sites and using them for longtime capture of cadmium to prevent it from being spread further distances and contaminate the water resources. The remedial process was to utilize optimum conditions and proper sorbent mass ratios resulted from a batch study to achieve maximum removal efficiency of the dissolved Cd (II).

2- Experimental work

2.1 Materials

Certain quantities of ZVI and ZVAI scrap wastes have been collected from different commercial workshops in Baghdad; these proposed sorbents were separated from other foreign matters such as splinters, dirt, stubs, hairs, etc., the sorbents were crushed, pulverized, and sieved using vibratory sieve 75 mesh number and the sieved particles were finally prewashed using 0.1 M H₂SO₄ solution for 10 min for the preparation of ZVI and 10 ml concentrated HCl solution for 20 min for the preparation of ZVAI (Lien and Wilkin, 2004). A sample of wastewater was prepared by contaminating deionized water with 2.1 g Cd(NO₃)₂ dissolved in 250 ml of deionized water and kept at room temperature of (25°C). The pH of the prepared solution was varied using 0.1 M NaOH or 0.1 M HNO₃ to obtain different values of pH (3-6).

2.2. Batch Tests

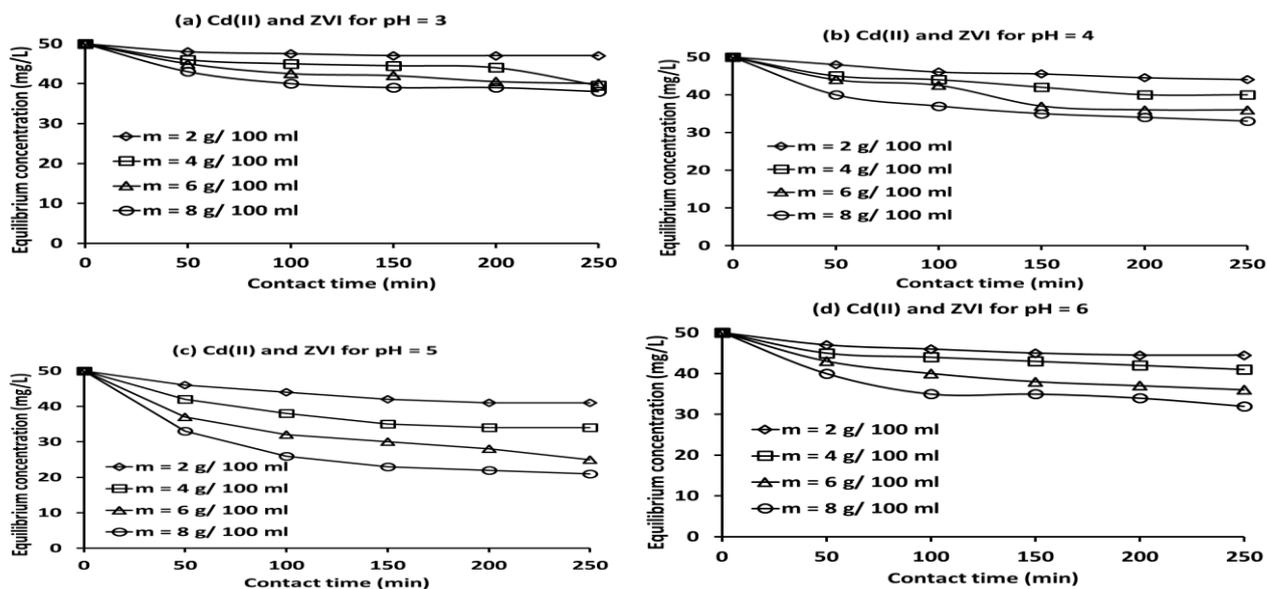


Fig. 1. Sorption of Cd(II) onto ZVI at different values of pH

Based on fixed temperature of 25 °C, several batch experimental parameters of contact time (0-250) min, initial pH (3-6), initial concentration (50-250) mg/L Cd(II), different ZVI/ZVAI dosage ratios (g/g) per 100 mL, and agitation speed (50-250) rpm were investigated on the removal of this contaminant.

Different masses of 0.25, 0.50, 0.75, and 1.00 g ZVAI and 2, 4, 6, and 8 g ZVI were placed into 100 ml of 50 mg/L cadmium solution contained in 250 mL flasks.

Different agitation speeds of (0- 250) rpm were used to vigorously shake the solid-liquid solution using shaker incubator type DAIKI, Korea. An aliquot of 20 ml was withdrawn and filtered to measure the residual concentration of heavy metal left in aqueous solution.

A sample of 10 ml of filtrate was withdrawn and measured for the concentration of dissolved metal ion using AAS flame (type Shimadzu, Japan). The number of cadmium milligrams captured by 1 g sorbent is given by Eq.(1):

$$C_s = (C_o - C_e) \frac{V}{m} \quad (1)$$

3- Results and Discussion

3.1. Sorbent Selectivity

A number of batch experiments were conducted to examine the reliability and effectiveness of ZVI and ZVAI at optimum conditions and varied pH values to achieve the desired removal efficiency:

- 1- The sorption of Cd(II) onto ZVI at different pH values revealed a 57% removal of cadmium at pH 5 as shown in Fig. 1
- 2- The sorption of Cd (II) onto ZVAI at different pH values revealed a 88% removal of cadmium using 1 g ZVAI/ 100 ml at pH 5.5 as shown in Fig. 2.

The replacement of the ZVI by ZVAI revealed good removal enhancement

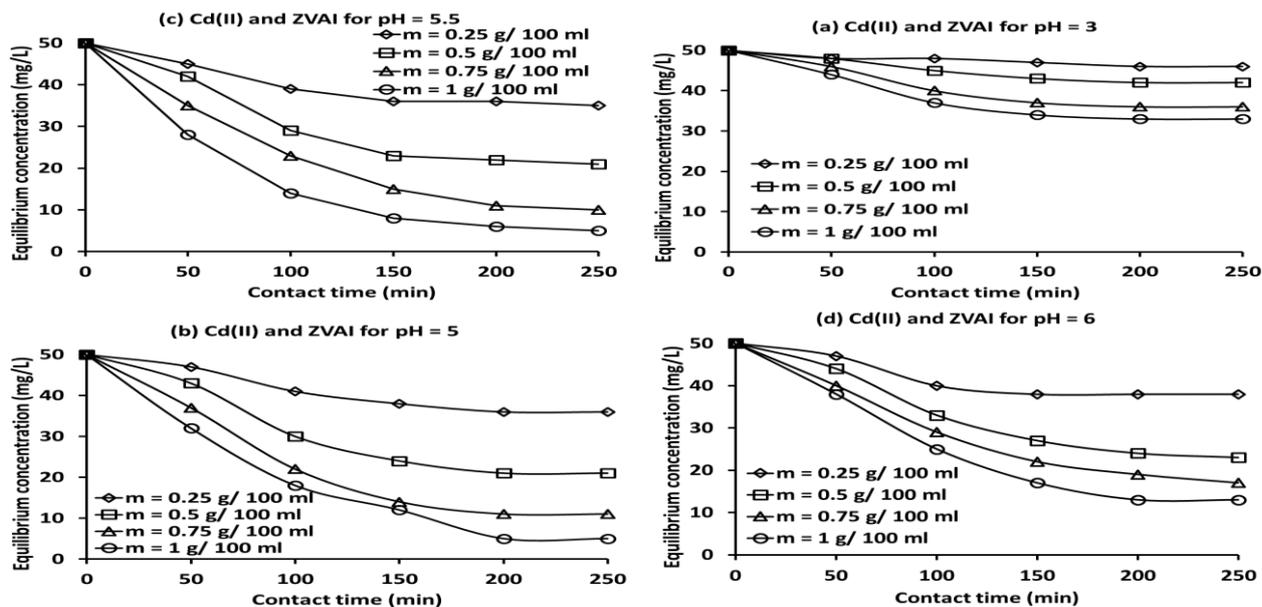


Fig. 2. Sorption of Cd(II) onto ZVAI at different values of pH

3.2. Equilibrium Time

A time interval of (50-250) min was used as contact time for the batch experiments. The driving force for the mass transfer has already ceased when a state of equilibrium was satisfied. Fig. 2 revealed a stabilization for the equilibrium concentration beyond 200 min and up to 250 min for the sorption of cadmium onto (0.25-1) g ZVAI at different pH values; this is due to the surface coverage by cadmium that has almost blocked most of the pore channel; therefore no further vacant sites were available to receive more cadmium ions that rendered the rate for the contaminant concentration approaches zero; this rate attains its maximum value during the first stages of the sorption process since no more active sites were fresh and available. The contact time for the removal of 88% of the cadmium was already determined as 250 min which is set as a reference contact time for other experiments.

3.3. Initial pH

The pH experimental parameter is considered as significant and sensitive for the dissolution or precipitation of heavy metals in water. Different values of pH values in the range of (3-6) were adjusted for the sorption of cadmium onto ZVI and/or ZVAI corresponding to 50 mg/L contaminant initial concentration and different times of contact at temperature of 25 °C.

Fig. 3 revealed maximum sorption capacity within pH (5-5.5) to yield maximum removal efficiency of 88% for pH less than 4, more protons H^+ were available to compete with cadmium for the adsorption over the sorbent surface while at pH greater than 4, the protons were eliminated and such competition subsided to cause an increase in the removal efficiency.

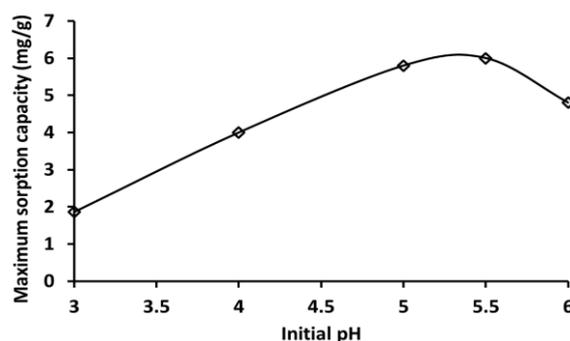


Fig. 3. Effect of initial pH on the removal of Cd(II) from aqueous solution

3.4. Effect of Sorbent Dosage

The individual masses or combination of ZVI and ZVAI were investigated for the removal of cadmium at the best experimental batch conditions of pH 5.5, 50 mg/L initial contaminant concentration, and 250 rpm agitation speed to achieve maximum removal efficiency.

Different sorbent dosages of (2-8) g ZVI and (0.25-1) g ZVAI per 100 ml of aqueous solution were used in this regard and found out that the higher removal efficiency is always associated with the higher sorbent dosage. Obviously, the higher dosage provides larger number of active sorption sites for the capture of this heavy metal species; furthermore, any further increase in the sorbent mass would promote surface coverage by the contaminant itself and hence stabilizes the removal efficiency.

3.5. Effect of Initial Contaminant Concentration

A concentration range of (50-200) mg/L cadmium ions were prepared to investigate the relationship between

initial concentration of the contaminant and the removal efficiency.

Fig. 4 depicted the inverse relationship between the initial contaminant concentration and the corresponding removal efficiency i.e., the higher the initial concentration, the lower the removal efficiency is associated, the figure also showed removal efficiencies of 88, 83, 75, and 43% corresponding to 50, 100, 150, 200 mg/L respectively.

It is evident that maximum driving force is attained for the solute transport from the higher concentration at the bulk solution to the lower concentration at the sorbent surface; therefore, maximum removal efficiency is always accompanied with higher initial concentration.

3.6. Effect of Agitation Speed

Different agitation speeds of (0-250) rpm were investigated on the removal efficiency of cadmium ions at fixed experimental parameters; pH 5.5, 50 mg/L initial contaminant concentration, and 250 min contact time.

The removal efficiency is directly proportional to the agitation speed in such a way that no cadmium removal is achieved when no agitation is induced while 88% of cadmium was removed corresponding to agitation speed of 250 rpm as shown in Fig. 5; this elucidates the most probable decrease in the thickness of the boundary layer surrounding the sorbent solid phase (Nernst film) which is in nature exhibits some resistance to the solute transport and hence causing maximum concentration gradient and additional mass loading from the bulk solution to the solid phase medium.

3.7. Sorption Kinetics

Sorption is generally influenced by intra particle diffusion and physicochemical processes **Error! Reference source not found.**

Table 1 exhibited the batch experimental kinetics for the sorption of cadmium ions onto the best mass ratio of the sorbent mixture ZVAI/ZVI and optimum conditions.

Rather than the fitted pseudo first order kinetics model Eq.(2), the last two columns of the table have revealed good agreement between the fitted pseudo second order model Eq.(3) and the experimental data.

These equations have been linearized and fitted for the kinetics data for the sorption of cadmium ions and the constants for best equation, i.e. pseudo second order model, are summarized in Table 2

$$\frac{dC_s}{dt} = k_1(C_{se} - C_s) \quad (2)$$

$$\frac{dC_s}{dt} = k_2(C_{se} - C_s)^2 \quad (3)$$

Table 1. Kinetics data for the sorption of Cd(II) onto ZVAI/ZVI mixture at optimum pH 5.5, 250 min contact time, 50 mg/L initial metal concentration, and 250 rpm agitation speed

Time (min)	C _e (mg/L)	C _s (mg/g)
50	25	0.3571
100	13	0.5286
150	9	0.5857
200	7	0.6143
250	5	0.6428

Table 2. Constants corresponding to the pseudo second order for the Cd(II) sorption onto the ZVAI/ZVI mixture

Metal	Parameter	Value
Cd(II)	C _{se} (mg/g)	0.6430
	k ₂ (g/mg min)	0.0960
	R ²	0.9652

Results proved that the sorbed amount at equilibrium for the pseudo second order kinetics of cadmium was equal to 0.603 mg/g and this value was almost as close as the experimental 0.6428 mg/g.

The results have elucidated that the chemisorptions is the most predominant mechanism for the sorption process under consideration.

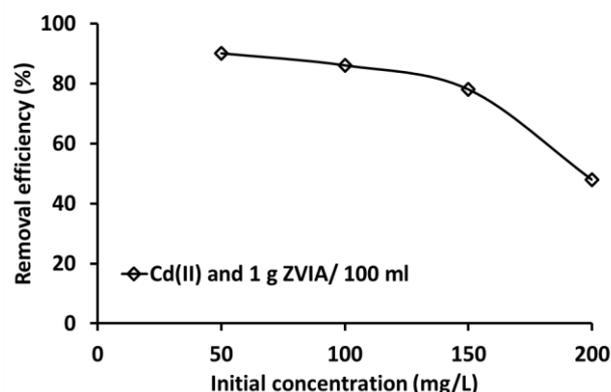


Fig. 4. Effect of initial concentration on the removal efficiency of cadmium ions onto ZVAI at pH 5.5, 50 mg/L initial contaminant concentration, and 250 min contact time

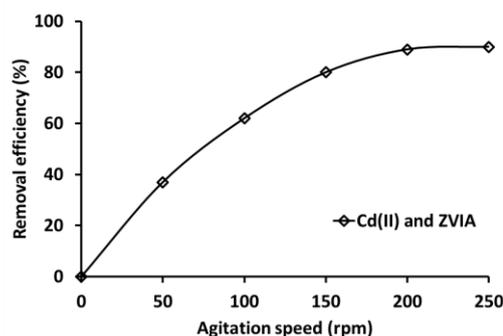


Fig. 5. Effect of agitation speed on the removal efficiency of cadmium ions onto ZVAI at pH 5.5, 50 mg/L initial contaminant concentration, and 250 min contact time

3.8. Selection of the Best ZVI/ZVAI Mass Ratio

The mixing up of certain amounts of ZVI and ZVAI has positive effect on the removal efficiency as shown in Fig. 6 Different proportions were roughly examined such that the equilibrium concentrations of the cadmium ions as a function of contact time for different proportions of ZVAI and ZVI were plotted. It is clear that the concentration has dropped from 50 to 28 mg/L to yield a removal efficiency of 44% using 0.75 g ZVAI/ 5 g ZVI per 100 ml, while dropped to 5 mg/L to yield a removal efficiency of 90% using 1 g ZVAI/ 6 g ZVI per 100 ml. The best mass ratio was found to be 1 g ZVAI and 6 g ZVI (equivalent to the 14% ZVAI and 86% ZVI) corresponding to contact time of 250 min, pH of 5.5 and agitation speed of 250 rpm for initial contaminant concentration of 50 mg/L.

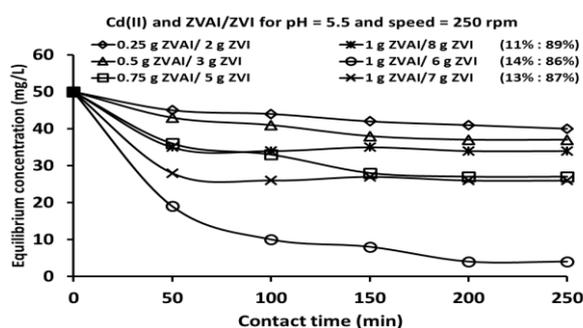


Fig. 6. Variation of equilibrium Cd(II) concentration as a function of contact time using different proportions of ZVAI / ZVI

3.9. Sorption Isotherms for Cadmium Uptake

At fixed temperature, sorption relationships relating the number of milligrams of contaminant captured onto 1 g of sorbent to the cadmium concentration at equilibrium in the form of mathematical or empirical equations is called isotherms [20]. Many sorption isotherms such as Hill De Boer, Temkin, Kesiliv, Elovich, etc., were performed by many researchers and the two most well-known isotherms are the Langmuir and Freundlich. Based upon the experimental sorption data, different forms of Langmuir I, II, III, and IV as well as Freundlich were proposed to investigate which one to well fits these data and according to the to the highest coefficient of determination (R^2).

Table 3 presents the linearized forms of Freundlich and Langmuir isotherm model.

Table 3. Linearized forms of Freundlich and Langmuir isotherm models used in the present study for the describing the uptake of Cd(II) onto ZVAI and ZVI

Model Isotherm	Linearized Formula	R^2
Freundlich	$\ln C_s = \ln k_F + n \ln C_e$	0.3209
Langmuir (I)	$C_e/C_s = (1/ab) + (1/a) C_e$	0.9115
Langmuir (II)	$1/C_s = (1/ab)(1/C_e) + 1/a$	0.4034

Langmuir (III)	$C_s = a - (1/b)(C_s/C_e)$	0.0835
Langmuir (IV)	$C_s/C_e = ab - b C_s$	0.0852

3.10. SEM Analysis

One of the most necessary analyses to conduct comparisons over what was going on before and after the cadmium sorption onto the sorbing media, the scanning electron microscopy (SEM) has turned up to depict such comparisons to reveal the surface shape, particles distribution, contaminant distribution, morphological changes, etc., Fig. 7 depicted the SEM images for the ZVI and ZVAI before and after the reaction with cadmium ions. The 500 times magnified SEM images Fig. 7 have revealed the followings:

- Before the reaction, the nature of the ZVI surface was characterized by rough homogenous texture with tremendous number of pore channels to considerably increase the sorption of contaminants and entrap them deep into these channels of the active sorption sites.
- The reaction, the nature of the ZVI surface was characterized by almost smooth homogenous texture with highly blocked channels and surface saturation of traces of contaminants in white color. The sorption; as a result; has considerably been reduced such that no more contaminants are sorbed thereafter.
- Before the reaction, the nature of the ZVAI surface was characterized by extremely smooth homogenous texture of remarkable abrupt change in surface morphological shape with descending grooves that have seemingly responsible for the sorption of contaminants.
- After the reaction, the nature of the ZVAI surface was characterized by groovy lumped and rough texture with remarkable traces of whitish color contaminants sorbed that almost covered the ZVAI surface and due to such coverage, the sorption consequently reduced.

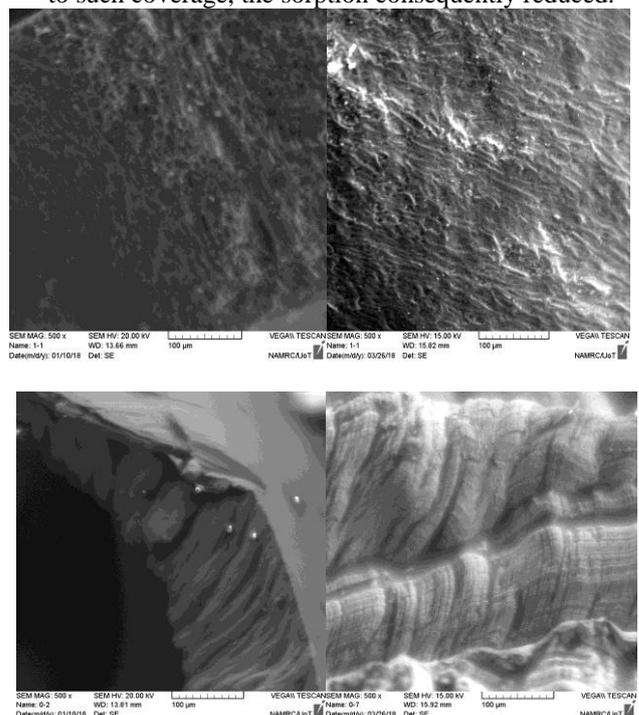


Fig. 7. SEM images for the ZVI (top) and ZVAI (bottom) sorbents before and after the reaction with Cd (II)

4- Conclusions

- 1- The cadmium sorption over ZVI and/or ZVAI has significantly been influenced by a set of batch experimental tests to determine the optimum batch experimental parameters to achieve maximum removal efficiency. These parameters included the initial contaminant concentration, contact time, initial pH, sorbent dosage, agitation speed corresponding to 50 mg/L, 250 min, 5.5, 1 g ZVAI/ 6 g ZVI per 100 mL, and 250 rpm respectively to achieve 88% Cd(II) removal.
- 2- The sorption of cadmium onto individual sorbent of either ZVI or ZVAI proved lower insignificant removal efficiency when compared with mixing up these sorbents i.e., a mass ratio of 1 g ZVAI/ 6 g ZVI was the best to achieve 90% Cd(II) ions removal rather than using 0.75 g ZVAI/ 5 g ZVI to yield 44% Cd(II) ions removal among several investigations over different sorbent mass ratios.
- 3- The Langmuir (I) was found to well represent the kinetics data for the sorption of cadmium ions onto the ZVAI/ZVI composite sorbent and at the best batch experimental conditions with coefficient of determination (R^2) greater than 0.9115; the Langmuir sorption constants were (0.307-6.34) mg/g as maximum sorption capacity and (0.19-1.54) L/mg as sorption affinity.

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ازالة ايونات الكاديوم من مياه الفضلات الملوثة باستخدام مخلفات برادتي الحديد والالمنيوم الصفر التكافؤ كملوثات مازة متوفرة محليا ورخيصة

الخلاصة

تقوم الدراسة الحالية على فحص مدى قابلية وفعالية استخدام مخلفات برادة الحديد والالمنيوم كفضلات متوفرة ورخيصة في اقتناص, اعاقه, وازالة اكثر العناصر الثقيلة خطورة وهو الكاديوم الذائب في الماء. لقد تم استخدام معالم تجريبية في اختبارات الوجبة مثل زمن تماس (0-250) دقيقة, جرعة (1-0.25) غم برادة المنيوم و(2-8) غم برادة حديدا 100مل من المحلول المائي الملوث, دالة حامضية (3-6), تركيز بدائي للملوث (50-200) mg/L وسرعة تقلب (0-250) دورة في الدقيقة حيث تحققت 90% ازالة للكاديوم مقترنة بأفضل معالم تجريبية وهي زمن التماس (250) دقيقة, جرعة (1) غم برادة المنيوم و(6) غم برادة حديدا 100مل من المحلول المائي الملوث, دالة حامضية (5.5), تركيز ملوث بدائي (50) mg/L وسرعة تقلب (250) دورة في الدقيقة ومن خلال نتائج تجارب الوجبة تبين ان موديل لانكمير (I) هو افضل تمثيل لبيانات امتزاز الكاديوم على برادة الالمنيوم والحديد وبمعامل ارتباط اكبر من 0.9115 وقد وجد ان بيانات حركيات التفاعل لامتزاز الكاديوم على خليط البرادتين وكنتيجه لمدى التقارب الحاصل بين النتائج النظرية والعملية تخضع لنموذج تفاعل الرتبة الثانية الكاذب حيث تكون الية الامتزاز الكيمائي هي المهيمنة على عملية الامتزاز.

لقد تم اجراء الفحص المجهرى لكل من برادة الحديد والالمنيوم قبل وبعد التفاعل بينها قبين الكاديوم وقد لوحظ بان هنالك تغييرات سطحه للمواد المازة نتيجة لتشبعها بالملوث وغلق قنواتها المسامية والتي كانت سبب في توقف عملية الامتزاز.