Removal of lead ions from wastewater using crushed concrete demolition waste

Alyaa F. Ali 1*, and Ziad T. Abd Ali 2

1 Department of Environmental Engineering, University of Baghdad, Baghdad, Iraq, alyaaafaris94@gmail.com
2 Department of Environmental Engineering, University of Baghdad, Baghdad, Iraq, z.teach2000@yahoo.com

* Corresponding author: Alyaa F. Ali, email: alyaaafaris94@gmail.com

Published online: 31 December 2019

Abstract— The sorption of Pb²⁺ ions from synthetic wastewater using crushed concrete demolition waste (CCDW) which collected from a demolition site was investigated in a batch sorption system. Factors influencing on sorption process such as shaking time (0-300 min), initial concentration of contaminant (100-750 mg/L), shaking speed (0-250 rpm), and adsorbent dosage (0.05-3 g/ml) have been studied. Batch experiments confirmed that the best values of these parameters were (180 min, 100 mg/l, 200 rpm, 0.3 g CCDW/100 ml) respectively where the achieved removal efficiency is equal to 100%. Sorption data were described using four isotherm models (Langmuir, Freundlich, Redlich-Peterson, and Radke-Prausnitz). Results proved that the pure adsorption and precipitation are the main mechanisms for removal of lead ions from aqueous solution onto CCDW and sorption data can be represented by Langmuir model. The lead ion was successfully removed from aqueous solution during batch experiments using (CCDW) in the particle size range 2–1 mm. The principal mechanism of uptake of Pb²⁺ was found to be by diffusion into the cement matrix and this was detected by Scanning electron microscopy.

Keywords— Sorption, Recycling, Concrete Demolition waste, Heavy metal ion, Isotherm.

1. Introduction

Each year industrial activities output of materials and chemicals bring about very large amounts of wastes containing heavy metals. Heavy metals possibly present in a diversity of forms, like sulphate, fluoride and chloride. Most of them are toxic, carcinogenic and mutagenic. Wastes containing toxic pollutants consider a dangerous threat to animal and human health because the concentration of pollutants in wastes diverse in a broad range and may exceed the approval threshold of the environment and need treatment [6]. Traditional wastewater treatment processes like coagulation, membrane separation flocculation, ion exchange, and reverse osmosis have long been managed to supply better quality of water and to treat wastewater prior discharging it into water bodies [18]. But, these methods are costly, and cost reduction is needed [7]. Lately, scientists have been studying a cheap and plentiful sorbent to remove heavy metals from wastewater. Natural and industrial geomaterials and biosorbsents are well known sorbents, and researchers have done many tests to identify the adsorption capacity of those materials [16]. Rapid civilization, industrialization, and population growth in developing and developed countries produce millions of tons of construction and demolition waste (CDW) per year. Consequently, researchers predict that countries will produce massive amounts of CDW materials in the future, creating many environmental problems. Therefore, investigation of the efficient recycling and usage of those abundantly available resources for different activities is timely. The utilize of alkaline cement and other portland cement compounds can be chemically categorized as a highly heterogeneous material, thus, dissolved metals in the aqueous solution can be removed by adsorption and precipitation [26, 27]. In order to describe the precipitation phase and the simultaneous adsorption–precipitation phase it is favored to adopt a
gradually operation manner for the description of these mechanisms. The variance between these phases can be clarified by the adsorption phase, as follows [13]:

- Precipitation by metal (M) hydrolysis
  \[ X_2O + H_2O \rightarrow 2X(OH) \]  
  \[ MSO_4 + X(OH) \rightarrow M(OH)_2 \downarrow +XSO_4 \]
  where X: Ca, Mg, K; Na; M: Pb, Cu, Ni … etc
- Adsorption of metal onto Cement compounds (CC) particles
  \[ M(OH)_2 + CKD \rightarrow CC - \{ - M(OH)_2 \} \]

Accordingly, it is visualized that the basis of demolition waste is concrete maybe affect the removal of toxic pollutants from contaminant water current. The scientist announced herein has been conducted to examine crushed concrete demolition waste (CCDW) and to define the kind of the reaction of aqueous containing metal ion with it. It has been investigated in a batch sorption study the removal of heavy metals from contaminant aqueous solutions by the 1–2mm fraction of CCDW, the granules of CCDW loaded metal ions were tested by scanning electron microscopy and energy dispersive X-ray analysis to define the kind of the CCDW–metal ion interactions.

2. Isotherm models

In the current study, a range of isotherm models are used to simulate the performance of CCDW in removing of heavy metals ions from wastewater. A summary of these models is presented below:

- **Langmuir model:** presume regular energies of sorption, upon the surface and no emigration of sorbate in the plane of the surface. It can be written as follows:
  \[ q_e = \frac{q_m b C_e}{1 + b C_e} \] (4)
  where \( q_m \) is the maximum sorption capacity (mg/g) and \( b \) is the constant related to the free energy of sorption (l/mg) [17].

- **Freundlich model:** is quantified by:
  \[ q_e = K_f C_e^{1/n} \] (5)
  where \( K_F \) is the Freundlich sorption coefficient and \( n \) is an empirical coefficient indicative of the intensity of the sorption [17].

- **Redlich–Peterson Model:** In some combination of both Langmuir and Freundlich features, a Redlich–Peterson isotherm comes like a hybrid isotherm model often utilize to represent solute adsorption data on heterogeneous surfaces with incorporation of three parameters into an empirical equation as follows:

  \[ q_e = \frac{K_RC_e}{1 + a_RC_e^{\beta R}} \] (6)

where \( KR \), \( aR \), and \( \beta R \) are constants. The \( \beta R \) takes the values ranged from 0 to 1.

The Redlich–Peterson model is taken the form of Langmuir model when \( \beta R \) equal to 1, while it is reduced to the form of Freundlich model for \( \beta R \) equal to 0[14].

- **Radke–Prausnitz Model:** this model is given as follows:
  \[ q_e = \frac{qmRP_KR_{RP}C_e}{qmRP_KR_{RP}+C_e^{mRP}} \] (7)
  where \( qmRP \) is the maximum adsorption capacity (mg/g), while \( KRP \) and \( mRP \) are constants [24].

3. Experimental work

3.1 Materials

Waste concrete was collected from a demolition site and then manually washed with tap water to remove any other undesirable material. It was crushed with miller, sieved into (2 - 1) mm, and then it was washed before being used with distilled water to remove fine powder and then dried. This was used for the batch experiments and characterization. The physical properties of the crushed concrete such as surface area=11.0956m2/g, bulk density=1.0481g/cm3, real density=2.6202g/cm3, and Porosity=0.6 were measured at Oil Research and Development Center-Ministry of Oil. Lead was selected as a representative of heavy metal contaminants. To simulate the water’s lead contamination, the stock solution (1000 mg/L) of Pb(NO3)2 (manufactured by BDH, England) was prepared by dissolving an appropriate quantity of metal salt in distilled water and then stored in glass container at room temperature.

3.2 Characterization of CCDW

Samples of CCDW were tested by energy dispersive X-ray analysis (EDX) (TESCAN, Vega III, Czech Republic). Energy Dispersive X-Ray analysis (EDX) is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM) used to recognize the elemental composition of materials. The data produced by EDX examination includes of spectrum showing crests identical to the elements making up the true composition of the sample being analyzed [23].

3.3 Batch experiments

The batch experiments were conducted through a set of four experiments to identify the conditions affecting the highest removal efficiency of the pollutant. These...
conditions included shaking time, initial concentration of contaminant, shaking speed and sorbent dosage. The first set included shaking time variation (0-300 min) at initial concentration of contaminant, shaking speed and sorbent dosage of 250 mg/l, 200 rpm and 0.2 g CCDW/100 ml of contaminant solution respectively. The second set included a solution variation in the initial concentration of contaminant (100, 150, 250,500 and 750 mg/l) at an optimum time of shaking obtained from the results of the first set. While maintaining shaking speed and sorbent dosage at their former values. The third set included variation in shaking speed (0, 50, 100, 150, 200 and 250 rpm) at optimum initial concentration of contaminant obtained from the outcome of the second set; while the values of the rest of the factors remained the same as in the second set. Finally, the last set included variation of CCDW dosage (0.05-3g/ml) with an optimum shaking speed obtained from the outcome of the third set; while the value of the rest of the factors remained the same as in third set. In the experiments mentioned above, 250 ml flasks were utilized, where in every flask 100 ml of contaminant solution with a certain amount of sorbent dosage were added. The flasks were shaken by an incubator shaker (ISO 9001, Model: LSI-3016, Korea). At the end of any specific experiment, a 20 ml of solution sample pulled from the flask and subsequently filtered using filter paper. 10 ml sample was withdrawn from the filtered supernatant to determine the concentration of metal by using atomic absorption spectrophotometer (AAS) (Model: 210 VGP, USA). However, the efficiency of heavy metal removal (Removal %) was calculated as follows:

\[
R = \left[\frac{(C_0 - C_e)}{C_0}\right] \times 100
\]

Where Co and Ce are the initial and the equilibrium contaminant concentrations, respectively. R is the removal efficiency (%). From a mass balance it can be specified the amount of sorbed contaminant (qe) retained in the CCDW phase, by taking into consideration its initial and equilibrium concentrations, therefore pure sorption can be calculated:

\[
q_e=(V(C_o-C_e))/m
\]

where Co and Ce are the initial and equilibrium concentrations of contaminant in the solution (mg/l), V is the amount of solution in the flask (l), and m is the mass of adsorbent material in the flask (g).

4. Results and discussion

4.1 Characterization of CCDW samples

It is essential that the cement matrix of CCDW chosen for this study was adequately ancient because immature cement pastes contains appreciable ratio of residual anhydrous phases and contains unrefined pore networks which may affect the nature of their interactions with heavy metal ions [9]. For this reason, new concrete was not used and CCDW was selected for old buildings. A corresponding energy dispersive X-ray (EDX) spectrum confirmed the existence of Ca, Si, Al, S, Fe, Mg, Na, and K as the major components were found to be approximately 27.13%, 9.26%, 3.48%, 1.24%, 1.15%, 0.81%, 0.78%, 0.41% respectively. These elements are representative constituents of Portland cement, therefore, constituent concentrations is different according to the ratio of phases existent in a given position, though, it must be indicated that hydrated cement is heterogeneous on a microscopic scale [9].

4.2 Influence of Batch Operating Parameters

4.2.1 Effect of Contact Time

Fig.1 presents the influence of shaking time on Pb\(^{2+}\) removal using 0.2 g CCDW add to 100 ml of contaminated solution with initial pH=4, as shown in Fig.1. This figure represents the removal efficiency of the contaminant significantly raise with an increment in shaking time. It is obvious that the removal process was initially rapid and gradually began to slow down after a while [22]. Therefore, diminishing in the sorption sites of the reactive material lead to slower sorption. The kinetic data for CCDW presented that 81% Pb\(^{2+}\) was removed utmost at 180min. There was no evident change in remaining concentration of contaminants after this time of 180 min. So that the other batch experiments were performed with these value of shaking time. CCDW generally contains alkali and alkaline earth metals such as Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\)and Na\(^{+}\) which are primarily presented from fresh water, So that, when CCDW reacts with heavy metals bearing solution, the light metals released causing an increase in the pH of the solution due to the form of light metal alkalis, as illustrated in Fig.1.

4.2.2 Effect of initial concentration of contaminant

Fig.2 presents that when the initial concentration increases from 100 to 750 mg/L, the removal efficiency decreases from (91 to 35%) for Pb\(^{2+}\) by keeping all other parameters constant. The results present that there was a higher removal percent of the metal at the lower value of initial
concentration. The curve in Fig.2 represent that less desirable sites became included in the process when increasing concentration of metal ion due to the saturation of the effective sites obtainable on the CCDW to interact with the contaminant [21].

The simple hydrolysis of generality divalent metal ions particularly Pb2+ can be written as follows:

\[ M^{2+} + HOH \rightleftharpoons M(OH)^+ + H^+ \]  

(10)

where M2+ is either Pb2+ or any other metal ion.

The final pH increases when concentration of the solution decreases and this happens when M2+ (metal ions) is being taken up by the adsorbent, the reaction above shifts to the left, leading to the depletion of protons and hence a rise in pH [20].

The dependence of Pb2+ sorption on CCDW dosage was studied by varying the amount of sorbent within the ranges added to 100 ml of contaminated solution with conservation rest parameters constant as illustrated in Fig.4 This figure explain the greater obtainability of effective sites increases the removal efficiency as increasing the amount of dosage and this has been expected as a result of the high dosage amount of sorbent in the solution. In addition, this supposed that after a certain dosage amount of sorbent, the greatest sorption sets in and hence the amount of Pb2+ attached to the substance and the remaining amount of this contaminant in solution remain consistent even with the further increase with dosage amount of sorbent [1]. However, the best values of dosage were found to be 0.3 g CCDW/100ml for Pb2+ the value of final pH almost consistent between 7 and 8 as the mass of sorbent were increased. This explains solution had arrived state of saturation. Increases in pH because of presence carbonate content (HCO3−) in sorbent material which gives buffer capacity (alkaline condition) to the sample and this was increased due to increase the dosage amount of sorbent. Adding sorbent particles to an acidic aqueous solution, they will dissolve equalizing acids and will increase concentration of dissolved calcium [3].

\[ \text{Precipitate} = \text{initial} \ - \ (\text{bound to CCDW} + \text{remain in solution}) \]  

(11)

4.2.4 CCDW Dosage

Through the course of the study, a small amount of loose floc was observed to have deposited in the nearness of the CCDW particles. For this reason, that the word ‘removal’ has been more suitable than of ‘sorption’ or ‘uptake’ in this instance. The uptake of Pb2+ by attaching (bounded) to CCDW was specified by nitric acid digestion according to (Chaney/Mielke Method) [5] of the recovered CCDW and the corresponding proportions of Pb2+ present in the loose floc deposited was then calculated by a mass balance for the metal ion as follows:

Through the course of the study, a small amount of loose floc was observed to have deposited in the nearness of the CCDW particles. For this reason, that the word ‘removal’ has been more suitable than of ‘sorption’ or ‘uptake’ in this instance. The uptake of Pb2+ by attaching (bounded) to CCDW was specified by nitric acid digestion according to (Chaney/Mielke Method) [5] of the recovered CCDW and the corresponding proportions of Pb2+ present in the loose floc deposited was then calculated by a mass balance for the metal ion as follows:

\[ \text{Precipitate} = \text{initial} \ - \ (\text{bound to CCDW} + \text{remain in solution}) \]  

(11)
The final partitioning of the metal ion among that bounded to CCDW, precipitated, and that which remained in solution is depicted in Fig. 5.

**Figure 5:** The final partition of lead ion after 180 min.

### 4.4 Isotherm models

Four isotherm models are used to simulate the performance of CCDW in removing of heavy metal ion from contaminated wastewater. These models have been applied separately as mathematical (fitting) equations for pure sorption data (bounded to CCDW) and pure precipitation data (precipitated at the bottom of the flask), and then find the most consistent model which describes the two simultaneous processes (present model). Accordingly, the constants with the coefficient of determination for each model was determined by using nonlinear regression method in the Microsoft Excel (2007) [4]. Its summarized in Table 1 that there is a low matching between experimental (bounded & precipitated) and theoretical (isotherm models) data in comparison with present model, and this may be due to a high heterogeneity of CCDW material [8]. However, Langmuir isotherm models have the highest value of $R^2$ in each case. Accordingly, Langmuir model can be used to represent the bounded and precipitated portions for Pb$^{2+}$ as illustrated in Table 2.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Pb$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bounded</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g)</td>
<td>86.297</td>
</tr>
<tr>
<td></td>
<td>$b$ (l/mg)</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.907</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>22.824</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.296</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.877</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>$K_R$</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>$a_R$</td>
<td>0.306</td>
</tr>
<tr>
<td></td>
<td>$B_R$</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.338</td>
</tr>
<tr>
<td>Radke-Prausnitz</td>
<td>$q_{mRP}$</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>$K_{RP}$</td>
<td>0.376</td>
</tr>
<tr>
<td></td>
<td>$m_{RP}$</td>
<td>0.049</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.374</td>
</tr>
</tbody>
</table>
Table 2: Present model constants with coefficient of determination for removal of Pb$^{2+}$ onto CCDW.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Present model</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>$q_e^{total} = \frac{q_mb_{c_e}}{1 + bC_{ce}}$</td>
<td>$q_m\lambda_B$ (mg/g) 43.140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b\lambda_B$ (l/mg) 0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$q_m\lambda_P$ (mg/g) 43.140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b\lambda_P$ (l/mg) 0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$ 0.999</td>
</tr>
</tbody>
</table>

5. Scanning electron microscopy (SEM)

Secondary electron images of the surfaces of CCDW specimens before and after loading of heavy metal Pb$^{2+}$ using scanning electron microscope (TESCAN, Vega III, Czech Republic) are illustrated in Fig. 6. The scattered, shatter, irregular surface of CCDW before loading is depicted in Fig. 6(a,b). Fig. 6(c,d) displays the secondary electron image of a unique crystal cluster on the surface of Pb-CCDW; by checking of the surface failed to detect the rest substances of similar morphology. In general the surface of Pb-CCDW involved a reticular, lead-loaded, calcium-rich, distorted polygons, lead-loaded, calcium silicate network and rare [12]. The morphology of the reticular, lead-loaded network nearly look like that of sort II CSH (one of four calcium silicate hydrate morphologies that are created during cement [12, 26]. The electron images reveal that the removal of Pb$^{2+}$ by CCDW happen through diffusion into the cement matrix. As if the mechanism applied is isomorphic exchange by Pb$^{2+}$ for Ca$^{2+}$ in the calcium silicate hydrate phase. Identical, exchange by Pb$^{2+}$ for Ca$^{2+}$ (ionic radii 1.17 and 1.00Å, respectively [11]) in crystalline calcium silicate hydrates has been reported by other scientist [19].

![SEM images of CCDW and Pb-CCDW surfaces](image1)

Figure 6: Electron micrographs depicting the surfaces of: (a, b) CCDW; (c, d) Pb-CCDW
6. Conclusion

- Shaking time, initial concentration of contaminant, shaking speed, and CCDW dosage were the most important factors affecting the removal process of heavy metals. The best conditions were (180 min, 100 mg/l, 200 rpm, 0.3 g CCDW/100 ml), for Pb2+.
- The SEM images detect that the Pb2+ removal by CCDW happens through diffusion into the cement matrix. The results indicate that a rough surface of solid media, high sorptive capacity are beneficial in the removal of heavy metals from water. Thus, CCDW offers the possibility for cheap and effective media for remediation ground water contamination with heavy metals using permeable reactive barrier. Sorption and precipitation as metal oxide were two of the mechanisms that contribute to the removal of metal from the solution.

References


