

**Pb(II) Adsorption From Aqueous Solutions Onto Activated Zeolite 5A****<sup>1</sup>Alwan Nasif Jassim, <sup>2</sup>Dhafer Faza Ali, <sup>2</sup>Ikhlas H. Shamoon, <sup>2</sup>Waleed M. Abood, <sup>2</sup>Firas Shams Abbas, <sup>2</sup>Alaa T. Yassin**<sup>1</sup>General Commission for Industrial Research and Development, Ministry of Industry and Minerals,<sup>2</sup>Energy and Environment Research Center, General Commission for Industrial Research and Development, Ministry of Industry and Minerals,

Alwan Nasif Jassim, Dhafer Faza Ali, Ikhlas H. Shamoon, Waleed M. Abood, Firas Shams Abbas, Alaa T. Yassin: Pb(II) Adsorption From Aqueous Solutions Onto Activated Zeolite 5A

**ABSTRACT**

The present study is focused on removal of Pb( II) from aqueous solutions using thermally activated zeolite 5A as adsorbent. Factors that effect the lead removal include the optimum dosage, pH, and temperature. The maximum removal of lead was observed at pH = 7. Removal of Pb (II) increased from 82 % to 98.8% with increasing adsorbent dosage from 0.5g to3g, the adsorption process was found to obey Langmuir adsorption isotherm and Freundlich adsorption isotherm. From all that we can conclude that zeolite 5A is of practical importance and expected to be economical.

**Key words:** Divalent lead, Zeolite 5A, Adsorption, AFM microscope.**Introduction**

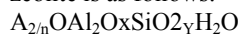
The presence of trace metals in the aquatic environment has been of great concern, because of their toxicity and non-biodegradable nature. There are high incidences of lead poisoning resulting from untreated industrial wastes [11,6,16].

Lead and its compounds are widely used as an industrial raw material for storage battery manufacture, printing, paint dyeing processes, and lead pipe. The potential environmental impact of waste water from metal and electroplating industries was evaluated by the examination of lead content [14,3].

Lead is chemically very similar to calcium, and so it is then distributed to different sites of the body where calcium plays an important rule in teeth and in bones of all ages . Lead primarily affects the nervous system, viral function and blood cells. Acute high lead exposure can cause serious physiologic effect like long damage to brain function and organ system.

Many investigations on the use of zeolite to remove heavy metals contamination before discharge into water basins have been reported [12,25,10,1] .

Zeolite is crystalline solid with small pores. It has pores with dimension of 3 to 10 Angstroms. They are called molecular sieves. Zeolite A and X are well known for higher removal of heavy metals than other types. They exhibited higher specific surface area and ion exchangeable capacity [20,30,5,19]. All of zeolites have 10-20 percent water in their composition. They loose their water at heat without any destruction in their structure. This process is returnable [7,8,27]. Empirical formula for zeolite is as follows:



Where A is an alkaline cation and n is cation capacity. The values of x and n vary from 2 to 10 and 2 to 7 respectively [22].

The aim of the present study is therefore to evaluate exchange behavior of zeolite 5A for removal of lead (II) from aqueous solutions in batch process. The effect of pH, temperature and adsorbent amount on adsorption capacity has been studied and equilibrium parameters have been evaluated.

**Materials And Method****Adsorbent:**

Industrial zeolite 5A (purchased from Fluka, Germany) has been used in this work for the removal of lead (II) ions from aqueous solution .Zeolite is in the form of cylindrical pellets with 3mm diameter and 6mm length. The zeolite samples were activated

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by heating for 12h in a stepwise manner from room temperature to 450 C°.

#### *Chemicals and reagents:*

Chemicals used for the experiments are of AR grade. Double distilled water is used for all experiments. Lead(II) ions standard solutions were prepared from standard ampoules purchased from Riedel-deHaen.

#### *Buffer preparation:*

Different pH buffers (acetic acid+sodium acetate) have been used over a range of 3-7 to study the effect of pH on the removed efficiency of the adsorbent.

#### *Characterization and Morphology Analysis:*

The infra-red analysis was conducted on SHIMADZU FT-IR-8900S spectrophotometer. X-ray powder diffraction analysis were performed by using a XRD-Shimadzu 6000 diffractometer equipped with graphite secondary monochromator. Also, atomic force microscope (AFM) (AA300 scanning probe microscope-Angstrom Advanced Inc.) was used for morphology study of zeolite. AFM is relatively new imaging technique for studying the morphology of particles such as clay [9,4].

#### *Equilibrium studies:*

Batch equilibrium experiments have been carried out to find the optimum pH, temperature and equilibrium isotherms. A series of 100 ml conical flask are employed. The procedure involved filling each flask with 50 ml of Pb(II) ions solution of 50 ppm. Certain amount of zeolite is added into different flasks and shaken intermittently in an electrical horizontal bench shaker for four hours and the flasks have been sealed and kept for 24h to achieve equilibrium. A known volume of the solution was removed and filtered for Pb(II) analysis by atomic absorption spectrophotometer (AAS). The effect of pH, for lead ions removal using zeolite is studied in a pH range of 3 to 7. The amount of zeolite is varied from 0.5 to 3.0 gm. In this investigation temperature range varied from 280K° to 318K°.

The amounts of Pb(II) sorbed by zeolite (q) in the sorption system were calculated using the mass balance:

$$q = V(C_1 - C_e) / m \quad (1)$$

Where V is the solution volume (L), m is the amount of sorbent(g), and C<sub>1</sub> and C<sub>e</sub>(mg/L) are the

initial and equilibrium metal concentration respectively.

## **Results and Discussion**

Adsorption of Pb(II) ions was studied on zeolite 5A under the optimize conditions of pH, amount of adsorbents and temperature. The results are summarized in figure 1, 2 and 3.

The physical properties of zeolite 5A used in this study are prented in Table1.

#### *X-ray diffraction patterns of zeolite 5A:*

Fig.4 shows the XRD pattern of zeolite 5A. The diffractogram exhibits many significant peaks from  $2\theta = 5^\circ$  to  $50^\circ$  indicating that the sample is in crystalline form [17,28]. Furthermore, when this pattern was matched up with peaks corresponding to the standard zeolite A [15,29], it shows that zeolite 5A used in this study was high purity one because all the peaks were well matched with peaks of standard zeolite structure. In addition the diffractogram also demonstrates that no other significant peaks corresponding to other phases emerged which confirmed the absence of impurities and other phases in the sample.

The d-spacing values reported in the literature [21] for zeolite 5A (11.99, 8.59, 7.01, 4.07, 3.68, 3.39, 2.73, 2.60) have been used as the basis for identification of crystalline phases in this study.

#### *Ft-Ir Spectrum:*

FT-IR spectrum for zeolite 5A sample used in this study is given in Fig 5. This spectrum shows a peak with high intensity at  $(900-1000)\text{cm}^{-1}$ . This strong vibration is assigned to the Si-Al-O asymmetric stretching vibration. The less intense a band at  $466.7\text{ cm}^{-1}$  can be assigned to the Si-Al-O bending mode. It is observed that the band recorded at  $665.4\text{cm}^{-1}$  which can be assigned to the Si-Al-O symmetric stretching has less intensity compared to the asymmetric stretching of Si-Al-O band. Another intense and sharp band occurs at  $565\text{cm}^{-1}$ , which is related to the presence of double ring in the framework structure of zeolite A sample. The broad band observed at  $3436.9\text{cm}^{-1}$  is characteristic of OH hydrogen bonded to the oxygen ions of the framework. In addition, an intense band at  $1647.1\text{cm}^{-1}$ , which is characteristic of the bending mode in the water molecule, is also observed. The intense band corresponding to the water of hydration indicates higher percentage of water of hydration.

It may be concluded that IR spectrum of zeolite 5A sample and standard zeolite A match quite closely, indication presence of similar structural units [21,23].

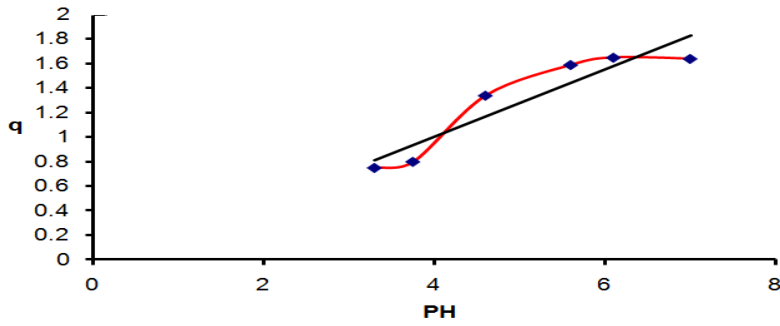


Fig. 1: Influence of pH on the Pb(II)adsorption on zeolite 5A

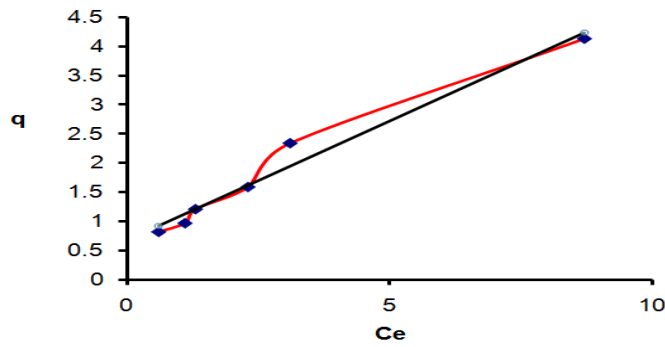


Fig. 2: Adsorption isotherm of zeolite 5A for the removal of Pb(II)

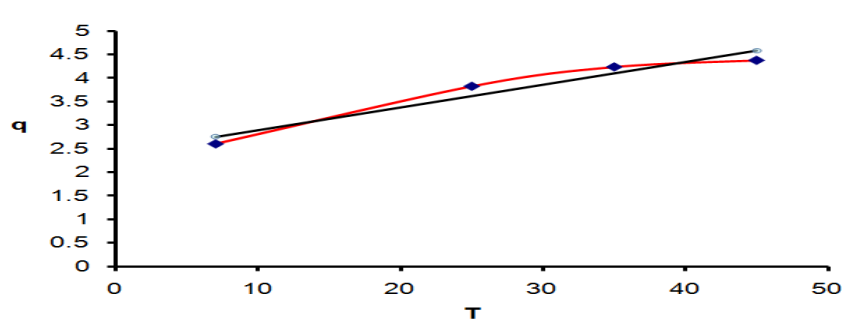


Fig. 3: Influence of T on the Pb(II)adsorption on zeolite 5A

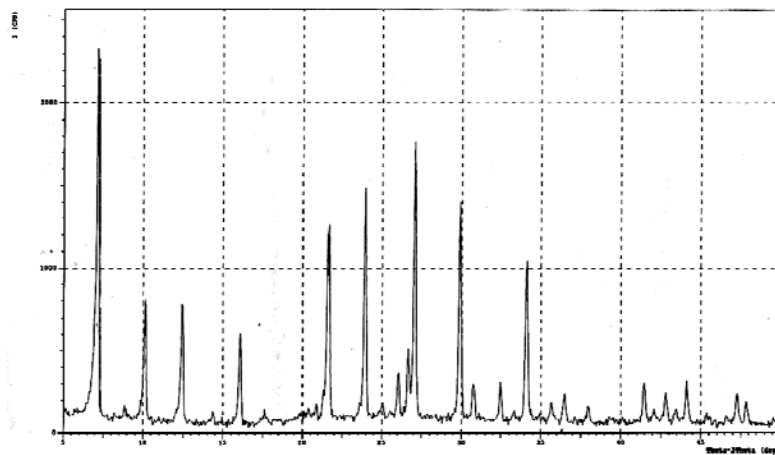


Fig. 4: XRD patterns of zeolite 5A sample

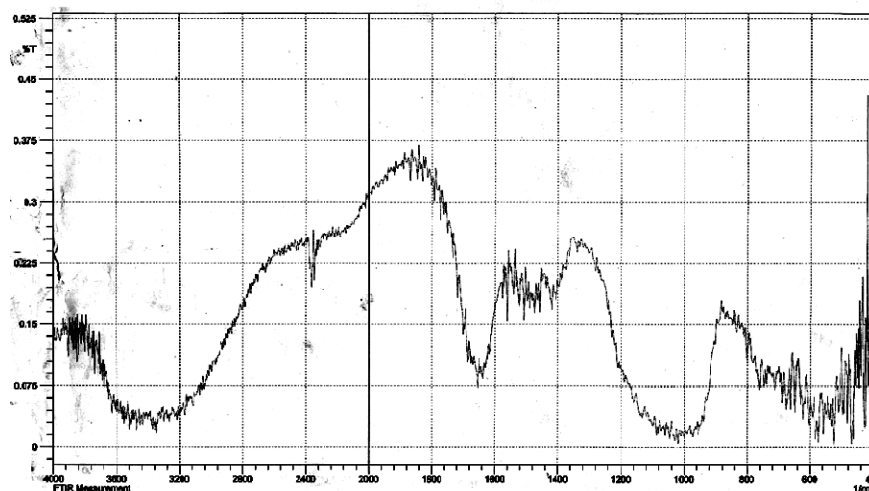


Fig. 5: FT-IR spectra of zeolite 5A sample

*Surface Morphology:*

The surface morphology of zeolite 5A was studied through AFM on 2\*2µm² area is shown in Figures 6 and 7. AFM can provide information on the cross-sectional analysis and roughness analysis. From Figures 6 and 7 it is apparent that zeolite 5A particles exhibit cylindrical like structure. The section analysis obtained through the selection of the transect line across the sample (not shown here) shows that the grain size has abroad distribution ranging from 0.45 – 0.58 µm .The average surface roughness (Ra) of the surface can be calculated from the roughness profile determined from the AFM image [24]. The value of Ra is found to be 17.9nm.

*Effect of pH:*

The pH is varied from 3 to 7 during this study. The effect of pH on the removal of lead ions by zeolite 5A is found to be significant as shown in Figure1. The uptake capacity of zeolite is found maximum at pH of 7 and within the limits of the experiment, for this reason a buffer with a pH of 7 was used in all subsequent studies. The loss in removal capacity at lower pH can be described to the collapse of the structure of zeolites [26].

*Effect of temperature:*

Many sets of experiments are conducted at different temperatures at 280, 298, 308, 313 K° and it is evident in the Figure 2 that adsorption of lead increases with increase in the temperature. This endothermic process is due to increase in adsorbing tendency of the adsorbate species on the surface of adsorbent, or due to simultaneous decrease in the real adsorption of the solvent [13].

*Effect of amount of zeolite:*

The effect of amount of adsorbent on the uptake of lead at optimum pH is examined. Percentage of lead ions removed versus amount of zeolite shows that the percentage removal of metal ion increases with an increase in the amount of zeolite. There is a substantial increase when the dose of zeolite increase from 0.5gm to 1.0gm, and then the removal efficiency increased gradually when zeolite further increased as could be seen from Fig 8.

*Isotherm models:*

The sorption data have been subjected to two sorption isotherm namely, Freundlich and Langmuir. The Freundlich isotherm based on a heterogeneous surface is as follows:

$$q_e = K C_e^{1/n} \tag{2}$$

Where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  the equilibrium concentration (mg/L),  $K$  and  $n$  equilibrium constants. The linearized form of Freundlich sorption isotherm is:

$$\text{Log } q_e = \text{logK} + 1/n \text{ log } C_e \tag{3}$$

Freundlich plots for  $\text{Pb}^{+2}$  adsorption onto zeolite 5A at 298 K° and at pH =7 is given in Fig 9. It illustrates that adsorption of this metal ion onto zeolite 5A obeys the Freundlich isothermal model well. The corresponding Freundlich isotherm constants  $K$  and  $n$  together with the correlation coefficients ( $r^2$ ) is listed in Table 2. The parameter  $n$  is a characteristic constant for the adsorption system. The numerical value of  $n$  in Table 2 suggests favorable adsorption of  $\text{Pb(II)}$  onto zeolite 5A [2].

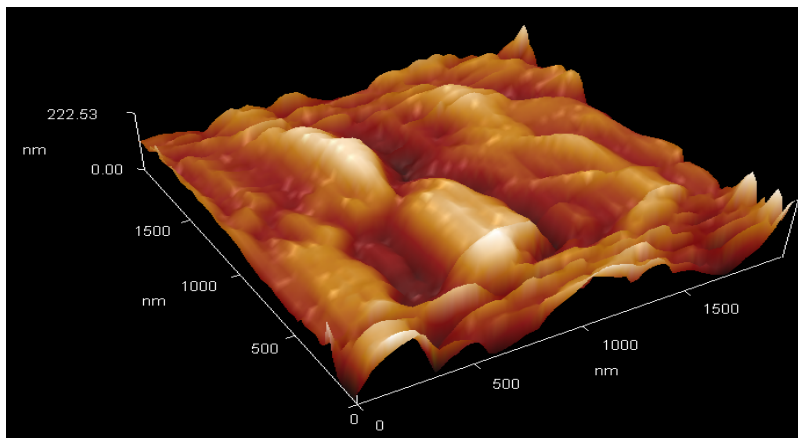


Fig. 6: 3D AFM image for Zeolite 5A sample

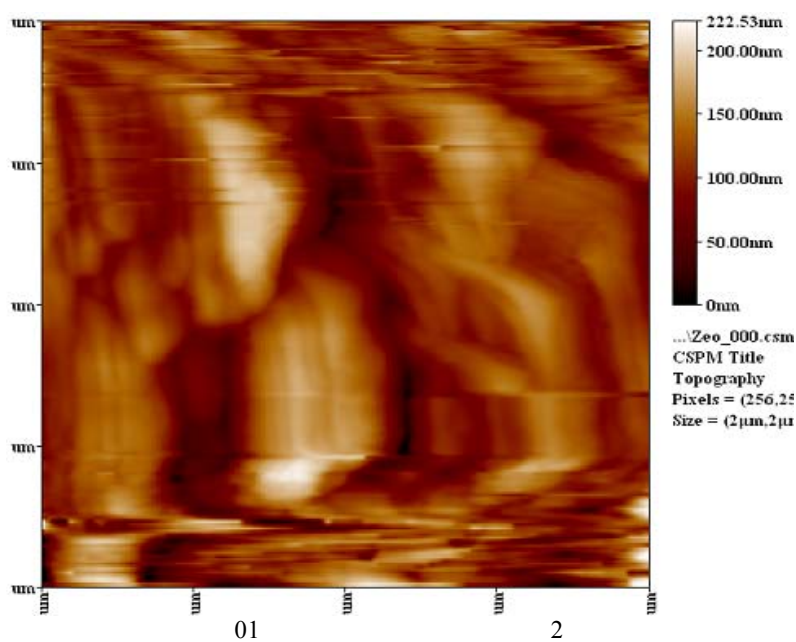


Fig. 7: 2D AFM image for Zeolite 5A sample

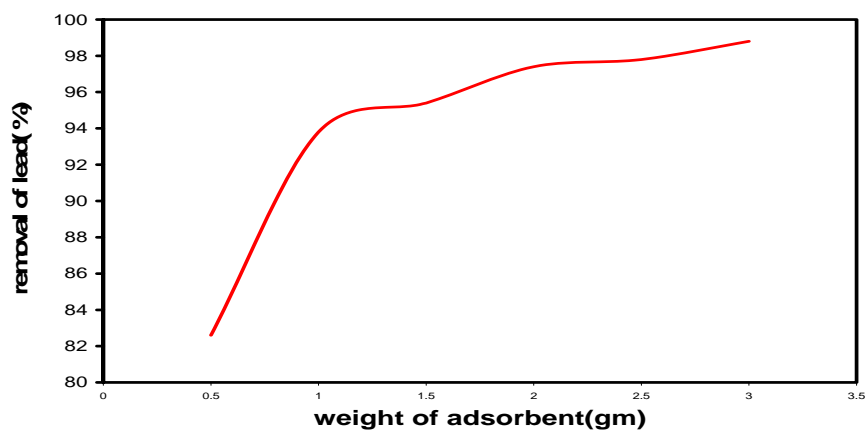


Fig. 8: Influence of amount of zeolite on the adsorption of lead (II)

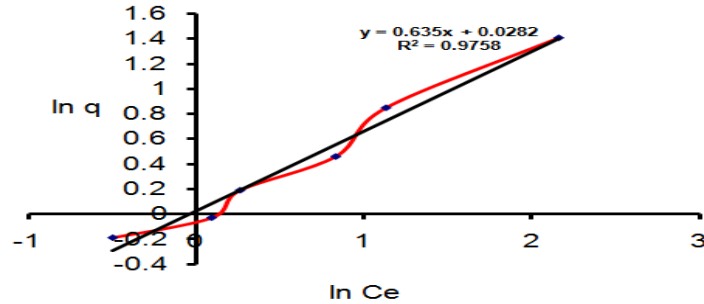


Fig. 9: Freundlich isotherm of zeolite 5A for the removal of Pb(II)

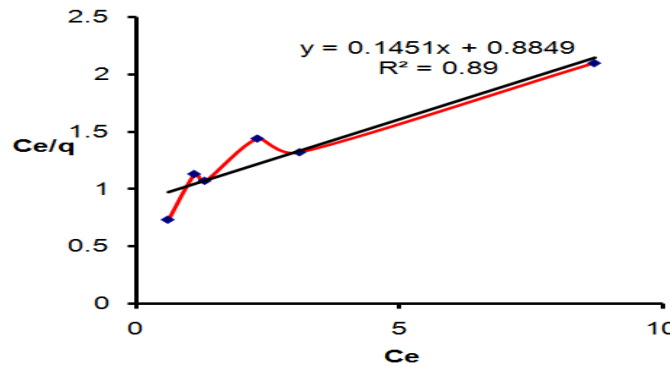


Fig. 10: Langmuir isotherm of zeolite 5A for the removal of Pb(II)

The langmuir equation was developed by Irving Langmuir in 1916 to describe the adsorption of gas molecules on a planer surface. The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogenous surface by monolayer sorption without interaction between sorbed molecules. This Langmuir equation can be described by the linearized form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (4)$$

Where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  the equilibrium concentration (mg/L),  $b$ , a constant related to the adsorption energy (L/mg),

and  $q_m$  the maximum adsorption capacity (mg/g). By plotting  $(C_e/q_e)$  versus  $C_e$ ,  $q_m$  and  $b$  can be determined from the straight line obtained.

The Langmuir plot for Pb(II) isothermal adsorption at 298 K<sup>o</sup> and at pH =7 is shown in Fig 10. The calculated constants  $q_m$  and  $b$  together with correlation coefficients are given in Table 3. The  $r^2$  value suggests that the Langmuir isotherm provides a good model of the sorption system. The Langmuir constant  $q_m$  which is a measure of maximum sorption capacity corresponding to complete monolayer coverage, shows the zeolite 5A had a high adsorption capacity for Pb(II) (6.896 mg/g).

Table 1: Physical properties of zeolite 5A

pH	6.9
Cation exchange capacity by methylene blue (mg/100gm)	78
Specific surface area BET (m <sup>2</sup> /g)	385.498
Specific pore volume BET (cm <sup>3</sup> /gm)	0.34
Maximum water adsorption % (water content)	21.06%
Specific gravity (gm/cm <sup>3</sup> )	0.7967

Table 2: Freundlich constants K and n with the correlation coefficient(r<sup>2</sup>)

K	n	r <sup>2</sup>
1.0286	1.57	0.9758

Table 3: Langmuir constants q<sub>m</sub> and b with correlation coefficient (r<sup>2</sup>)

q <sub>m</sub> (mg/g)	b (L/g)	r <sup>2</sup>
6.896	164	0.89

The Gibbs free energy ( $\Delta G^\circ$ ) of the adsorption process is calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The Gibbs free energy change of the process is related to equilibrium constant (K) by equation (5) as below:

$$\Delta G^\circ = -RT \ln K \quad (5)$$

Where K is equilibrium constant ( $L \text{ gm}^{-1}$ ) that is calculated from the langmuir constant b [18]. The negative  $\Delta G^\circ$  value ( $-4.06 \text{ KJ mol}^{-1}$ ) confirmed the thermodynamic feasibility of the sorption process and the spontaneous nature of adsorption.

#### Conclusion:

The results of present investigation show that lead under the optimized conditions can be removed quantitatively (98.8%) by using adsorbent like zeolite 5A. Zeolite 5A provides as substitute for the use of activated carbon as adsorbent due to its availability and its low cost.

#### Acknowledgement

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