For the first time, an irradiated mineral was used as a novel modified adsorbent for lead removal of aqueous solutions. The effects of gamma radiation doses and temperature on the lead adsorption capacity of an unknown mineral were evaluated. The results show that, in the chemisorption process, the highest adsorption capacity (9.91 mg/g) and the maximum percentage of lead removal (99.1%) were reached at 40°C when using an irradiated mineral at 150 kGy. The improvement on the lead adsorption speed was the most important feature of the irradiated mineral. The experimental results were successfully correlated with the pseudo second-order kinetic model. For all results, the average absolute relative deviations (AARD) were less than 13.20%, and the correlation factor ($r^2$) was higher than 0.998. Moreover, the average values of the thermodynamic parameters ($\Delta G_0 = -10612$ J/mol, $\Delta H_0 = -12360$ J/mol, and $\Delta S_0 = 171$ J/mol K) suggest the feasibility of the proposed process, in terms of the endothermic and irreversible chemisorption results; moreover, ion exchange was evaluated through the EDS results. The X-ray diffraction analysis showed that the unknown irradiated mineral is mainly composed of quartz (SiO$_2$), calcite (CaCO$_3$), and calcium magnesium silicate (Ca$_{0.15}$Mg$_{0.85}$) Mg (SiO$_3$).

1. Introduction

Despite the strict regulations on environmental issues imposed in many countries [1, 2], today, it is still possible to find some heavy metal ions in the wastewater because of industrial processes. However, true environmental damage may occur when such polluted water is unconsciously discharged into natural water flows. Not only aquatic animals and plants but also the human health is at risk [3–5]. Lead is one of the most dangerous metals for the human health, especially for children because their growing bodies can absorb a higher quantity than adults [6–8]. Although lead is prohibited in many products, it is still used in commercial products as automotive batteries, paints, cookware, and some Mexican potter glazes [9, 10]. At low concentrations of lead ions in the blood, some not dangerous diseases such as anemia, diarrhea, and headaches are observed, but, at a higher concentration (>10 $\mu$g/L), the liver, kidney, and neurological and reproductive systems can be severely affected [11, 12].

Many treatments for wastewater polluted with lead ions have been proposed, including an adsorption process which...
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does not have high effectiveness, unless the adsorbent mate-
rial shows certain physicochemical and mechanical proper-
ties. In recent years, some physical, chemical, and biological
treatments on natural raw minerals have been done in order
to modify their structure, thus increasing the adsorption
capacity or the selectivity [13,14].

In this tenor, many works have been published; for exam-
ple, the chemical surface modification of mesoporous silica
with a tertiary aminosilane using supercritical carbon dioxide
showed that the structural ordering of silica was preserved,
but the grafting density increased, and the specific surface
area and the average pore diameter decreased in the modified
adsorbent material [15]. Specifically, for lead adsorption, a
chemically modified adsorbent nanoparticle based on the
treated low-value agricultural byproduct rice husk was used
and it is reported that a maximum lead adsorption capacity
of 93.45 mg/g was achieved [16]. Even the biological modifi-
cation for mineral adsorbents has been done; such is the case
of the functionalized cells with intracellular CaCO
ions was markedly increased [17].

Thermal treatments to obtain spherical mesoporous silica
materials by pseudomorphic transformation of silica fume
were used too; this modified adsorbent was employed as an
effective adsorbent for removing Pb\(^{2+}\) and its capacity
demonstrated great improvement [18].

A novel magnetic composite bioadsorbent, graphene
oxide and magnetic chitosan-ionic liquids, for removing
Pb(II) from water was developed. The mixture of ionic liquids
and graphene oxide and magnetic chitosan resulted in a
material to be applied in the adsorption of metal ions. The
addition of ionic liquids can not only improve the dispersion
of the adsorbent, but also increase the adsorption sites [19].

There is a reported study where gamma radiation was utili-
zied to synthesize a modified adsorbent of chitosan grafted
with acrylic acid. Grafting degree was evaluated as a function
of a radiation dose, and the removal of Pb and Cd ions from
aqueous solutions was investigated with both ungrafted and
grafted chitosan adsorbents [20]. Gamma radiation was also
used as a technique for inducing polymerization in the syn-
thesis of some materials utilized in the removal of heavy
metals from wastewater [13, 21].

Gamma radiation is a current tool that is used as a decon-
tamination or sterilization process, as well as for modification
of the physicochemical properties of materials. In this work,
gamma radiation is used for the modification of physico-
chemical properties of a natural mineral and for improving
its adsorption capacity for removing lead ions from industrial
wastewater. The main novel aspects in the present work are
the validation of the mechanism of the kinetic adsorption
process and application of gamma irradiation as a technique
to improve the lead adsorption capacity of a mineral.

2. Materials and Methods

2.1. Mineral. The natural mineral (from mines located in
Oaxaca, Mexico) was provided by Lumogral S.A. de C.V.
Enterprise (Iztapalapa, Mexico City), which has a particle size
of 0.149 mm on average (100 Tyler mesh size).

2.2. Lead Adsorption Experiments. Aqueous solutions with
100 mg/L lead concentration were prepared by dissolving
dried salt (159.8 mg) of lead nitrate \([\text{Pb(NO}_3\text{)}_2]\) in distilled
water (1 L). Then, in 100 mL of such solution, 1 g of nonirra-
diated or irradiated mineral was added. These heterogeneous
mixtures were heated at constant temperature (20, 30, and
40\(^\circ\)C) and stirred with a shaker at 200 rpm (Lab-Line
Incubator-Shaker, USA). Finally, separation of solid adsor-
bents was obtained by a filtration process, at different contact
times (1, 15, 30, 60, 120, 180, 240, and 300 min).

2.3. Gamma Irradiation Treatment. The mineral was exposed
different gamma radiation doses using a \(^{60}\)Co source. In
this case, the mineral was placed into glass flasks and the
applied doses were 10, 50, 100, and 150 kGy at the dose rate
of 3.5 kGy/h. The experiments were performed in air at
room temperature by using a Transelektro irradiator LGI-01
manufactured by IZOTOPE Institute of Isotopes Co. Ltd.,
Budapest, Hungary, and located at the National Institute of
Nuclear Research (ININ, Mexico).

2.4. Characterization of the Absorbent Material. The adsorb-
ent material was dried and its morphological surface was
characterized by using a scanning electron microscope (JEOL
model JSM-6510LV) coupled with an energy dispersive X-ray
probe (EDAX) for semiquantitative elemental analysis. The
metal concentrations in the liquid solutions were analyzed by
using Atomic Absorption Spectrophotometer (Perkin-Elmer
model AA300), according to the standard method for lead
detection [22].

Mineral samples were also characterized by X-ray diffra-
tion (XRD), before and after irradiation. The analyses were
conducted in a Siemens D5000 diffractometer with Cu Ka
radiation. Data were collected in the radiation angle range
from 2\(\theta\) of 5° to 2\(\theta\) of 75°.

3. Results and Discussion

Chemical composition of nonirradiated and irradiated min-
erals is shown in Table 1. As in many natural minerals, the
most abundant component is oxygen followed by silicon and
calcium. The received energy by the mineral after irradiation
only modified its ratio of each chemical element. For instance,
in the irradiated mineral at 10 kGy, concentrations of four of
the seven chemical components decreased, when compared
with nonirradiated mineral. To compensate it, the concentra-
tion of the others increased in the same ratio, such that the
final concentration is always 100%. Therefore, each chemical
element shows slight variation in the weight percentage
after the irradiation process. As it is known, interactions of
gamma irradiation with matter may cause different effects;
one of them is breaking of chemical bonds, which may be
combined and allow the formation of other chemical species.
Another effect is the cross-linking of chemical bonds that
cause changes in the morphology of matter [21, 23].
Table 1: EDS analysis of nonirradiated and irradiated minerals.

<table>
<thead>
<tr>
<th>Element</th>
<th>Nonirradiated</th>
<th>10 kGy</th>
<th>50 kGy</th>
<th>100 kGy</th>
<th>150 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>58.22</td>
<td>54.05</td>
<td>59.59</td>
<td>52.10</td>
<td>53.07</td>
</tr>
<tr>
<td>Mg</td>
<td>2.16</td>
<td>1.09</td>
<td>0.88</td>
<td>0.87</td>
<td>0.86</td>
</tr>
<tr>
<td>Al</td>
<td>2.22</td>
<td>2.90</td>
<td>2.63</td>
<td>2.13</td>
<td>2.17</td>
</tr>
<tr>
<td>Si</td>
<td>18.93</td>
<td>24.02</td>
<td>19.67</td>
<td>14.45</td>
<td>10.63</td>
</tr>
<tr>
<td>K</td>
<td>1.53</td>
<td>1.44</td>
<td>1.71</td>
<td>1.03</td>
<td>1.24</td>
</tr>
<tr>
<td>Ca</td>
<td>13.75</td>
<td>14.79</td>
<td>14.52</td>
<td>28.55</td>
<td>31.38</td>
</tr>
<tr>
<td>Fe</td>
<td>3.19</td>
<td>1.71</td>
<td>1.00</td>
<td>0.87</td>
<td>0.65</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2: Diffraction peaks of each compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diffraction peak (2θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>21.0 26.8 50.1</td>
</tr>
<tr>
<td>Calcite</td>
<td>23.1 29.5 36.2 39.4 43.3 47.5 48.6</td>
</tr>
<tr>
<td>Calcium magnesium silicate</td>
<td>26.8 27.9 30.9 35.0 42.3</td>
</tr>
</tbody>
</table>

According to the literature, Si/Al ratio is an important parameter in such minerals [24, 25]. In this case, as it can be seen in the results of Table 1, for nonirradiated mineral, a value of 8.5 is obtained, with the lowest value of 4.9 for irradiated material at 150 kGy. Diminution of the Si/Al ratio is due to gamma irradiation; this result provides guidelines for future research as acid catalyst. It is observed that as the Si/Al ratio decreases, acidity increases [26, 27].

Chemical elements are part of three main compounds: quartz, calcite, and calcium magnesium silicate, as it is shown in the diffraction pattern of the nonirradiated and irradiated minerals (Figure 1). Diffraction peaks of each compound are summarized in Table 2. Moreover, calcium magnesium silicate compound gives the mineral interesting features as adsorbent material.

As it can be seen, at doses of 100 and 150 kGy, the most stable phase represented by the calcium magnesium silicate is highlighted, and probably at these highest radiation doses the porosity of the material was increased. So, it is inferred that the highest adsorption capacity is due to the highest radiation dose.

In Figure 2, the lead concentration in the aqueous solution versus time is shown. The values of the removal of lead are shown in Table 3. Such values are obtained by mass balance between the initial lead in the solution \( C_0 = 100 \text{ mg/L} \) and the lead concentration at any time.

Faster lead adsorption on irradiated mineral was observed with respect to the nonirradiated one. The highest adsorption values were obtained for higher doses (150 kGy) with time less than 60 minutes. Moreover, according to the removal rate and adsorption capacity results, the highest adsorbent properties are developed for irradiated mineral at 150 kGy.

As it is observed in Table 3, during the first 15 minutes of contact, the adsorption rate is high, due to the high gradient of the lead concentration between the liquid and the adsorbent surface; this is a common behavior in the mass transfer phenomena as ion exchange and chemisorption processes. Moreover, 80% of lead is adsorbed for different combinations of contact time and irradiation dose: (a) 30 minutes and 100 kGy or (b) 60 minutes and 10 kGy. Thus, diminution of the irradiation dose requires more contact time. At the highest contact time (300 minutes), where the state of equilibrium is almost reached.
Table 3: Lead removal percentage of nonirradiated and irradiated minerals ($C_0 = 100 \text{mg/L}, T = 20^\circ \text{C}, w = 1 \text{g}$, and $V = 0.1 \text{L}$).

<table>
<thead>
<tr>
<th>$t$ (min)</th>
<th>Nonirradiated</th>
<th>10 kGy</th>
<th>50 kGy</th>
<th>100 kGy</th>
<th>150 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.5</td>
<td>55.3</td>
<td>64.1</td>
<td>68.7</td>
<td>71.6</td>
</tr>
<tr>
<td>15</td>
<td>56.8</td>
<td>67.7</td>
<td>73.3</td>
<td>77.7</td>
<td>81.1</td>
</tr>
<tr>
<td>30</td>
<td>66.8</td>
<td>73.3</td>
<td>76.8</td>
<td>81.2</td>
<td>85.4</td>
</tr>
<tr>
<td>60</td>
<td>75.9</td>
<td>80.1</td>
<td>81.8</td>
<td>85.9</td>
<td>89.3</td>
</tr>
<tr>
<td>120</td>
<td>85.5</td>
<td>87.2</td>
<td>88.6</td>
<td>90.2</td>
<td>93.3</td>
</tr>
<tr>
<td>180</td>
<td>91.4</td>
<td>92.7</td>
<td>92.7</td>
<td>93.8</td>
<td>95.8</td>
</tr>
<tr>
<td>240</td>
<td>92.6</td>
<td>93.8</td>
<td>94.8</td>
<td>95.6</td>
<td>96.9</td>
</tr>
<tr>
<td>300</td>
<td>94.7</td>
<td>95.9</td>
<td>96.1</td>
<td>96.8</td>
<td>97.5</td>
</tr>
</tbody>
</table>

happens, the adsorption capacity values are almost constant for nonirradiated and irradiated minerals, with only 3% difference between them. A similar behavior was observed for the other temperatures.

The experimental adsorption capacity was evaluated with the following equation:

$$q = \frac{(C_0 - C) V}{w},$$  \hspace{1cm} (1)

where $q$ is the adsorption capacity (mg/g), $C_0$ is the initial lead concentration (mg/L), $C$ is lead concentration of the filtered solution at any time (mg/L), $V$ is sample volume (L), and $w$ is adsorbent mass (g).

As it is known, kinetics of the adsorption process are related to the rate at which the adsorbent material retains a certain quantity of lead. By experimental data of the concentration and contact time, elucidation of the adsorption mechanism was done.

In the case of the adsorption of lead ions on nonirradiated and irradiated minerals, it was assumed that the adsorption rate is proportional to the square of the number of linking atoms. A lead ion [Pb$^{2+}$] present in the aqueous solution would be interacting with 2 oxygen atoms [-O-] in the chemical structure of the mineral surface [28]. Similar results have been found in other systems [3, 4].

According to the chemical equation

$$[\text{Pb}^{2+}] + 2[\text{O}^{2-}] \rightarrow [\text{O-Pb-O}]^\#$$  \hspace{1cm} (2)

the kinetic equation is

$$\frac{dq}{dt} = k \left[\text{Pb}^{2+}\right] \left[\text{O}^{2-}\right]^2,$$  \hspace{1cm} (3)

where

$$k \left[\text{Pb}^{2+}\right] = k_2$$  \hspace{1cm} (4)

$$\left[\text{O}^{2-}\right] = (q_e - q)^2.$$  \hspace{1cm} (5)

Then, the kinetic equation can be written as

$$\frac{dq}{dt} = k_2 (q_e - q)^2,$$  \hspace{1cm} (6)

where $q$ is the adsorption capacity (mg/g), $q_e$ is the adsorption capacity at equilibrium (mg/g), and $k_2$ is the kinetic constant of the pseudo second order.

The differential equation is written in an integrated form:

$$\frac{t}{q} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2},$$  \hspace{1cm} (7)

The experimental results of the adsorption capacity were adjusted with (6), in order to obtain $q_e$ and $k_2$ parameters; later, the calculated adsorption capacity was estimated and the results are shown in Tables 4 and 5. The comparison between experimental and calculated adsorption capacities was made considering the average absolute relative deviations (AARD), which were determined by

$$\text{AARD} = \frac{1}{n} \sum \frac{|q_{\text{cal}} - q_{\text{exp}}|}{q_{\text{exp}}},$$  \hspace{1cm} (8)

where $n$ is the number of data, $q_{\text{exp}}$ is the experimental adsorption capacity obtained with (1), and $q_{\text{cal}}$ is the calculated adsorption capacity through (6).

According to the AARD and $r^2$ results shown in Tables 4 and 5, the pseudo second-order kinetic model represents satisfactorily the adsorption process of lead on nonirradiated and irradiated mineral, regardless of the irradiation dose or temperature. The AARD values were lower than 14%, and $r^2$ was higher than 0.998.

Determination of the main thermodynamic parameters of the adsorption process allows knowing the feasibility of the separation process as well as deciding whether it is controlled by physisorption or chemisorption. Such parameters include free energy ($\Delta G_0$), enthalpy ($\Delta H_0$), and entropy ($\Delta S_0$), which are evaluated by using the equilibrium constant ($K_{eq}$) value, as follows:

$$K_{eq} = \frac{C_{ads}}{C_i},$$  \hspace{1cm} (9)

where $C_{ads}$ is the concentration of adsorbed lead by the mineral and $C_i$ is the concentration of lead in the supernatant solution.

The relation between $K_{eq}$ and the free energy is given by

$$\Delta G_0 = -RT \ln K_{eq},$$  \hspace{1cm} (10)

where $T$ (K) is the absolute temperature and $R$ is the universal gas constant.

The dependence of $K_{eq}$ on the temperature is expressed by

$$\ln K_{eq} = \frac{\Delta H_0}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_0}{R}.$$  \hspace{1cm} (11)

Since (10) represents a straight line, plotting $\ln K_{eq}$ versus $(1/T)$, it is possible to obtain both $\Delta H_0$ and $\Delta S_0$ from the slope and intercept, respectively.

Although the adsorption process is a natural phenomenon, in order to get the highest adsorption capacity, it is necessary to work at higher temperatures. In this case,
Table 4: Experimental and calculated lead adsorption capacity of nonirradiated and irradiated minerals ($C_0 = 100 \text{ mg/L}, T = 20^\circ \text{C}, w = 1 \text{ g}, \text{ and } V = 0.1 \text{ L}$).

<table>
<thead>
<tr>
<th>$t$ (min)</th>
<th>Nonirradiated</th>
<th>10 kGy</th>
<th>50 kGy</th>
<th>100 kGy</th>
<th>150 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.35</td>
<td>0.80</td>
<td>5.53</td>
<td>1.06</td>
<td>6.41</td>
</tr>
<tr>
<td>15</td>
<td>5.68</td>
<td>5.56</td>
<td>6.77</td>
<td>6.29</td>
<td>7.33</td>
</tr>
<tr>
<td>30</td>
<td>6.68</td>
<td>7.07</td>
<td>7.33</td>
<td>7.64</td>
<td>7.68</td>
</tr>
<tr>
<td>60</td>
<td>7.59</td>
<td>8.18</td>
<td>8.01</td>
<td>8.56</td>
<td>8.18</td>
</tr>
<tr>
<td>120</td>
<td>8.55</td>
<td>8.88</td>
<td>8.72</td>
<td>9.10</td>
<td>8.86</td>
</tr>
<tr>
<td>AARD (%)</td>
<td>12.15</td>
<td></td>
<td>13.19</td>
<td></td>
<td>13.19</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.9981</td>
<td></td>
<td>0.9985</td>
<td></td>
<td>0.9988</td>
</tr>
</tbody>
</table>

Table 5: Experimental and calculated lead adsorption capacity of irradiated mineral at different temperatures (150 kGy, $C_0 = 100 \text{ mg/L}, w = 1 \text{ g}, \text{ and } V = 0.1 \text{ L}$).

<table>
<thead>
<tr>
<th>$t$ (min)</th>
<th>20\textdegree C</th>
<th>30\textdegree C</th>
<th>40\textdegree C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.16</td>
<td>2.03</td>
<td>7.46</td>
</tr>
<tr>
<td>15</td>
<td>8.11</td>
<td>7.82</td>
<td>8.39</td>
</tr>
<tr>
<td>30</td>
<td>8.54</td>
<td>8.24</td>
<td>8.24</td>
</tr>
<tr>
<td>AARD (%)</td>
<td>10.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.9997</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Thermodynamic parameters of the lead adsorption process (150 kGy, $C_0 = 100 \text{ mg/L}, w = 1 \text{ g}, \text{ and } V = 0.1 \text{ L}$).

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\Delta G_0$ (J/mol)</th>
<th>$\Delta H_0$ (J/mol)</th>
<th>$\Delta S_0$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20\textdegree C</td>
<td>-8929.0</td>
<td>-10546.8</td>
<td>41326.4</td>
</tr>
<tr>
<td>30\textdegree C</td>
<td>-8929.0</td>
<td>-10546.8</td>
<td>41326.4</td>
</tr>
<tr>
<td>40\textdegree C</td>
<td>-8929.0</td>
<td>-10546.8</td>
<td>41326.4</td>
</tr>
</tbody>
</table>

the higher the temperature, the greater the spontaneity, as an endothermic process (Table 6). Furthermore, a higher value of $\Delta H_0$ suggests a chemisorption mechanism for the process. According to the results, it is possible to establish a set of process variables and the conditions to scale up the process to an industrial wastewater treatment plant.

According to the EDS results, a great capacity to adsorb lead ions is observed in Table 1. The ion interchange is present; the Mg and Fe ions were substituted by Pb ions as it is shown in Table 7 by comparing with the results shown in Table 1.

Morphological changes are observed in nonirradiated and irradiated minerals after the lead adsorption process, as it is shown in Figure 3. At higher radiation doses (50, 100, and 150 kGy), the porosity of this material increased because the size of the particle decreased drastically; this is most evident at 150 kGy which corresponds to the XRD results. On the other hand, as mentioned earlier, one of the effects of gamma irradiation is the cross-linking of chemical bonds, which produces morphological changes, with an increment on the porosity between them.

4. Conclusions

A novel natural mineral adsorbent was obtained, through its structural modification by gamma radiation, in order to increase the adsorption capacity and the percentage of removal of lead from aqueous solutions. The ionizing energy submitted by gamma rays on the mineral allows a high crystallinity degree as well as high chemical stability. The effects of gamma radiation doses and the temperature on the lead adsorption capacity of the mineral were evaluated. The highest adsorption capacity (9.91 mg/g) and the maximum percentage of lead removal (99.1%) were reached at 150 kGy and 40\textdegree C, for industrial wastewater with a content of lead of 100 mg/L. The improvement on the lead adsorption speed was the most important feature of the irradiated mineral. The experimental results were successfully correlated with the pseudo second-order kinetic model. In all cases, the average absolute relative deviations (AARD) were lower than 13.20%, and the correlation factor ($r^2$) was higher than 0.998.
Moreover, the thermodynamic parameters values ($\Delta G_0$, $\Delta H_0$, and $\Delta S_0$) revealed a feasible, endothermic, and irreversible process, where lead ions are mainly chemisorbed or ion-exchanged. The mineral showed specific characteristics: (a) its adsorption capacity is not too high compared with the bioadsorbents, (b) it was insoluble in water, and (c) it had high mechanical strength; thus, the proposed adsorbent can be regenerated and reused, mainly in large-scale processes such as adsorption columns, where large pressure drops are present.

### Additional Points

**Highlights.** More than 95% of lead ions contained in industrial wastewater were removed by using an irradiated mineral. The lead adsorption kinetic process was successfully correlated with the pseudo second-order model. The lead adsorption is a spontaneous and endothermic process that achieved higher adsorption capacity at 40°C. The highest values for lead adsorption capacity were obtained for irradiated mineral at 150 kGy, which were 17.5% higher than that obtained by the nonirradiated one.

**Competing Interests**

The authors declare that they have no competing interests.

### References


[7] A. Chen, K. N. Dietrich, J. H. Ware, J. Radcliffe, and W. J. Rogan, "IQ and blood lead from 2 to 7 years of age: are the effects in older children the residual of high blood lead concentrations in 2-year-olds?" *Environmental Health Perspectives*, vol. 113, no. 5, pp. 597–601, 2005.


