Study of chemical and physical parameters affected on purification of water from inorganic contaminants

Waleed R. Abdullah ¹, Yasir A. J. Alhamadani ², Ishraq Khudhair Abass³, Mohammed Nsiaf Abbas⁴

¹ Environmental Engineering Department, College of Engineering, Mustansiriyah University, Iraq
² Directorate of Construction and Building, Ministry of Higher Education and Scientific Research, Iraq
³ Environmental Engineering Department, College of Engineering, Mustansiriyah University, Iraq
⁴ Environmental Engineering Department, College of Engineering, Mustansiriyah University, Iraq

ABSTRACT

The ability to remove perchlorate anions was investigated by the adsorption technique in a laboratory scale and by a batch type unit from contaminated aqueous solutions prepared at specific concentrations. The adsorption process was carried out using banana peels, which were chosen as an available, cheap, and low-cost adsorption media. The studied operating conditions in the treatment process were the acidic function, shaking speed, contact time, temperature, in addition to the initial concentration of perchlorate, which ranging from 1-10, 100-400 rpm, 10-180 min, 20-50 ºC, 50-1000 ppb respectively, while the dose of adsorbent media ranged between 0.5-6 g and the particle size ranged from 0-Pan. The experimental results showed that the removal efficiency of perchlorate changes directly with the shaking speed, contact time, particle size and the dose of adsorbent, while it was inversely with the remaining variables for certain levels. Thus, two types of contaminants were disposed of simultaneously in a beneficial, and eco-friendly manner, reaching to Zero Residue Level (ZRL).

Keywords: inorganic contaminants, perchlorate, adsorption, banana peels and ZRL

1. Introduction

There is no trustworthy evidence until now that life can exist anywhere else in this universe than on Earth. In spite of this well-known actuality, man, since his presence on the blue planet, continued to deplete its natural resources and pollute his environment [1]. With the exception of some natural factors - which are sometimes caused by humans - all other environmental problems are caused by various human activities, and one of the most important of these environmental issues is pollution [2]. After this pollution was limited to a specific time and place, it became a major problem that began to exacerbate since the mid-1940s of the twentieth century [3]. It continued to grow and develop and took new forms until it now includes all the elements of the environment, namely air, soil and water, even exceeds that to pollute space [4]. One of the most important of the previous types is water pollution due to its association with agriculture and the life of living organisms in general, not just humans [5]. There are many types of human-caused pollution of surface and groundwater, including vision pollution, oil pollution, thermal pollution, physical pollution, biological pollution, and chemical pollution [6]. The last type is considered one of the most serious types due to its ability to pollute large areas in a short time and its effects will last for a long time [7]. Chemical pollution results from the dispose of toxic alien chemical elements entering the water environments or raising the concentrations of the elements present in them as a result of industrial, agricultural, military and other activities on a continuous basis so that the environment cannot reduce these concentrations in timely manner [8]. This type results in a
great danger to human health as a result of the contamination of water and food sources with these elements and the transfer of pollutants to him through the food chain [9]. There are several types of pollutants that fall under the heading of chemical pollution, including pollution with organic substances such as dyes [10], phenols [11] and Humic acid [12], pollution with positive ions such as, manganese [13], cobalt [14], lead [15], cadmium [16], zinc [8], copper [1], antimony [17], nickel [18] and the other heavy elements [14], and pollution with negative ions such as phosphates [19], and cyanide [20], etc. These ions and elements mentioned above, if they exceed the permissible limits, have different effects on human health and lead to various diseases that may lead to death at different times [21]. However, there is a type of these negative ions whose effect is harmful even in small concentrations, which are perchlorate ions [22]. It drew the attention of researchers to their effect about 50 years ago, and their toxic effect on various human organs is still being studied [23].

The current known toxic effect of perchlorate ions is to disrupt neurodevelopment, particularly in infants and pregnant women and thus interfere with the endocrine systems of the brain [24]. On the other hand, it is considered the most effective chemical in inhibiting the absorption of iodide by the thyroid gland, which limits its ability to produce the hormones necessary for metabolism, growth and normal development of the body of the organism, namely, thyroxine and triiodothyronine [25]. This condition is medically known as hypothyroidism (including dry and itchy skin, dry and brittle hair, sluggishness, muscle and joint pain, and headaches) and may cause cretinism, hypothyroidism or cretinism (i.e., mental retardation) [26]. Even low levels of perchlorate can cause severe imbalances in the production of thyroid hormones, and may lead to cancer [27]. This substance has been widely used since the middle of the last century to treat toxic goiter known as Grave's disease, which is an autoimmune disease that affects the thyroid gland. It is the most common cause of an overactive and enlarged thyroid gland. Treatment with this substance continued until the mid-1960s, when its use decreased due to the emergence of serious blood disorders and cases of fatal aplastic anemia in patients who underwent treatment for long periods [28]. Although some perchlorates are naturally produced, most of them are anthropogenic and are considered an important chemical due to their wide use in many industrial applications. Perchlorate is used in the manufacture of fireworks, rocket propellant, airbags, matches, ammunition capsules and explosive fuses, dyes, some types of epoxies, and some types of batteries such as lithium-ion batteries. All types of perchlorates have high solubility in water (except for potassium perchlorate, which is the least soluble compared to its counterparts), and is characterized by kinetic inactivity and high stability in water for decades without change. Therefore, attention must be focused on removing this substance from polluted water and wastewater [29]. The maximum acceptable dose of perchlorate ions in drinking water was set at about 0.015 mg/l or 0.0007 mg/kg/day, equivalent to 0.0245 mg/l, according to the US Environmental Protection Agency (USEPA) and the US National Academy of Sciences, respectively. The maximum acceptable dose varies between US states, being 0.002 mg/l in Massachusetts, 0.005 mg/l in New York, 0.006 mg/l in California, and 0.014 mg/l in Arizona. While the maximum acceptable dose in Canada was 0.006 mg/l and in Germany 0.0067 mg/l. In general, the available data show that 0.004-0.018 mg/l is an acceptable exposure level, while the maximum permissible dose shows clear differences between countries or between states [30]. Many researchers studied different treatment methods in order to remove anions from water or reduce its concentration to the permissible concentration, including biological treatment, physical methods, and chemical reduction [15]. All these methods have limitations and obstacles, the most important of which are the high cost, energy requirements, primary treatment, special units, and the ability to deal with low concentrations of pollutants [4]. From the study of these methods, it was found that the adsorption method is the best method that can be used to treat water contaminated with perchlorate ions [30]. The adsorption method is considered one of the most effective methods for treating polluted water as it does not require high energy consumption and does not need special systems or pre-treatments and is acceptable in cost and efficiency [31]. If activated carbon (which is the most famous substance in adsorption experiments due to its high efficiency) is expensive, studies have shown the possibility of using industrial and agricultural waste as alternative adsorption media [9]. Agricultural wastes are considered as sources of many benefit materials like acetone [4], nano-material [32], and have different applications such as enhanced concrete [33], and purified soil, water and crude oil from contaminants. Many types of agricultural waste were used as adsorption media and proved effective in water treatment, including rice husk [34], lemon peel [8], orange peels [5], tea waste leaves [1], egg shells [17], aluminum foil [7], water melon rinds [16], algae [35], and water hyacinth [6]. Although the adsorption method is limited in efficiency under normal conditions and leaves large quantities of substances that are often toxic [36], these obstacles were overcome by adjusting the operating conditions and investigating the use of polluted residues in an environmentally friendly manner through the zero residues level (ZRL) concept [37]. The purpose of ZRL concept is disposing the toxic waste to produce a useful
substance such as pesticides [38], and this is the aim of the current paper. This research aims to investigate the possibility of using banana peels as a low-cost adsorbent to treat aqueous solutions contaminated with perchlorate anion in a batch type adsorption unit with suitable ranges of different design conditions reaching to the concept of zero residue level (ZRL).

2. Research method

Adsorbent media: Ripe yellow banana peels were collected for the period from 01/03/2022 to 01/05/2022 from the domestic uses. Each batch of collected peels were washed with an excess of tap water to ensure that they are free of any dirt or dust attached to them. Then they were washed once with distilled water and left to dry naturally in sunlight at a temperature ranging between 25-38 ºC for 72 hours in closed transparent glass mason jars to ensure that they are not contaminated. After that, the peels were cut manually using sharp kitchen knife into small pieces, the lengths of which ranged between 3-5 cm. Then crushed by a laboratory grinder (RT-02, Mill Powder Tech., Taiwan). The peels were dried using a drying oven (VO29cool-Memmert, Germany) at a temperature of 50ºC for 12 hours and kept in dark, airtight glass amber jars until use. A sieve analysis was carried out for a sample of one hundred grams to provide graduated particles sizes as shown in Table 1. All samples for sieve analysis had a surface area test (BET) performed and the values are listed in Table 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Mesh size (mm)</th>
<th>Retained Mass (g)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Peel</td>
<td>-</td>
<td>-</td>
<td>16.86</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>2.23</td>
<td>9.714</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>1.68</td>
<td>39.825</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>1.19</td>
<td>20.442</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.841</td>
<td>8.125</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.707</td>
<td>7.068</td>
</tr>
<tr>
<td>6</td>
<td>Pan</td>
<td>-</td>
<td>14.826</td>
</tr>
</tbody>
</table>

Stock solution: To conduct the adsorption experiments, perchlorate solutions of specified concentrations were prepared using sodium perchlorate monohydrate which has the molecular formula (NaClO₄·2H₂O) purchased from Merk company of 140.46 g/mol molecular weight, and a purity >98%. To obtain a perchlorate stock solution of a concentration of 1 mg/l (or 1000 µg/l), 1.45 mg of sodium chlorate monohydrate was dissolved in a liter of double distilled water prepared in the laboratory via the distillation apparatus (GFL 2012).

Spectrophotometric calibration curve: To achieve any spectrophotometric calibration curve, several solutions of different and known concentrations are prepared and tested spectrophotometrically. The corresponding absorbance is recorded at the wavelength corresponding to the highest absorbance. By plotting the relationship between concentration and absorbance, getting a straight line representing the calibration curve. The method described by [39] [40] was adopted, where a spectrophotometer (NU-T3A, NANBEL, China) of ±1nm wavelength accuracy was used to determine the concentrations of perchlorate at 292 nm wavelength. All samples were tested triplicate and the arithmetic mean was taken to reduce the error rate. Figure 1 shows the calibration curve used in this study.

![Figure 1. The calibration curve of ClO₄⁻ anions](image)
Adsorption unit: Adsorption experiments were carried out in a batch type adsorption unit, which is an orbital water bath shaker (GYROMAX 929-Amerex Instruments, Inc.; USA) in which the dose of the studied adsorbent is placed in addition to adsorption solutions of specific concentrations and pH, all put in 100 ml conical flask (CORDIAL MedLab 1122 Borosilicate Glass, China). The pH was adjusted using standard solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) purchased from Merck company, Germany at a concentration of 0.1M each. After setting the shaking speed and the temperature of the adsorption unit, the experiment is started and continues for a required contact time until stops finally. The studied operating conditions were pH, shaking speed, contact time, temperature of unit, adsorbent dose, perchlorate initial concentration, and particle size of banana peels, which ranging from 1-10, 100-400 rpm, 10-180 minutes, 20-50 ºC, 50-1000 ppb, 0.5-6 g, and 0-Pan, respectively. After ending the time of experiment, the samples are extracted from the unit and filtered using the filtration kit (250ml, Glass Filter Funnel Kit, Model: B00501, Xiying Labwear-China) and filter paper (Whatman 43). Finally, the non-adsorbed concentration of perchlorate was determined using the spectrophotometric method and calibration curve, and the final concentration and removal efficiency were calculated from equations 1 and 2.

\[
\% E = \frac{C_{in} - C_f}{C_{in}} \quad ...\text{(1)}
\]

\[
q = \frac{V}{m} (C_{in} - C_f) \quad ...\text{(2)}
\]

Where: \(\% E\): is the percentage efficiency of perchlorate adsorption, \(C_{in}\) and \(C_f\): are the initial and final concentrations of perchlorate anions before and after adsorption respectively (ppb), \(q\): is the capacity of perchlorate adsorption (mg/g), \(V\): is the volume of selenium solution used in adsorption experiment (0.1 L), and \(m\): is mass of banana peels used in test (g)

Effectiveness of pH: The effect of the pH function on the adsorption of perchlorate ions by banana peels was studied within a range of 1-10 to include all pH ranges, acidic, basic and neutral. The obtained results shown in Figure 2 showed that the adsorption of perchlorate ions decreases with the increase of the pH and that the highest adsorption capacity was 5.957 μg of perchlorate per gram of banana peels obtained at a pH value of 1. The reason for this is due to the fact that the acidity function is closely related to the concentration of hydrogen ions, as a low acidity function means that the concentration of hydrogen ions is high. This, in turn, means a high susceptibility to charge the adsorption surface with positive ions, and thus increases the chance of perchlorate ions binding to the adsorbent surface by van der Waals forces. On the other hand, by increasing the pH, the concentration of the negative hydroxide ions (OH\(^-\)) will increase, which will increase the competition between them and the perchlorate ions on the active sites, and this will reduce the chance of adsorption of the perchlorate ions on the adsorbent surface, and thus the efficiency of the adsorption process will decrease. Similar results were reported by [40].

![Figure 2. Effectiveness of pH](image-url)

Effectiveness of temperature: The effect of this important factor on perchlorate adsorption by banana peels was investigated within the general temperature range in Iraq, which ranges between 20-50 ºC, keeping other
design factors constant. The results obtained from the practical experiments shown in Figure 3 showed that the highest adsorption efficiency was approximately 77% which occurred at a temperature of 20 °C. The adsorption efficiency continued to decrease with increasing temperature until it reached a little more than 4.5% at 50 °C. It is clear that increasing the temperature leads to the adsorbed perchlorate molecules possessing the kinetic energy necessary for liberation from the forces capturing them on the adsorption surface. Or increasing the temperature will help to expand the adsorption surface pores, which contributes to the liberation of the adsorbed particles. Consequently, it will return to the solution, causing increasing the perchlorate concentration, which means a decrease in the adsorption efficiency. This is consistent with what was mentioned by [5].

![Figure 3. Effectiveness of temperature](image)

Effectiveness of contact time: The studied range of contact time for the adsorption process ranged from 5-180 minutes with the rest of the operational variables were kept constant. The results shown in Figure 4 showed that the adsorption efficiency increased with increasing contact time, and that 165 minutes was the best time required by banana peels to reach the highest adsorption efficiency of perchlorate ions, while the increase in contact time did not have any effect on the efficiency after 165 minutes. Increasing the contact time will provide the adsorbent with the time required to adsorb a larger number of perchlorate ions, in other words, it will provide a higher chance for the ions to reach the active sites on the surface of the adsorption media. Vice versa, the short time means that a number of ions will not be allowed to bind with the adsorption sites, and thus the adsorption efficiency will decrease. Thus, the truism will be confirmed that the relationship between adsorption efficiency and contact time is a direct relationship. These same results have been referred to in most similar studies such as [1].

![Figure 4. Effectiveness of contact time](image)
Effectiveness of adsorbent dose: Practical experiments were conducted with a range of 0.5-6.0 g of banana peels, keeping other variables constant. Increasing the dose of banana peels has a positive effect on increasing the adsorption efficiency of perchlorate ions from the aqueous solution, and that a dose of 5.75 g of adsorption media is the perfect dose to reach the maximum adsorption efficiency, as shown by the experimental results shown in Figure 5 to investigate the effect of this operational factor. As it is known, the adsorption process is a surface phenomenon, i.e., depends mainly on the surface area per unit mass of the adsorption media, which varies in its values among the adsorbents. As increasing the dose of adsorption medium, leads to increase the surface area of adsorbent. Thus, the number of active sites that contain the functional groups required to adsorb more molecules of the adsorbent material will increase, and this leads to an increase in the adsorption efficiency. After reaching the adsorption dose of 5.75 g, it is noticeable that the adsorption efficiency remains constant despite the increase in the adsorbent dose. This is due to several reasons, including that the adsorption media has reached a state of equilibrium, so it cannot adsorb an additional amount of perchlorate ions. Or, increasing the adsorption dose led to the accumulation of the adsorbent material on top of each other, which leads to not allowing perchlorate ions to reach the active adsorption sites, thus the efficiency of adsorption will be constant. This is consistent with [41].

Effectiveness of the perchlorate initial concentration: By keeping the other operating factors constant, and within a range of 50-1000 µg/L, the effect of the initial concentration of perchlorate ions on the adsorption capacity of banana peels was investigated. As it is clear in Figure 6, that the relationship between adsorption efficiency and initial concentration is inverse, and that the concentration of 50 ppb is the concentration at which the maximum adsorption efficiency was achieved. This result is considered intuitive, as an increase in the initial concentration means an increase in the amount of perchlorate ions for the same unit volume, and the same dose of the adsorbent. Which means the same surface area of the adsorption media will be exposed to an increasing amount of adsorbent. Thus, banana peels cannot adsorb an additional number of ions that exceed the number that can be absorbed at that dose. As a result, the number of free perchlorate ions in the solution will increase with an increase in the initial concentration, which leads to a decrease in the adsorption efficiency. It is noted from Figure 6 that the adsorption capacity increases with the increase of the initial concentration, and this result is attributed to the increase of the adsorbent concentration (despite the decrease in efficiency) and the reason is that the increase of the initial concentration. One of the conclusions similar to the above result was reached by [42].

Effectiveness of shaking speed: The effect of the shaking speed factor on the adsorption of perchlorate by banana peels within a range of 100-500 rpm was investigated, fixing the rest of the other operational factors. The obtained results revealed that the shaking speed directly affects the adsorption efficiency and that the efficiency increases steadily between 100 to 350 rpm until it reaches the highest value as shown in Figure 7. After that, the increase in shaking speed does not have any significant effect on the removal efficiency and remains constant.
As mentioned earlier, increasing the speed of shaking will increase the access speed of the perchlorate ions to the active sites on the adsorption surface, which increases the chance of those ions being attached to the functional groups scattered inside the pores of the banana peels. On the other hand, increasing the speed of shaking may lead to the destruction of the film layers formed on the surface of the adsorption, which lead to blocking the access of particles to the adsorbent surface, and this in turn increases the efficiency of adsorption.

As for the value of the removal efficiency after 350 revolutions per minute, it may be due to the reaching to equilibrium adsorption with the equal amount of the liberated ions with the adsorbed ions. Thus, the increase in the shaking speed will not have any effect on the adsorption efficiency, as indicated by [43] in his study on removal of phosphorus ions.

Effectiveness of adsorbent particle size: After drying and crushing banana peels in the previously described manner, the sieve analysis process was carried out for the grinding peels, as well as the surface area of each section was tested as shown in the Table 1. Equal amounts of each sieve section were used to carry out the adsorption process for perchlorate ions to conclude the best particle size among the mentioned sections, which ranged from virgin banana peels of 3-5 mm length to the lowest particle size obtained which is pan. The results showed that the adsorption efficiency decreased gradually with increasing particle size, and the maximum removal percentage was achieved at the particle size pan. The reason for this intuitive result is that the surface area of the section Pan was the highest compared to the size of other particles, because the section has the smallest particle size. The effect of adsorbent particle size is presenting in Figure 8.
3. Conclusions

This paper highlighted several points, the first of which is the importance of removing perchlorate anions when their concentrations are higher than acceptable levels, as they can cause harmful effects to human and animal life through their competition with the thyroid gland to absorb iodine. Also, the possibility of using low-cost and non-valuable materials to purify water from pollutants, which added importance to these wastes that are still thrown with household and municipal waste. The current study indicated the possibility of using banana peels as an efficient adsorption media in removing perchlorate anions from contaminated solutions according to several design variables. The obtained results showed that the optimal operating conditions were in terms of acid function, shaking speed, contact time, banana peel dose, initial concentration, and temperature of 1, 350 rpm, 165 min, 5.75 g, 50 ppb, 20 ºC, respectively, while pan was the best particle size. The results also showed that the adsorption efficiency is directly proportional to the shaking speed, contact time, adsorbent dose and particle size, while it is inversely proportional to the other variables.

Declaration of competing interest

The authors declare that they have no recognized non-financial or financial competing interests in any materials conversed in the current work.

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