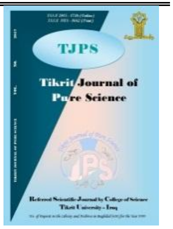
TJPS

TIKRIT JOURNAL OF PURE SCIENCE

Journal Homepage: http://main.tu-jo.com/ojs/index.php/TJPS/index



UTILITY OF CYANIDE ION REMEDIATION RESIDUES TO PREPARE ACTIVE RODENTICIDE ACCESSING TO ZERO RESIDUE LEVEL: SPRAGUE DAWLEY RATS *Rattus rattus* AS CASE STUDY

Suadat Mustafa Mohammed[1], Nisreen Sabbar[2], Ahmed Alaa Hussain[3], Mohammed Nsaif [3]

[1] Department of Biology , College of Science , Tikrit University , Tikrit , Iraq
Department of Biology , College of Education for Pure Science , Diyala University , Diyala , Iraq
[3] Environmental Eng. Dep. , Faculty of Engineering , Mustansiriyah University , Baghdad , Iraq

DOI: http://dx.doi.org/10.25130/tjps.23.2018.025

ARTICLE INFO.

Article history:

-Received: 12 / 9 / 2017

-Accepted: 18 / 10 / 2017

-Available online: / / 2018

Keywords: *pomegranate peel, cyanide ion, adsorption, Sprague Dawley Rats and* zero residue level (*ZRL*)

Corresponding Author:

Name:

Suadat Mustafa Mohammed

E-mail:

zaid.almahdawi@yahoo.com

Tel:

Affiliation:

Abstract

This study was examined the possibility of pomegranate peel residue (PPR) (*which remains after extraction of antioxidants* (*phenolics*)) for removing polluted cyanide ions from aqueous solutions using several operational factors via adsorption technique. The operational factors studied included initial concentration of (CN^-), pH of aqueous solution, flowrate of the aqueous solution inside the adsorption unit, height of adsorption media and time of treatment. By means of changing the aforementioned variables within particular empirical ranges, the best operational conditions were identified that gave the highest percentage removal of cyanide ion from aqueous solutions which reach to 95.75%. The samples of PPR remaining after completion the adsorption process explained above have been used to prepare an effective toxic material for rodents. The lethal effect of this cheap rodenticide was investigated using laboratory rats of type Sprague Dawley (which has the scientific name *Rattus rattus*) as a case study. These toxic residues exhibited a fatal effect on this type of rats depending on the calculated half lethal dose (LD_{50}) of its which was compared with the (LD_{50}) mentioned in literature and scientific references and showed that it was within the required range. In this method, more than one type of toxic and non-toxic wastes was disposed by simple, benefit, non-cost and environment friendly way. This way represents by eliminating the cyanide ions from aqueous solutions to minimum possible concentration using non-valuable agricultural wastes (PPR) and in the same time preparing a cheap and active rodenticide according to lethal dose (LD_{50}) calculated accessing to zero residue level (ZRL).

1. Introduction

Cyanide is a chemical substance (inorganic in itself) either gas or liquid or solid and it be colourless to white like a powder form of small granular. It is very flammable and extremely toxic. Cyanide is formed as a compound produced from combination a carbon element with a nitrogen element by triple-bond [1]. Cyanide does not exist alone in nature, but it is usually associated with other chemicals to compose cyanides i.e. cyanide compounds. Cyanides are either organic compounds like acetonitrile () and benzonitrile () or as acid like hydrogen cyanide (HCN) (which is also called prussic acid or formonitrile) or inorganic compounds such as cyanogen chloride (ClCN) (which known as CK) or as complexes like $K_2Zn(CN)_4$, $K_2Cu(CN)_3$ and $K_2Fe(CN)_6$. In other words, cyanide compounds can be defined as any compound containing a cyano group (CN^-) [2]. All types of cyanides are not dissolved in water except alkaline metal cyanides i.e. sodium cyanide (NaCN) and potassium cyanide (KCN) (Both are white powder) and mercuric cyanide ($Hg(CN_2)$) which is dissolved in water and has boiling point of 630 °C. There is no individual separated substance called cyanide, but there is a wide range of chemicals called cyanides [1,2]. Cyanide is founded in some bacteria, algae and fungi producing cyanide, also some types of millipedes (known as Sierra luminous millipedes or *motyxia*) secrete a poisonous sap of hydrogen cyanide gas by microscopic pores located on both sides of its body as a mechanism of itself defended and this is considered as secondary defences [3]. Cyanide also exist naturally with very small quantities in the seeds of some fruits and plants like apple, apricot, peach, sweet and bitter almond, soybean, spinach, bamboo shoots (*Cathariostachys madagascariensis*) and cassava roots (Which is the main source of food in the countries of tropical regions) [4]. Cyanide is known among toxicologists as one of the fastest and most lethal poisons in the world. Generally, most cyanide compounds are fatal, but not every chemical compound containing cyano group (CN^-) is necessarily toxic cyanide. However, there are certain types of this ion toxic and other are non-toxic at all. The difference between what is toxic and what is nontoxic is the ability to liberate cyano compound from the substance containing it [5]. The most toxic compounds of cyanide are hydrogen cyanide (HCN) and the salts derived from it such as potassium cyanide (KCN), sodium cyanide (NaCN) and calcium cyanide (CaCN) as well as mercuric cyanide ($Hg(CN_2)$) and others [6]. Therefore, it is not recommended to eat the seeds of cyanide-containing fruits aforementioned above because the digestion of 50 almonds or 50-60 apricots or 20 apples continuously, for instant, is enough to kill an adult human [7]. Although the cyanides found in the seeds of these fruits are harmless on their own, the destruction of seeds with the presence of water and the enzymes needed release the toxic cyanide ion due to the presence of cyanide in the form of amygdalin (classified as a cyanogenic glycoside), which eventually turns into highly toxic hydrogen cyanide [8]. The permission level of cyanide in air is ranging between 0.160-0.166 ppm (0.180-0.187 mg/m^3) while in water the maximum acceptable level for drinking and aquatic biota does not exceed to 50 and 200 µg/l respectively [9,10]. Inhalation of 200-500 ppm of hydrogen cyanide for 30 minutes leads to kill the human while the lethal dose of cyanide for adult person reach to 75 mg which is sufficient to cause the death in less than 2 minutes, whilst a dose of 0.2 g eliminates the human life in a few seconds [11]. The effects of toxic cyanide are very important matter because the risk of cyanide lying when it can enter the body through the skin or inhalation by the mucous membranes or via the volatile vapours. When taking cyanide salts through the mouth, it mixing with the acids founded in stomach precisely hydrochloric acid. The results of their reaction are salts of cyanide and acid of hydrogen cyanide which in turn occurs poisoning in the body [12]. Symptoms of exposure to cyanide begin with irritate the eyes, respiratory system and skin accompanied by redness, while the inhalation of it causes breathing problems leading to breakdown [13]. The nervous system can be affected by the compound, leading to dyspnoea and pulmonary circulation. Exposure to cyanide also leads to headache, dizziness, imbalance of movement, heart arrhythmias, vomiting and convulsions, damage the nerves and thyroid and in some cases the human enter into coma and may reach the outskirts of death [12]. Chronic exposure to small and continuous amounts of cyanide resulted in elevate its ratio in blood which lead to gradual weakness in body muscles and nervous system [14, 15]. Cyanide is applied industrially in several fields including cleaning, polishing and finishing precious metals such as silver and gold, also used in industry of plastic, synthetic rubber, as well as heat treatment of steel, electroplating, and in different chemical processes, and mining aiming to extract the valuable metals from their ores in different methods like MacArthur-Forrest process [16]. Cyanide also used in several pharmaceutical compounds does not pose any danger to human health, such as Cimetidine (Tagamet®) [17], Verapamil HCl [18], Nitroprusside [19], Citalopram (Celexa) [20] and other types of drugs. Also copper cyanide was used in the treatment of tuberculosis and leprosy by Japanese doctors in the early of 20th century [21]. Furthermore, cyanide is used as an insecticide for fumigation of ships and their cargoes [22]; moreover cyanide salts have been and are still used in some regions as a toxic killer for mice rats and other types of rodents and as pesticides to eliminate ants [23]. So, generally the cyanide compounds form a great proportion of residues disposed from coke oven, blast furnace, mining activities, electroplating operations etc. These residues are highly toxic industrial wastes due to the cyanide salts it's contain. To be disposed of, these wastes are usually stored in specially constructed, open-air tanks that are not fully ventilated in the form of dams. Under the influence of the sun and wind, these sludges are dried by evaporation which may make the cyanide fading and form the cyanates then carbonates, which are non-toxic substances. But the capital mining companies avoid this process due to their high costs. Therefore, these highly toxic wastes are disposed directly into valleys and nearby water streams leading to contaminate the soil and groundwater. Also, these toxic compounds are combined with the local food chain, resulting in malignant diseases and sustainable health impairments [24]. On the other hand, cyanide is one of the most known poisons used in fishing and cyanide fishing is widespread in North-East Asia and the South Pacific where cyanide is used in coral reefs for the purpose of obtaining fish and marine organisms live by affecting on the respiratory system of fish making it easier to catch them after they surface. The use of cyanide in fishing has destroyed vast areas of coral reefs in the Philippines and Indonesia and has adversely affected for environmental tourism in some regions, which were among the best and most popular for tourists [23]. The soil contaminated with cyanide as soon as it touches by the human body or animal, it is poisoning. The risk of this substance will increase when rain falls on soil contaminated with cyanide, where the water sweep the polluted soil with them, so these toxics will dissolve in water that consumed by human or animals in outlying areas without any treatment [24]. In addition to that, part of this contaminated water will reach to the aquifer, which is also contaminated. If the cyanide wastes dispose to the river, very soon, all the fish and animals in the area will kill and float on the surface [25]. Therefore, as a precautionary measure, the Environmental Protection Agency (EPA) has set very strict limits on the permitted concentrations of cyanide ion disposed from industrial wastewater streams. Among the current methods used to remove cyanide ion from water are biodegradation process and adsorption technique [26]. Adsorption technology is a known and famous process and is an effective way of treating municipal and industrial effluents. The adsorption method either in the batch or continuous mode is a very efficient method for removing the cyanide ion from wastewater because it is a simple method comparing to other methods of treatment and does not require large operational costs in addition to the high removal percent obtained due to this process especially when using activated carbon [26-29]. However, since activated carbon is considered to be a high cost, researchers have sought cheaper cost alternatives to this material. One of the proposed alternative materials is the agricultural waste for its availability and because it is non-toxic and non-valuable substances and its ability to be effective adsorbent materials. Among these agricultural wastes are pomegranate peels [30]. Pomegranate is a plant that is heavily consumed in many regions of the world, the ration of peels wasted to the fruit ranging from 10-15% from the all pomegranate product. These peels are considered as one of the most important sources of antioxidants as well as their known ability to adsorb many of heavy metals such as zinc, lead, copper, chromium, dyes and other contaminants [30,31]. This paper is dealing with study the ability of removing toxic cyanide ions from contaminated aqueous solutions with known concentrations of (CN^-) using a cheap, available and non-toxic material which is Iraqi pomegranate peel (*after extraction of antioxidants* (*phenolics*) *from them*). Then try to find a way to get rid of the toxic waste left after finishing the removal process via preparing of an effective rodenticide by testing it on Sprague Dawley Rats (*Rattus rattus*) as a case study. Thus, most of toxic cyanide ion is removed from the water by pomegranate peels, which is considered as one of the useless types of agricultural waste. Then prepare an effective rodenticide by an economical, simple and eco-friendly method, up to the zero residue level (ZRL) of wastes.

2. Experimental work:

2.1 Pomegranate Peels Residue (PPR): Pomegranate peels residue (PPR) were collected after anti-oxidant extracted from them as described in **[30]**. PPR were washed three times with excess of distilled water, boiled to remove any type of impurities or dust that from PPR. Finally leave dried in sun for 24 hours.

2.2 Stock Solution: With a view to avoid the overlapping with another elements or compounds existing in real wastewater, the cyanide ion adsorption experiments in this study were achieved using simulated synthetic aqueous solution (SSAS) with different concentrations from one of the cyanide salts. The cyanide stock solution with 1000 mg/l was prepared by dissolving 1.88 g of sodium cyanide (NaCN) in a liter of distilled water. All the solutions used in the laboratory experiments had come from dilution of the stock solution to the coveted concentration using distilled water. The concentration of cyanide ions in the solution was measured by spectrophotometer devise using the calibration curve prepared for this purpose at wavelength of 520 nm as elucidated in Figure 1 as explained in [32] using spectrophotometer thermo – genesys 10 UV, USA.

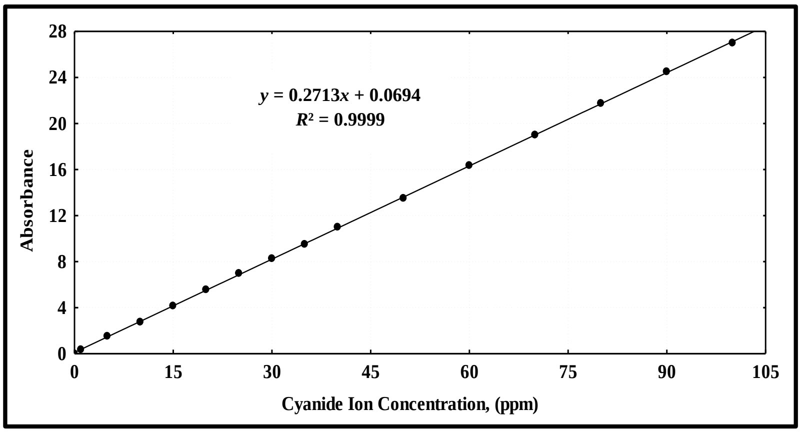


Figure (1) Calibration Curve of Cyanide Ions Using Spectrophotometer

2.3 Adsorption Unit:

Continuous adsorption unit of packed bed was used to perform the cyanide ion adsorption from SSAS at different initial concentrations, multiple heights of adsorbent media (which was PPR), various flowrates of cyanide contaminated solutions (SSAS), numerous treatment times and several pH of SSAS. The pH of cyanide solution was fixed using suitable solutions which were 0.1 N of potassium hydroxide (KOH) as a base and 0.1 N of hydrochloric acid (HCl) as an acid. The continuous adsorption unit consists of a plastic storage tank of 5 L capacity for SSAS, plastic column as packed bed containing the filling (which was PPR) of 60 cm height and 5 cm diameter, pump to withdraw the SSAS from storage tank to packed bed column at different flow rates determined by the rotameter. Before starting the experiments the packed column stuffed with distilled water down from top to bottom and the adsorption media (PPR) adding with the distilled water gradually and carefully as a slurry to the required height to avoid any bubble formation inside the unit between the adsorbent. When the adsorption column and the packing are ready, the adsorption process will begin by allowing the SSAS with coveted cyanide concentration to enter the packed bed with the flowrate determined using rotameter. To predict the best operational conditions that gave the maximum percentage removal of cyanide ions from SSAS. The adsorption experiments are conducted under a range of cyanide initial concentration, pH of SSAS, adsorbent media height, SSAS flowrate of and treatment time varied between (1-100) ppm, (1-8), (10-50) cm, (5-100) ml/min and (1-120) minutes respectively. All experiments carried out at laboratory temperature (25±2) °C. Samples are taking from the bottom of packed column each 5 minutes and analysed spectrophotometrically to detect the remaining cyanide concentration unadsorbed during treatment process.

3. Results and discussion

The ability of PPR to remove cyanide ion from SSAS using fixed bed of continuous mode at various parameters are explained below.

3.1 Initial concentration influence: as describe from Figure 2, the results showed that the percentage removal of cyanide ions using PPR increased with decreasing the initial concentration of contaminated compound when all other operational factors keeping constant. This may be explained by knowing that the adsorbent media (which is PPR) has finite active sites which will be saturated at given concentration of cyanide. This lead to increase the ions jostled on active sites at the surface of adsorbent media. Since the little concentration of cyanide contains a small number of cyanide ions compared to the high concentrations of the same ion, therefore the percentage removal of cyanide from SSAS is increased with lowering the initial concentration of cyanide in SSAS. The maximum percentage removal reaches to 95.75% at cyanide initial concentration of 1 ppm.

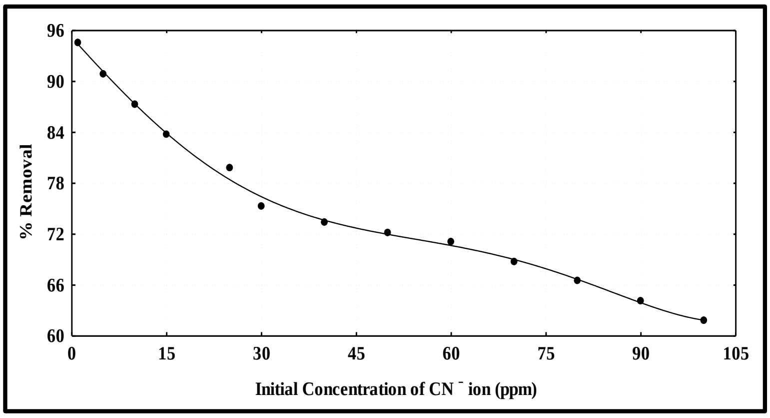


Figure 2 Effect of initial concentrations on the percentage removal of cyanide ion

3.2: pH influence: Generally, the pH of the solution effects on the ionization degree of the polluted solution and also on the surface charge of the adsorption medium as well as with the polluting substances which may be of different charges, depending on the Point of zero charge (pzc). So, the influence of pH will be obvious on the adsorption of cyanide ions at the surface of PPR as characterize in Figure 3. It is clear that the percentage removal increase when the pH of SSAS increase too when all other operating factors keeping constant. This result may be attributed to the pzc value which is equal to 7.827 which is playing an important role in the stability of cyanide ions. According to pzc the surface will charged with positive charge decreases gradually until reach the maximum density at pzc value. So, when the pH is less than pzc the cyanide ion will be in the form of hydrogen cyanide (HCN) which is weak acid and very soluble in water so it is difficult to adsorb CN^- ions on the surface of PPR due to attracting forces between the hydrogen ion in water and cyanide ions in solution. While when the pH increases and approach to pzc the positive charge at the PPR surface will increase too and the cyanide ions will adsorbed on the surface of adsorbent media because the de-protonation process from the surface of the adsorbent media will be more difficult due to increase the availability of effective groups of chemical adsorption on the surface, which suffers from ion exchange as a type of interaction with the cyanide ion. Therefore, the percentage removal of cyanide ions will increase with pH increase. The adsorption equilibrium between the adsorbent media and cyanide ion indicates that the adsorption range highly depends on the pH at the range between (7-10). Thus, the value of the optimal pH for adsorbing the cyanide ion is 8. This result is agreed with[29-31].

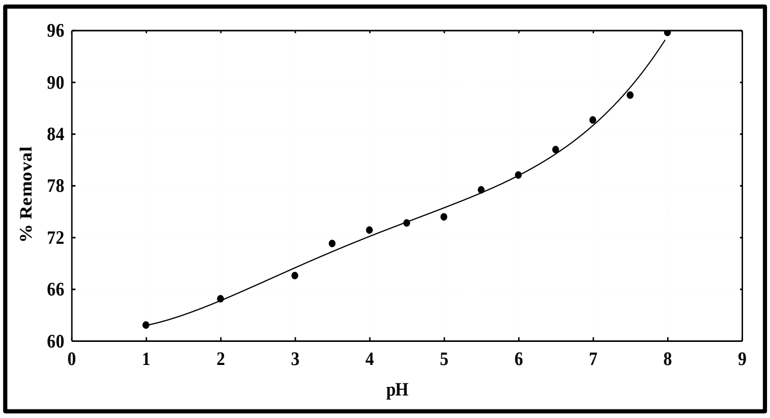


Figure 3 Effect of *pH* on the percentage removal of cyanide ion

3.3: Adsorbent media bed height influence: The results illustrate that when the adsorbent media (PPR) bed height is increased the percentage removal of cyanide ions from SSAS is increasing too, as depicted in **Figure 4**, when all other operators are keeping without change. The increase in the bed height means increase in the amount of adsorbing media inside the adsorption unit. This lead to increasing the number of active sites that will be adsorbed the cyanide ions from SSAS; as a result, the availability of bonding sites for adsorbing has increased. Consequently, the removal of cyanide ions on the surface of the active sites will be also increased. This will increase the portability of PPR to adsorb more amounts of cyanide ions from SSAS at different initial concentrations; eventually the percent removal of cyanide from aqueous solutions will be increased.

3.4: Flow rate of SSAS influence: The effect of changing SSAS flow rates in the adsorption unit was investigated at constant of all other operating conditions. From Figure 5, it ca be observed that the relation is inversely between the cyanide percentage removal and the flow rate of SSAS. When the SSAS flow rate is increased inside the adsorption unit, the velocity of solution is also increased. Thus, the solution will spend low retention time in the packed bed if the flow rate of solution was less. It will therefore undergo less processing time than solutions with low flow rates. Ultimately, the cyanide ion percentage removal will be reduced when the flow rate of SSAS is increased. The results show that the maximum percentage removal of cyanide ions from SSAS using PPR was took place at flow rate of 5 ml.min^{-1}.

3.5: Treatment time influence: The effect of treatment time on the efficiency of cyanide ion adsorption by PPR was studied within a range of (10-120 min) and immutability of all other operational factors. Figure 6 exhibits the results obtained by changing this operational factor. It is noted from this figure that there is direct relation between cyanide ion percentage removal and the time of treatment until 60 minute, i.e. increasing the removal efficiency with increasing the treatment time inside the packed bed. The reason of this is due to fixed fact that is when the treatment time of SSAS is longer and the flow velocity of the solution within the packed column is fixed, the solution is spent longer time than the solutions of short retention time, which means a greater removal percentage of cyanide ions from SSAS. While when the time exceeds 60 minutes, it is observed that the adsorption percentage will fixed and not change. This may be that the active sites in PPR becomes saturated with cyanide ions and cannot adsorb any additional ions. So, increasing the treatment time more than 60 minutes will not change the adsorption efficiency of cyanide. Thus, it can say that the optimum time of treatment for best cyanide percentage removal from SSAS using PPR is 60 minutes.

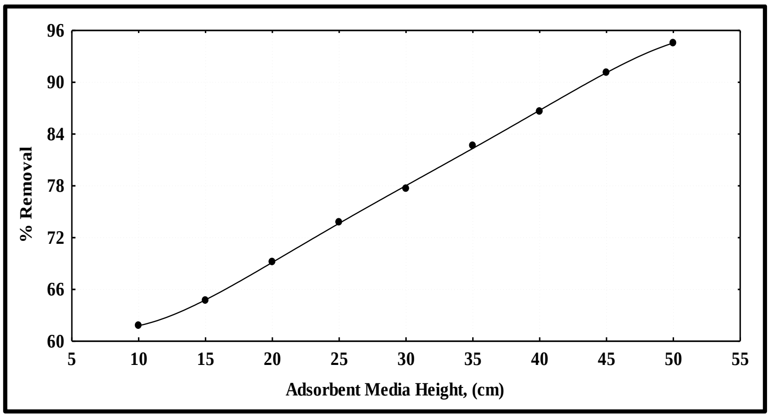


Figure 4 Effect of adsorbent media bed height on the percentage removal cyanide ion

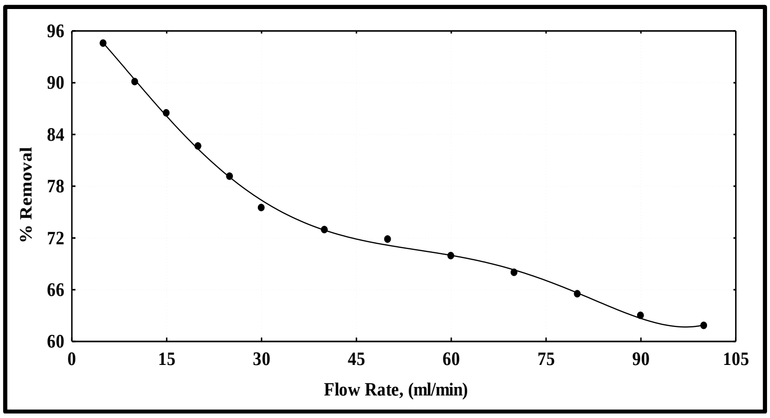


Figure 5 Effect of aqueous solution flow rate on the percentage removal of cyanide ion

4. Adsorption Isotherm

Langmuir and Freundlich models are used to describe the adsorption isotherm behaviour in the present study.

4.1: Langmuir isotherm model: the Langmuir adsorption isotherm model supposes the adsorption surface is monolayer, homogeneous and the adsorption sites have similar adsorbate ability and each side in the adsorption surface independent on the adsorption in the neighbouring sites. Langmuir isotherm model can be described by equation (1):

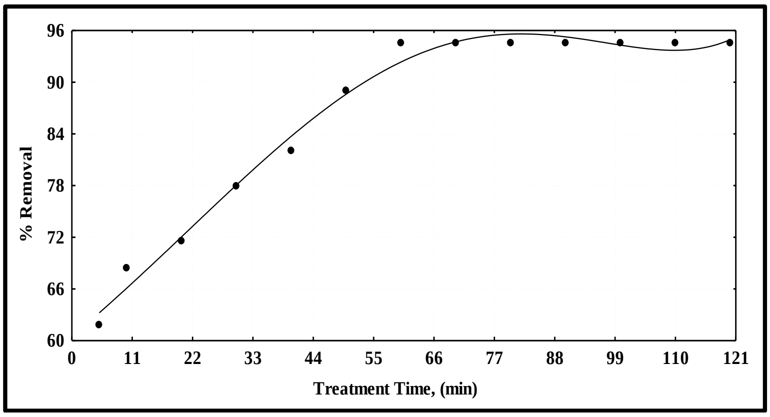


Figure 6 Effect of treatment time on the percentage removal of cyanide ion

$$\boxed{q_{eq} = \frac{q_m . K_L . C_{eq}}{1 + K_L . C_{eq}}} \dots (1)$$

where: q_{eq}: is the cyanide ion quantity adsorbate per unit mass of adsorbent at equilibrium concentration C_{eq} , C_{eq} : is the adsorbate concentration in the solution at equilibrium, q_m: is the amount of solute adsorbed per unit mass of adsorbent in forming a complete monolayer on the adsorbent surface and K_L: is a constant related to the energy or net enthalpy of adsorption (l/mg).

For very small amount of adsorption, when $K_L C_{eq} << 1$ it yields a linear adsorption isotherm: $q_{eq} = q_m K_L C_{eq}$. For large amount of adsorption, when $K_L C_{eq} >> 1$ it will be equal: $q_{eq} = q_m$, Thus, the

Langmuir isotherms model can be represented by linear form as:

$$\boxed{\frac{C_{eq}}{q_{eq}} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_{eq}} \ldots (2)$$

Plotting of C_{eq}/q_{eq} against C_{eq} will give a straight line, has an intercept of $(1/K_L q_m)$ and the slop is $(1/q_m)$.

4.2: Freundlich isotherm model: the Freundlich adsorption isotherm model is an empirical equation and has been widely used for long time ago. This model depicts the equilibrium on heterogeneous surfaces and assumes multilayer capacity. Usually, for moderate concentrations, Freundlich model is completely concurred with Langmuir model and the experimental data, but in contrast, this isotherm model cannot represent a linear form in very low concentrations as in Langmuir adsorption isotherm model. However, Freundlich isotherm model can be described by equation (3) bellow:

$$\boxed{q_{eq} = K_F C_{eq}{}^{\frac{1}{n}}} \ldots (3)$$

Where n and K_F are the Freundlich isotherm constants.

Equation (3) can be rearranging to obtain the linear form of Freundlich adsorption model. The Freundlich isotherm model can be represented by linear form as:

$$\boxed{\log q_{eq} = \log K_F + \frac{1}{n} \log C_{eq}} \ldots (4)$$

The calculation of n and K_F values can be performed via plotting $\log q_{eq}$ vs. $\log C_{eq}$ where the intercept is $\log K_F$ and the slop is $1/n$

4.3: Adsorption isotherms calculations: The adsorption isotherm constants were calculated from the slopes and intercepts of (Langmuir isotherm) and (Freundlich isotherm) and presented in **Table 3**. The values of calculated correlation coefficients R^2 were higher for Langmuir isotherm than the Freundlich isotherm; that means Langmuir isotherm model represented the adsorption process well than Freundlich isotherm model. The maximum capacity of pomegranate peels residue (PPR) for cyanide ion removal CN^- was calculated in the range of 15.228 mg/g at constant temperature that indicated the best adsorbing capacity of PPR for cyanide ion removal CN^- .

Table 3: Values of Langmuir and Freundlich isotherm constants for the adsorption of cyanide on pomegranate peels residue (PPR) at Optimum Conditions (C_o = 1 mg.l^{-1}, pH = 8, l = 0.6 m, F = 5 ml.min^{-1}, and t = 60 min).

Langmuir Isotherm Model				Freundlich Isotherm Model		
q_m	K_L	R_L	R^2	K_F	n	R^2
15.228	0.03575	0.7810	0.9957	0. 5077	1. 2511	0.9053

5- Adsorption Kinetics:

In this paper, the adsorption kinetics is studied due to the important of it's to determine the physical and chemical behaviour of the adsorbent media and also to predict the mechanism of adsorption process occurred. Three kinetic models are proposed to investigate the experimental data obtained from the adsorption of cyanide ions on PPR. These kinetic models are first order reversible model, pseudo first order model and pseudo second order model.

5.1: Pseudo-first order model: This model is depended on the capacity of solid adsorbate. It is assumed that adsorption between liquid and solid occurred on one layer on the adsorption surface (adsorbate). The mathematical expression of this model is described by Equation (7):

$$\boxed{q_{eq} - q = e^{-k_1 t}} \ldots (7)$$

Where: q_{eq}: is the cyanide ion quantity adsorbate per unit mass of adsorbent at equilibrium (mg/g), q: is the cyanide ion quantity adsorbate per unit mass of adsorbent at any time (mg/g), t : is the time and (k_1) : is the first order rate constants (min^{-1}). The linear form of this model can be represented by equation (8):

$$\boxed{\ln(q_{eq} - q) = \ln q_{eq} - k_1 t} \ldots (8)$$

So from the plot of $\ln(q_{eq} - q)$ vs. t it can be calculating the rate constant k_1 which appears as the slop of the equation, while the intercept is equal to $\ln q_{eq}$.

5.2: Pseudo-second order model: Ordinarily it is the best model for expressing the kinetic model of adsorption process. It is assumed that adsorption between adsorbent (solid phase) and adsorbent (liquid phase) performed on two layer on the adsorption surface (adsorbate). This model is described by Equation (9):

$$\boxed{q = \frac{q_{eq}{}^2 k_2 t}{1 + q_{eq}{}^2 k_2 t}} \ldots (9)$$

Where: q_{eq}: is the cyanide ion quantity adsorbate per unit mass of adsorbent at equilibrium (mg/g), q: is the cyanide ion quantity adsorbate per unit mass of adsorbent at any time (mg/g), t : is the time (min) and (k_2) : is the first second order rate constants (g.mg^{-1}.min^{-1}). The linear form of this model can be represented by equation (10):

$$\boxed{\frac{t}{q} = \frac{1}{q_{eq}{}^2 k_2} + \frac{1}{q_{eq}} t} \ldots (10)$$

From linearized form it is clear when plotting (t/q) against t the slop of equation 10 is $(1/q_{eq})$ while the intercept is $(1/q_{eq}{}^2 k_2)$

5.3: Adsorption kinetic calculations:

The adsorption kinetic constants and correlation coefficients of three models used in this study were calculated and given in **Table 4**. Good correlation coefficients R^2 were observed for the cyanide ion CN^- uptake process and can be approximated with the pseudo second order kinetics model. Constants k_1 and k_2 for all kinetics models tested have been calculated and summarized in **Table 4**. Thus, the pseudo second order kinetics was pathway to reach the equilibrium.

Table 4: Values of pseudo first order and pseudo second order for the adsorption of cyanide on pomegranate peels residue (PPR) at Optimum Conditions (C_o = 1 mg.l^{-1}, pH = 8, l = 0.6 m, F = 5 ml.min^{-1}, and t = 60 min)

Pseudo first order			Pseudo second order			Experimental
q_{eq}	k_1	R^2	q_{eq}	k_2	R^2	q_{eq}
2.7129	3.61×10^{-3}	0.8825	4.2261	3.86×10^{-4}	0.9800	4.99537

6. Utilization of Wastes after Adsorption Process:

PPR after uses as an adsorption media to remove cyanide ions from SSAS (as explained in experimental work mentioned above) was collected and set up to the next step which is exploited it as a raw material for preparation of a simple and cheap rodenticide, the main goal of this paper. To perform this purpose, 20 groups (10 groups for males and 10 groups for females) of outbred multipurpose breed of albino rats, which are (Sprague dawley) and have scientific name (*Rattus rattus*). Each group (cage) contain 10 rats. Their weight ranged between (250-300) g and their age ranged between (6-10) months. In addition to that, there are another two control groups, (CG 1) and (CG 2) where the rats in which (males and females) were feeding with natural rat provender only and natural with non-contaminated PPR (*non-adsorbed cyanide ions*) respectively to compare the results. Before testing, all rats were left for one week in clean cages and laboratory conditions suitable for living. The rats were feeding with normally rat provender to ensure that no rats suffer from any disease or ill-treatment that leads to change the results and for adapting to the place and food (provender) before starting experiments. The temperature was between (25±2°C) and the lighting was 14 hours per day using an ordinary light bulb [32]. After adoption to the place and provender, 120 male rats and 120 female rats were divided randomly to 12 groups for males and females as 10 rats/group, and the rats were treated daily for one week. After the week, the rats were feeding by PPR that adsorbed cyanide ions directly (without any further treatment) mixed with provender with very little of sweet food in order to entice the rats. These sweet foods were replaced continuously to avoid any aversion by the rats. The results showed that there were fatalities among males and female rats in all cages (except for rats in the control groups CG1 and CG2). The fatalities occur at unlike ratios and at different times depending on the amount of cyanide ions loaded on PPR consumed by rats. The half lethal dose (LD_{50}) was also calculated, and the results determined were as explained in Table 1. From Table 1 it is noted that the value of LD_{50} calculated for prepared rodenticide in this study is identical with the LD_{50} cited in the literature and references. Thus, this way can be considered as one of the means that dispose of more than one type of harmful and contaminated wastes at the same time with non-cost, simple and eco-friendly method accessing to zero residue level (ZRL).

Table 1: The Half Lethal Dose (LD_{50}) for Rodenticide Prepared from PPR Loaded with CN^- ions

Type of food consumed by rats	**The Half Lethal Dose (LD_{50}) Calculated for Male Rats (according to this study) , (mg/kg)**	**The Half Lethal Dose (LD_{50}) Calculated for Female Rats (according to this study), (mg/kg)**	**The Half Lethal Dose (LD_{50}) for Rats according to Literature**
Control Group 1 (CG1): Feeding: Ordinary rat provender	There are no fatalities	There are no fatalities	-
Control Group 2 (CG2): Feeding: Ordinary rat provender + non-contaminated PPR only	There are no fatalities	There are no fatalities	-
Other Groups: Feeding: Ordinary rat provender + PPR loaded with CN^- ions	5.53	5.17	5 – 5.72 **[34]**

Generally, the inorganic rodenticides are one of important pesticide types which are used to prevent or expel or kill or control rodents. The active components in these pesticides predominantly are compounds of chromium, arsenic, lead, tin, zinc, phosphorus and cyanide as inorganic compounds [26]. There are many ways to use rodenticides which contain inorganic materials as active compounds, some of which are placed near their whereabouts as poisonous baits food that can be consumed by rats through oral nutrition. Another type of rodenticides is sprinkled like a powder in the path of rodents, attach to their bodies and enter the digestive system by cleaning the body. Or the poisonous pesticide is putting on an adhesive and when rat attach by the adhesive material, the toxic substance enters the body and is able to kill it. The rodenticide presents in this investigation follows the first type. PPR loaded with toxic cyanide ions were given to the rats by mixing it with very little sweet material approximately (1-5 wt %) of given food amount. Cyanides are considered as one of distinctive substances that can be successfully used in the preparation of rodenticides due to their guaranteed effectiveness and highly toxic effects. Moreover, they are non-degradable and can remain for a long time without changing their composition.

The follow-up of morphological and anatomical changes in the defunct rats showed the mechanism by which the cyanide ion acts on rodents, which were as follows:

1. Very high concentration of cyanide ion (>10 mg/kg) leads to a very rapid and overall precipitation to the living (Deoxyribonucleic acid DNA) cell protein, because it attacks the sulfur bonds, which play an important role in maintaining the distinctive form of protein and thus the rat is defunct. It is noted that the effect of the cyanide ion is focused on the epithelium of the central gastrointestinal tract of the rodents exposed to rodenticide tested.

2. High concentrations of cyanide ion (1-10mg/kg) lead to bind of a cyanide ion with important enzymes required by the body and deviate or inhibit its action. From these enzymes is dehydrogenase, which the inhibitions of its action lead to myocardial infarction. Also effect on cytochrome c oxidase enzyme which is necessary in respiratory processes converts the oxygen molecule into two water molecules and plays an important role in the synthesis of adenosine triphosphate (ATP). Cyanide ion may influence on phosphatase enzyme which is necessary for many biological functions, because phosphorylation and opposite phosphorylation act in different roles in cellular regulation and cryptographic signalling. The inhibition of the action of these enzymes alone or in combination leads to an imbalance in the chemical and biological processes in the body, which eventually lead to the destruction of the organism.

3. Medium concentrations of cyanide ion (0.05-1mg/kg) acts to inhibit the phosphorylation process of adenosine diphosphate (ADP) [an important organic compound in the metabolic process and is essential for the flow of energy in cells and present in all tissues of living organisms, provides energy for physiological processes such as muscle contraction] in the oxidative phosphorylation process and thus prevents the formation of adenosine triphosphate (ATP), which is the required and necessary material to store energy in the body of the organism.

4. Low concentration of cyanide ion (<0.05 mg/kg) leads to inertia, inability to stand on its lists, breakdown of the immune system and inability to reproduce (infertility) from rodents.

7. Conclusions

The following conclusions can be drawn:

1. Pomegranate Peels Residue (PPR) (*which remains after extraction of antioxidants* (*phenolics*)) exhibit a good ability to remove cyanide ions from SSAS and the maximum percentage removal was 95.75% at laboratory temperature and initial concentration, pH, height of PPR, treatment time and feed flowrate equal to, 1 mg/l, 8, 60 cm, 60 min and 5 ml/min respectively.

2. The percentage removal of cyanide ions using PPR was increased with increasing pH, treatment time and height of adsorbent media while it is increasing with decreasing initial concentration and feed flow rate.

3. After ended the adsorption process, it can utilize from the huge amount of toxic waste remaining by preparation a simple and cheap rodenticide. By this way it can dispose more than one type of waste in benefit, non-cost and eco-friendly method accessing to zero residue level (ZRL).

8. References

[1] Dunbar, K. R. and Heintz, R. A., (1996), “Chemistry of Transition Metal Cyanide Compounds: Modern Perspectives”, in Progress in Inorganic Chemistry, Volume 45 (ed K. D. Karlin), John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9780470166468.ch4

[2] Dzombak D. A., Ghosh R. S. and Wong-Chong G. M., (2006), “Cyanide in Water and Soil: Chemistry, Risk, and Management”, CRC Press. Taylor & Francis Group.

[3] Jones D. A., (1998), “Why Are So Many Food Plants Cyanogenic?”, *Phytochernistry*, Volume 47, No. 2, pp. 155-162, PMID 9431670. doi:10.1016/S0031-9422(97)00425-1

[4] Vetter J., (2000), “Plant Cyanogenic Glycosides”, *Toxicon*, Volume 38, Number 1, pp: 11-36. PMID 10669009. doi:10.1016/S0041-0101(99)00128-2.

[5] Surleva A., Gradinaru R. and Drochioiu G., (2012), “Cyanide Poisoning: From Physiology to Forensic Analytical Chemistry”, *International Journal of Criminal Investigation*, Volume 2, Issue 2, pp: 79-101.

[6] Müller K. R., Bromley J., Farquhar J. T., Gidley P. T., James S., Martinetz D., Robin A., Schomaker N., Stephens R. D. and Walters D. B., (1986), “Chemical Waste: Handling and Treatment”, Springer-Verlag Berlin Heidelberg, DOI: 10.1007/ 978- 3-642-69625-1

[7] Bolarinwa I. F., Orfila C., Morgan M. R.A., (2014), “Amygdalin Content of Seeds, Kernels and Food Products Commercially-available in the UK”, *Food Chemistry*, Volume 152, pp: 133–139, http://dx.doi.org/10.1016/j.foodchem.2013.11.002

[8] Holzbecher M. D., Moss M. A. and Ellenberger H. A., (1984), “The Cyanide Content of Laetrile Preparations, Apricot, Peach and Apple Seeds”, *Journal of Toxicology: Clinical Toxicology*, Volume 22, Issue 4, pp: 341-347. http://dx.doi.org/10.3109/15563658408992565

[9] Water Quality Standards Handbook: Second Edition. EPA-823-B-12-002; March 2012. Retrieved November 13, 2012 from http://water.epa.gov/scitech/swguidance/standards/handbook/index.cfm

[10] Young C. A. and Jordan T. S., (2004), “Cyanide Remediation: Current and Past Technologies”, *Proceedings of the 10th Annual Conference on Hazardous Waste Research*, pp. 104-129.

[11] Encyclopædia Britannica, Science, (2014), “Hydrogen cyanide”, October 20.

https://www.britannica.com/science/hydrogen-cyanide

[12] World Health Organization, (2004), "Hydrogen cyanide and cyanides: human health aspects", Concise international chemical assessment document; 61.

[13] Dhas P. K., Chitra P., Jayakumar S., Mary A. R., (2011), "Study of the effects of hydrogen cyanide exposure in Cassava workers", *Indian Journal of Occupational and Environmental Medicine*, Volume 15, Number 3, pp: 133-136. doi:10.4103/0019-5278.93204.

[14] Bhattacharya R. and Flora S .J. S., (2009), "Chapter 19 – Cyanide Toxicity and its Treatment", Handbook of Toxicology of Chemical Warfare Agents, Pages 255–270. Academic Press, Elsevier. https://doi.org/10.1016/B978-0-12-374484-5.00019-5

[15] Obiri S., Dodoo D. K., Okai-Sam F. and Essumang D. K., (2006), "Non-Cancer Health Risk Assessment From Exposure To Cyanide by Resident Adults from the Mining Operations of Bogoso Gold Limited In Ghana", *Environmental Monitoring and Assessment*, Volume 118, pp: 51-63. DOI: 10.1007/s10661-006-0773-6.

[16] Fui L. K., (2011), "Removal Of Cyanide Using Photocatalysis-Membrane Hybrid System", BSc. Thesis, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Petaling Jaya, Malaysia.

[17] Piyapolrungroj N., Li C., Pisoni R. L. and Fleisher D., (1999), "Cimetidine transport in brush-border membrane vesicles from rat small intestine", *The Journal of Pharmacology and Experimental Therapeutics*, Volume 289, Number 1, pp: 346-353.

[18] Wikipedia, (2017). https://en.wikipedia.org/wiki/Verapamil

[19] Rindone J. P.and Sloane E. P., (1992), "Cyanide Toxicity from Sodium Nitroprusside: Risks and Management", *Annals of Pharmacotherapy*, Volume 26, Issue 4, pp: 515-519. https://doi.org/10.1177/106002809202600413

[20] Ramdharane S. M., Vyas K. B., Nimavat K. S., (2016), "A sensitive spectrophotometric determination of cyanide content in Citalopram Hydrobromide API in parts per million levels", *Journal of Pharmaceutical Science and Bioscientific Research*, Volume 6, Number 1, pp: 168-171.

[21] Wikipedia, (2017). https://en.wikipedia.org/wiki/Cyanide

[22] Baur X., Budnik L. T., Zhao Z., Bratveit M., Djurhuus R., Verschoor L., Rubino F. M., Colosio C. and Jepsen J. R., (2015), "Health risks in international container and bulk cargo transport due to volatile toxic compounds", *Journal of Occupational Medicine and Toxicology*, Volume 10. DOI: 10.1186/s12995-015-0059-4

[23] Ibrahim T. A., Abbas M. N. and Abbas F. S., (2016), "Detoxification of Pesticides Wastewater by Adsorption Technique Feasibility of Agricultural Waste Utilization", LAMBERT Academic Publishing, **ISBN-10:** 365983243X, **ISBN-13:** 978-3659832437.

[24] Kuyucak N. and Akcil Ata, (2013), "Cyanide and removal options from effluents in gold mining and metallurgical processes", *Minerals Engineering*, Volumes 50–51, September, Pages 13-29. https://doi.org/10.1016/j.mineng.2013.05.027

[25] Kjeldsen Peter, (1999), "Behaviour of Cyanides in Soil and Groundwater: A Review", *Water, Air, and Soil Pollution*, Volume 115, pp: 279-307. Kluwer Academic Publishers

[26] Al-Hermizy S. M. M., (2017) "Preparation of Rodenticide for (Sprague Dawley Rats *Rattus rattus*) from the Residue of Tin Adsorption Arriving to Zero Residue Level (ZRL)", *Tikrit Journal of Pure Science*, volume 22, Number 4, pp:10-18. (*in Arabic*).

[27] Eletta O. A. A., Ajayi O. A., Ogunleye O. O. and Akpan I. C., (2016), "Adsorption of cyanide from aqueous solution using calcinated eggshells: Equilibrium and optimisation studies", *Journal of Environmental Chemical Engineering*, Volume 4, Issue 1, March, pp: 1367-1375. https://doi.org/10.1016/j.jece.2016.01.020

[28] Pirmoradi M., Hashemian S. and Shayesteh M. R., (2017), "Kinetics and thermodynamics of cyanide removal by ZnO@NiO nanocrystals", *Transactions of Nonferrous Metals Society of China*, Volume 27, Issue 6, June, pp: 1394-1403. https://doi.org/10.1016/S1003-6326(17)60160-2

[29] Abbas M. N., Abbas F. S. and Ibraheem S. A., (2014), "Removal of Cyanide Ion from Wastewater Using Banana Peel and Utilization from Residue", *Journal of Asian Scientific Research*, Volume 4, Number 5, pp: 239-247.

[30] Abbas M. N., (2014), "Pomegranate Peels: Source of Antioxidants Extraction and Natural Dentifrices Preparation", *European Academic Research*, Volume II, Issue 3/ June, ISSN 2286-4822. www.euacademic.org

[31] Ibrahim T. A., (2016), "Study of the Using Effect of Chromium Adsorption Remnants as Rodenticide for Sprague Dawley Rats *Rattus rattus* Accessing to Zero Residue Level (ZRL)", *European Academic Research*, Volume IV, Issue 5/ August, ISSN 2286-4822. www.euacademic.org

[32] Pitschmann V., Kobliha Z. and Tušarová I., (2011), "A Simple Spectrophotometric Determination of Cyanides by P-nitrobenzaldehyde and Tetrazolium Blue", *Advances in Military Technology*, Volume 6, Number 2, December.

[33] Al-Kattan M. M., Abdul-Fattah J. H. and Al-Annaz R. M., (2012), "Effect of Salvia Powder on Blood and Histological Picture of Liver and Heart Muscle in Male Albino Mice", *Rafidain Journal of Science*, Volume 23, Number 2A, pp:1-14. (*in Arabic*)

[34] Ballantyne B., (1994), "Acute percutaneous systemic toxicity of cyanides", *Journal of Toxicology*, Cutaneous and ocular toxicology, Volume 13, Issue 3, pp: 249-262.

الإستفادة من متبقيات إزالة أيون السيانيد في تحضير مبيد قوارض فعّال وصولاً إلى مستوى المتبقيات الصفري: إستخدام الجرذان من نوع Sprague Dawley (*Rattus rattus*) كحالة دراسية

سعادت مصطفى محمد[1] ، نسرين صبار هاشم[2] ، احمد علاء حسين[3] ، محمد نصيف عباس[3]

[1]قسم علوم الحياة ، كلية العلوم ، جامعة تكريت

[2]قسم علوم الحياة ، كلية التربية للعلوم الصرفة ، جامعة ديالى

[3]قسم هندسة البيئة ، كلية الهندسة ، الجامعة المستنصرية

zaid.almahdawi@yahoo.com, dr.hishamtj@yahoo.com , malakaz08@yahoo.com ,
mohammed.nsaif.abbas@gmail.com

الملخص

يتناول هذا البحث دراسة إمكانية استخدام بقايا قشور الرمان (PPR) (والتي تبقت بعد استخلاص مضادات الأكسدة منها (الفينولات)) في إزالة أيون السانيد من المحاليل المائية الملوثة به باستخدام عدة عوامل تشغيلية بتقنية الامتزاز. كانت العوامل التشغيلية المدروسة تتضمن التركيز الابتدائي لأيون السيانيد (CN^-)، الدالة الحامضية للمحلول المائي (pH)، معدل الجريان للمحلول المائي الملوث داخل وحدة الامتزاز، ارتفاع وسط الامتزاز وزمن المعالجة. من خلال تغيير المتغيرات المشار إليها أعلاه بمديات تجريبية محددة، تّ/ اختيار أفضل الظروف التشغيلية التي أعطت أفضل نسبة إزالة لأيون السيانيد من المحلول المائي والتي وصلت إلى 95.75%. مخلفات نماذج قمتبقيات قشور الرمان بعد انتهاء عملية الامتزاز تم استخدامها لتحضير مادة سامة فعالة تستخدم كمبيد قوارض. تم اختبار التأثير القاتل لمبيد القوارض الرخيص المحضر باستخدام جرذان من نوع (Sprague Dawley) والتي تحمل الاسم العلمي (*Rattus rattus*) كحالة دراسية. أظهرت هذه المتبقيات السامة تأثير قاتل على هذا النوع من الجرذان المختبرية بالاعتماد على الجرعة النصفية القاتلة المحسوبة (LD_{50}) والتي تمت مقارنتها بالجرعة النصفية القاتلة المشار إليها في الأدبيات والمراجع العلمية ولوحظ بأنها تقع في نفس المدى . بهذه الطريقة ، تم التخلص من أكثر من نوع من المخلفات السامة بواسطة طريقة بسيطة ومفيدة وغير مكلفة وصديقة للبيئة. تمثلت هذه الطريقة بإزالة أكبر كمية ممكنة من أيون السيانيد من المحلول المائي بواسطة مخلفات زراعية عديمة القيمة وهي متبقيات قشور الرمان وفي نفس الوقت تحضير مبيد قوارض رخيص وفعّال بالاعتماد على الجرعة النصفية القاتلة وصولاً إلى مستوى المتبقيات الصفري (ZRL).

الكلمات المفتاحية: قشور الرمان ، أيون السيانيد ، الامتزاز ، جرذان نوع (*Sprague Dawley*) ، مستوى المتبقيات الصفري (*ZRL*) .