Plant Archives Volume 20 No. 2, 2020 pp. 3343-3353 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

ZERO RESIDUE LEVEL CONCEPT A NEW VISION FOR TOXIC WASTE MANAGEMENT : A REVIEW

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Abstract

Adsorption technology is one of the most promising techniques in many important areas. Although discovered in the 19th century, it is still widely used in many biological, medical, industrial, environmental and other applications. Pollution treatment is one of the environmental areas in which adsorption technology contributes effectively. This technology has proven its high ability to treat pollution in soil, air and water, especially using activated carbon because of its distinctive specifications. Therefore, activated carbon has become the most famous adsorption media among other adsorption materials. It is a porous material with a high surface area and has the ability to adsorb many types of organic and inorganic pollutants and can be regenerated several times in addition to the possibility of use in the treatment of water, air and soil. The observer of researches, papers and studies dealing with adsorption technique notes that one of the reasons for the spread of this technology in environmental treatment processes is due to its facility, simplicity, low operational cost and acceptable efficiency compared to other methods and techniques in addition to negligible toxicity of different adsorption materials. But, the problem of the high cost of activated carbon and other adsorbents production, especially high surface area is the most important constraints that called on researchers to find solutions through look for alternative adsorption materials. Agricultural and industrial wastes have been proposed as substitutes for activated carbon or as raw materials for its manufacture. They are cheap and available materials, with suitable operability and do not require a lot of initial preparations to use them. However, the problem of its accumulation and disposal after the completion of the process due to its transformation into toxic substances has not been addressed adequately so far. A number of researchers have limited their efforts to recover the toxic materials from the adsorbents media only. This review highlights a number of studies that have applied a new concept in waste management, is the zero residue level (ZRL), which aims to completely get rid several types of pollutants in different ecosystems simultaneously by an easy, safe, benefit economical and environmentally friendly manner accessing to ZRL.

Key words : zero residue level, wastes, pollution, environment, aqueous solutions, environmentally friendly.

Introduction

The environment suffers from two types of problems; the first type is the natural problems represented by earthquakes, volcanoes, floods and devastating hurricanes, while the second type is the human problems that occur due to the ongoing human activities (Knap and Rusyn, 2016). The second type is the most dangerous and the most widespread than the first type, and in some cases, be one of the reasons for the first type of environmental problems (Muralikrishna and Manickam, 2017). As a result of human revolution and increasing its social, industrial, agricultural, population, recreational and military requirements, this has led to the depletion of resources, climate change, acid rain and other environment problems. All of these activities directly affected the environment in all its components (water, air, soil and space) (Trenberth, 2018). Water pollution is one of the oldest topics of cared for by scientists and specialists in the field of pollution, so as to the importance of water and its necessity. It enters into all biological and industrial processes, and no living organism - whatever its shape, type or size - can live without it (Inyinbor *et al.,* 2018). Agricultural residues, industrial wastes and wastewater

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constitute a high proportion of aquatic environment pollution sources the with many organic and inorganic contaminants such as heavy metals, dyes, pesticides, oil spills, radioactive elements and other hazardous toxic pollutants on the environment (Muralikrishna and Manickam, 2017). Contamination of water with these pollutants causes an imbalance of the ecosystem and leads to the poisoning of aquatic plants, fish and other organisms, as well as the changing of natural water specifications (Ali *et al.,* 2019). In spite of all these horrific damages and serious problems, some industrial enterprises and mining companies that do not adhere to the right environmental standards release these hazardous substances directly to water sources without appropriate treatment in the absence of strict government control or have been managed to circumvent the law, especially in most developing countries (Kjellstrom *et al.,* 2006). The effect of high toxicity of those materials is not limited on the environment only but will be transferred to humans when they enter the food chain, causing serious health effects for many diseases, including cancer. Also, it can disrupt occur in the genetic makeup of the human being infected, and children category is the most age group affected by the damage of these contaminants (Engwa *et al.,* 2019). Therefore, it has become necessary to treat wastewater and reduce the proportion of pollutants in accordance with the standard specifications used before being released to water sources or stored properly and accurately in the ground until safe disposal and intensive observe of these activities to control the environmental pollution and preservation of human health and other organisms (Edokpayi *et al.,* 2017). Currently there are many methods used in the treatment of wastewater including chemical precipitation, ion exchange, membrane separation, adsorption by activated carbon, ultrafiltration, solvent extraction, electrophoresis and coagulation (Chisti, 2018). It has been found that the use of some of these techniques is limited because it requires high cost or its efficiency of wastewater treatment is not good, which does not give a solution to the problems of the environment (Crini and Lichtfouse, 2019). However, one of the most important techniques that drew attention, especially in recent times, is the adsorption technique using agricultural waste for its efficiency and low cost (Rashed, 2013). On the one hand, the accumulation of agricultural residues in large quantities causes damage to the aquatic environment, especially the disposal process requires effort, time and material costs, and on the other hand the issue of water wastewater treatment itself is also a problem (Abdel-Shafy and Mansour, 2018). Therefore, the researchers tended to solve both problems at the same time, by converting these materials from harmful wastes to a useful material by using these materials available in the treatment of toxic and hazardous wastewater (Ferronato and Torretta, 2019). However, the toxic waste remaining after the end of the adsorption process is another problem and generates another impediment to adsorption technology (Clavijo and Osma, 2019). To solve this problem, a number of researchers have introduced a new look at waste treatment in general, the concept of zero residue level (ZRL) (Abbas and Al-Madhhachi, 2015), which aims to make residues from any treatment process is zero or near to zero by using these residues in the preparation of useful materials, economical and eco-friendly materials (Abbas, 2015). This article reviews a number of researches that have applied the concept of zero residue level in the treatment of contaminated aqueous solutions.

Zero residues level (ZRL)

Definition

Is the limit at which the amount of waste (one or more, combined or single), whether raw material or residue from any practical activity (laboratory, pilot or field) or resulting from any treatment of one or more elements of the environment (water, air, soil or space) is equal to or near zero after recycling (physically, chemically or biologically) in one or several useful, economical, environmentally friendly and applicable ways compared to its original amount prior to recycling.

Applications

The concept of zero residue level has been applied in many environmental treatments through converting the residues from adsorption process into beneficial and cost-effective materials such as promoted catalysts, rodenticides or toothpaste, and other types such as vegetable and industrial oil residues have been converted successfully into bio- and Indu- fuels. This article reviews the researches that dealt with to safely dispose of residual toxic wastes after the end of the desorption process via using them as raw materials in the preparation of benefit and useful materials in an easy, economical and environmentally friendly manner applying the concept of zero residue level.

The researchers (Abbas *et al.*, 2012) studied the possibility of exploiting Iraqi rice husks to achieve the ZRL concept in three steps. The first step involved the conversion of rice husks into a zeolite, which was used in the next step as a medium for adsorption of heavy elements from aqueous solutions prepared in laboratory as simulations of industrial wastewater, while the final stage was the use of zeolite after treatment as a catalyst in the catalytic thermal cracking process. The zeolite type Y was prepared in the first step by preparing rice husks by

washing, treating with sulfuric acid (H_2SO_4), filtering, calcination and treated with NaOH by refluxing, then by concentrated hydrochloric acid (HCl) and washed again and finally dried. The prepared Y type zeolite was used as adsorbent media for divalent zinc ions removed from aqueous solutions prepared of zinc prepared using zinc sulfate ($ZnSO_4$) and the continuous process was carried out using a packed column and at different operational conditions of initial concentration of zinc, acidic function, flow rate, high of packed in the column, temperature and treatment time. The results obtained showed that the efficiency of the zinc removal using zeolite was inversely proportional to the initial concentration, the pH and flow rate while the increase with the increase in other variables. Prepared zeolite and residual zeolite from the adsorption process, after determination of its operational specifications and identification of surface area and SEM and FTIR, was used as a catalyst for thermal cracking of heptane under different operating conditions of temperature and amount of promoted catalyst. The results of the catalytic cracking process showed the efficiency of the promoted catalyst in converting the heptane to substances with higher octane number as well as selectivity compared to the non-promoted catalyst.

The ability of rice husks to remove a range of heavy metals from contaminated solutions was investigated by (Abbas and Abbas, 2013a) as a first step and in the second step, studied the utilization of the toxic residues in various methods up to the zero residues level (ZRL). The potential of rice husks for adsorption of seven heavy metals (mercury, cobalt, lithium, tungsten, vanadium, tin and antimony) from aqueous solutions prepared to simulate wastewater was studied. The adsorbent material was rice husks collected from the fields of Al-Shanafiya district - southern of Iraq, which was used after washing, drying, measuring X-ray diffraction and surface area and then used as adsorption media directly without any further treatment. Contaminated aqueous solutions of studied heavy metals were prepared from their nitrate, chlorides and ammonium salts. Adsorption unit was of continuous mode and the design factors used were initial concentrations heavy metals, acidic function, temperature, height of rice husks in the packed column, contact time, flow rate of contaminated solutions within the unit. The results showed that the removal efficiency was increased by increasing the packing height of rice husk, temperature and contact time while it was decreasing with increasing the initial concentration and flow rate of all heavy metal ions studied. But, the effect of the pH was different as the removal efficiency of lithium, tin, and tungsten metals were directly proportion to the acidic function, while the pH correlation with the other elements (*i.e.* cobalt, mercury, antimony, and vanadium) was inversely. In the second step of the research, the huge quantity of the leftover rice husks was sorted after the adsorption process was completed according to the loaded elements. The husks of cobalt, lithium, lithium, antimony, tungsten, vanadium, and tin ions were used to prepare promoted catalysts for the process of heptane catalytic cracking to produce materials used as additives to increase the octane number of gasoline fuel. While the preparation of a cheap rodenticide using rice husks loaded with cobalt, mercury, lithium and antimony ions was studied by mixing these toxic husks directly and without any additives or additional treatment with rodent food and calculating the time it takes to kill the rodent. The results obtained from the second stage showed that the catalytic agents showed higher selectivity and productivity than the catalyst prepared by the usual rice husk and that they are highly efficient for use as rodenticides. Finally, the researchers suggested that rice husks loaded with toxic metals should be used as fuel in some rural areas that depend on them for thermal or electric power generation. In this way, more than one type of waste is disposed of in a beneficial, economical, safe and environmentally friendly manner.

Rice husk susceptibility has been tested by (Abbas and Abbas, 2013b) to remove boron, barium, beryllium, bismuth and selenium elements from contaminated aqueous solution and study the disposal of residues loaded with these ions from the treatment process in a beneficial and environmentally friendly way accessing to zero residue level. Like in previous research, the ions of these elements were removed from the laboratory prepared solutions by adsorption in a continuous mode unit using raw rice husks. The operational conditions used in this study were acidic function, height of rice husk packing in adsorption column, temperature, initial concentration of metals and treatment time as well as flow rate of solutions within the unit. The results showed that the removal efficiency was directly proportion with the height of the husks packing, temperature and contact time of all elements and acidic function of barium, beryllium and selenium, while the correlation of acidic function was inversely for boron and bismuth elements. The maximum removal percentages were 95.09, 96.76, 96.84, 97.75 and 98.72% for barium, selenium, beryllium, bismuth and boron respectively. The remaining wastes were collected, sorted and divided into two parts to study their utilization in two different ways. The first way is prepared it for the synthesis of promoted zeolite type Y, and the second way is mixing it with the provender of laboratory rats and investigating their conversion into a rodenticide. The

results showed that the catalysts prepared from these elements was significantly better in terms of productivity and selectivity than the ordinary type in the process of heptane isomerization and that the best conversion ratio was 49.48% and was achieved using beryllium promoted catalyst. The results also showed that these residues could be used as a rodenticide effectively. The best results were using residues with a concentration of 5.5 ppm of selenium, where a 3-hour period was sufficient to kill animals after eating their food.

Aqueous solutions contaminated with magnesium, manganese and molybdenum elements have been tested for adsorption efficiency using Iraqi rice husks as adsorbent by (Abbas and Abbas, 2013c) and attempted to utilize their residues to achieve zero residue level (ZRL) concept. A unit of continuous pattern is designed to determine the optimal operating parameters that conduct maximum adsorption ratio. The operating parameters studied were the same as those used in the previous researches from the initial concentration of metal ions, acidic function, temperature, contact time, packing height and flow rate. After a series of laboratory experiments showing that all operational factors have a significant effect on the adsorption process. The maximum removal efficiency of 93.95% for magnesium, 95.26% for molybdenum and 97.18% for manganese was obtained at the lowest initial concentration, lowest flow rate, highest temperature, highest husks packing height, highest contact time and highest acidity of 1 ppm, 5 ml / min, 55 m, 1 meter, 60 minutes, 8 respectively. The used rice husks were collected, dried to 105 °C and reused as adsorption media for several times. It was found that its efficiency of adsorption gradually decreases with repeated usage until it reaches a constant level. Rice husk loaded with magnesium ions was the highest number of reuses and reached to 15 times, while the rice husks of molybdenum and manganese could be reused 12 and 10 times, respectively. After the adsorption process was ended, the remaining rice husks were collected, sorted and used as a raw material for the preparation of the promoted Y type zeolite catalyst for use in the process of heptane isomerization or as a rodenticide. The obtained results showed that the promoted catalysts were more than 6 times better than the usual catalyst, and the catalyst promoted with molybdenum was the highest yield while the catalyst promoted with manganese was the best selectivity. Wastes were also effective when used as rodenticides. The molybdenum-loaded wastes of various concentrations were the most efficient, while the low concentrations of magnesium and manganese elements had negligible effect on the rats. The high concentration of these two elements constituted half or less of molybdenum effect as rodenticide.

As a type of valueless agricultural waste available in large quantities, raw rice husks were used by (Abbas and Abbas, 2013d) without any further treatment as a media for adsorption of the 9 widely used, most prevalent, and most tremendously heavy metals elements of different water systems. The metals studied were lead, nickel, chromium, copper, iron, cadmium, arsenic, zinc and aluminum. In order to avoid interference with any other elements, compounds or substances in the real contaminated solutions, laboratory aqueous solutions of these metals were prepared from the sulfate salts of these elements excluding lead and chromium which were prepared from nitrate ($Pb(NO_3)_2$) and potassium dichromate ($K_2Cr_2O_7$). Adsorption experiments were carried out in a continuous unit using a packed bed column and at different operating conditions of temperature, acidity, contact time, elevation of adsorption media in the adsorption column, flow rate and initial concentration of metals. The results showed varying susceptibility to adsorb of these metal ions from polluted aqueous solutions and the optimum operating conditions were achieved at an initial concentration of 5 ppm, temperature of 45 °C, contact time of 60 minutes, a flow rate of 5 ml/min and a height of rice husk of 70 cm, while the maximum removal efficiency by rice husk was 95.05%, 95.75%, 95.78%, 95.82%, 96.21%, 96.24%, 96.33%, 97.61%, 98.73% for lead, copper, arsenic, nickel, cadmium, aluminum, zinc, iron, and chrome ions respectively. The results also showed that rice husks can be used for several times ranging from 5 to 13 times depending on the adsorbent metal, while the ability of these husks for adsorption of all elements together from the real wastewater was also varied and ranged between 34.78% - 50.17%. After the end of adsorption process, the remaining rice husks were sorted according to the loaded concentrations of metal ions and studied their use in a beneficial and environmentally friendly way up to the ZRL level. The first method was the preparation of promoted zeolite from rice husks loaded with zinc, nickel, cadmium, iron, chromium and copper (each one alone) for the heptane isomerization process, while the rice husks loaded with aluminum, arsenic, lead and zinc were used as rodenticides. The results showed that the highest conversion ratio and selectivity of heptane isomerization was performed by chromium-loaded zeolite while the nickel promoted catalyst was the lowest, whereas the lead-loaded husks and arsenic proved to have high and similar ability to kill laboratory rats and reached to 3 hours after eating food mixed with toxic husks.

As with heavy metals, the rice husks have been used by (Abbas and Abbas, 2014) to investigate their potential to treat water contaminated with humic acid. Laboratory aqueous solutions with different concentrations of humic acid were prepared and rice husks adsorption susceptibility was tested in a continuous type unit. The design conditions were contact time, temperature, acidic function, high of rice husks, and flow rate while the concentration of humic acid was measured spectrophotometrically. The treatment results showed that the removal efficiency was inversely proportional to the flow rate, acidity and initial concentration, while the correlation was positive with other variables and the highest percentage of removal was 98.24%. The treated husks were dried and reused as a adsorption media for humic acid several times and found to be usable 7 times, where their efficiency decreases gradually time after time before they become constant at the seventh time. Humic acid-treated husks have been studied to get rid it in a safe, inexpensive, useful and environmentally friendly way reaching to zero residue level (ZRL). The humic acid (0.05-1%) was used as fertilizer for the tomato crop. The results showed that the husks were remarkably efficient in increasing the yield amount to 15% by weight.

Type Y-zeolite was prepared from Iraqi rice husks as a source of silica by (Abbas *et al.,* 2013a) and used in this research as a catalyst to remove an organic acid from liquid hospital waste experimentally and theoretically in an environmentally friendly way accessing to zero residue level (ZRL) concept. The experimental work of this research included the study the oxidation process of phenolic acid (C_6H_6O) which conducted in a continuous bed reactor and at different operational parameters of initial concentration of phenol, the weight hourly space velocity (WHSV), the acidic function of the solution entering the system, catalyst charge height, partial oxygen pressure, gas flow rate and temperature which ranging from (2-10) mg/l, (1-5) h^{-1}, (40-80) cm, (3-11), (5-15) bar and (100-200) °C respectively, and the phenol concentration in laboratory samples was analyzed using spectrophotometer. The results obtained showed that the phenol oxidation process was inversely proportional to the acidic function, WHSV and the initial concentration of phenol while it was directly correlated with other variables. The highest conversion value was 98.79% using the prepared catalyst and the reaction was of the first order of phenol and half order of the oxygen while the activation value was 79.91 kJ/mol. In the theoretical part of the research, equilibrium and rate based models were developed using MATLAB and FORTRUN programs together, and MESHR equations, M: Material Balance, E: Equilibrium Relations, S: Summation Equations, H: Heat Balance and R: Reaction Equations were solved taking into account the effect of heat transfer and mass transfer on the energy and material balance. The results obtained from the theoretical side were very close to the practical side with a low error. Finally, a statistical model was accomplished to link the used variables together by a mathematical relationship.

(Abbas *et al.,* 2013b) studied the susceptibility of Iraqi rice husks (without any additives or further treatment) to remove of phenolic acid from laboratory preparations of aqueous solutions up to the zero residue level (ZRL). The removal process was carried out by adsorption technique using a continuous unit consisting of a column packed with rice husks at different heights ranging from (10-100) cm in addition to different values of other operating factors of acidic function, phenol initial concentration, the temperature of solution, contact time and flow rate of contaminated solution within the unit which were ranged between (1-8), (1-100) mg/l, (22-50) °C, (1-60) min, (5-100) ml/min respectively. The results showed that the efficiency of phenol removal was 89.73% and that it was increasing by increasing the packing of rice husks, contact time and temperature, while the efficiency was reduced by other design factors. A statistical model was performed to relate the studied variables to removal efficiency in one mathematical equation. Used rice husks were collected, dried and reused as an adsorption media for phenolic acid again. The results showed that the ability of these husks decreases gradually with each reuse and that reached to equilibrium after 10 times of reuse.

The hexavalent chromium ions in the tannery wastewater, which is considered as a carcinogenic agent, have been investigated to be removed from aqueous solutions using raw rice husks (without any additives or further treatment) as cheap and available material by (Abbas *et al.,* 2013c). The remediation method examined was adsorption technique and after that exploitation from the toxic residue in preparation of a useful catalyst for heptane isomerization process arriving to the zero residue level (ZRL). Adsorption was tested in a semi-continuous unit at different operating conditions of acid function, flow rate, processing time, weight of rice husks in packed bed and at two different concentrations of hexavalent chromium ions 120 and 150 ppm. The results showed that the highest removal efficiency was 99.99% at optimum conditions, namely the concentration of chromium ions 120 mg/l, acidic function 2, the amount of rice husks 50 g, contact time 120 minutes. The kinetic study confirmed that the results obtained followed the

pseudo first order with excellent correlation coefficient of 0.97 while the results of the isotherm study showed that the isotherm of the adsorption process is obeying Langmuir isotherm model better than Freundlich isotherm model where the correlation coefficients are 0.979 and 0.5959 respectively. A mathematical model was also completed to simulate the adsorption process and the conformity between the results of mathematical model with the experimental result was 94.6%. Chromium-loaded rice husks were used as a raw material for the preparation of type Y-zeolite which is used as a catalyst in the process of heptane isomerization at different operating conditions of temperature and amount of catalyst. The results showed that the efficiency of the isomerization process rises with increasing temperature and the amount of catalyst. Also, the promoted catalyst prepared from the residues of the chromium adsorption process had a better selectivity and conversion ratio than the ordinary catalyst prepared from rice husks only.

Continuous type adsorption unit was used by (Abbas, *et al.,* 2014a) to remove highly toxic cyanide ions (CN^-) from aqueous solutions prepared in the laboratory to simulate cyanide-containing wastewater and try to dispose of toxic residues in a beneficial, economical and environmentally friendly manner. The stock solution was prepared by dissolving a certain amount of sodium cyanide (NaCN) from which the experimental solutions were prepared by dilution the required volume of stock solution. The adsorbent material in this research was banana peels collected from household waste and was cut, washed carefully, boiled and dried for 24 hours at 50 °C. The surface area of the peels was then detected by BET method and X-ray diffraction was determined. The operating conditions studied in this research were the flow rate of the contaminated solution, contact time, temperature, the initial concentration of cyanide, the packing height in the packed bed, and the acidic function. The results showed that the efficiency of the adsorption process was decreasing by increasing the initial concentration of cyanide and flow rate, while the efficiency was directly related to other variables. The optimum operating conditions were 1 ppm, 8, 5 ml/min, 55 °C, 100 cm and 60 min for initial concentration, acidic function, temperature, packing height of banana peel, and contact time respectively achieved the highest removal rate of 95.65%. A statistical model that combines all variables in a single mathematical relationship to describe the behavior and results of adsorption process with a correlation coefficient of 0.989 was also completed. Banana peels loaded with cyanide ions were collected, dried and mixed with the provender feed to experimental rats to evaluate their potential to use as a rodenticide. Biological results showed a high ability of these residues to kill rats and the time of animal death ranged between 7 and 120 hours at concentrations of 1 and 0.1% by weight respectively, which indicates the severity of the toxicity and seriousness of this substance.

Used frying oils (UFO) and used automotive oils (UAO) were used by (Abbas, *et al.,* 2014b) as raw materials for the preparation of bio-diesel and industrial diesel (Indus-diesel) respectively. The preparation process was achieved by type Y-zeolite prepared from rice husks and egg shells as catalysts to get rid of these contaminated residues of soil and water in an economical and environmentally friendly manner up to the zero residue level of these oils. The production process of diesel fuel is carried out using different concentrations of concentrated sulfuric acid, which is added to gradually the oil and left for one hour. Then add the thermally treated eggshell powder in different amounts, leave for an additional half hour and then add the zeolite Y prepared from rice husks to prepare (Indu-diesel) and ethanol to prepare (bio-diesel) to the mixture, finally stir the mixture using the stirrer at different agitation speeds and at different periods. The results obtained by conducting 20 different tests proved that the fuel produced from both types of oil waste was very close to the standard diesel fuel. The highest yield of diesel fuel from UAO was 78% and from UFO was 75% and was achieved at optimum operating conditions (acid/raw material) ratio, (base/raw material) ratio, (zeolite/raw material) ratio, agitation speed, reaction temperature, treatment time is 7%, 8%, 8%, 500 rpm, 100°C, 150 minutes respectively for fuel indu-diesel and 8%, 8%, 10%, 450rpm, 80°C, 120 minute respectively for bio-diesel fuel.

Cooked tea leaf waste (CTLW) without any further treatment tested by (Joodi and Abbas, 2014a) for treating contaminated water using adsorption technique and trying to exploit from the residues of the treatment process. Adsorption of phosphorus ions from pre-prepared laboratory solutions was carried out in a continuous mode unit and concentrations of phosphate in different solutions were detected using spectrophotometer device. The results showed that the CTLW was able to remove phosphorus ions from aqueous solutions with an efficiency exceeding 97% at optimum operating conditions of 55 °C, 1 m, 1 ppm, 5 mL/min, 8, 60 minutes for temperature, elevation of adsorption column packing, initial concentration of phosphorus ions, solution flow rate, acid function and contact time respectively. A statistical model was developed to describe the results of the adsorption process and to correlate the operational variables studied

in this paper with one equation. The comparison between the practical results and the results of the statistical model showed high matching with correlation coefficient (R^2) of 0.9938. After adsorption, the residues were collected, dried and sorted according to the amount of phosphorus adsorbed to be used as fertilizer for the tomato crop. The results showed that the fertilized tomato crop of CTLW adsorbed phosphorus ions yielded 17.235% higher than the normal tomato crop. Thus, the residues of cooked tea leaves and water-contaminated phosphorus ions were disposed of in a useful way accessing to the zero residue level (ZRL). In the same way mentioned above, rice husks were used by (Abbas, 2015) to adsorb phosphorus ions from contaminated aqueous solutions and to prepare fertilizer for tomato crop with different results.

(Joodi and Abbas, 2014b) studied the potato capability in industrial wastewater treatment by two ways. The first was the usual adsorption technique, and the other way using a poly phenol oxidase (PPO) enzyme extracted from potato peels. The remaining potato peel after PPO extracted from it was used as a direct adsorption media without any further treatments. Phenol adsorption process was carried out in a continuous packed bed column unit using laboratory preparations of aqueous solutions. At different operational conditions of initial concentration, acid function, contact time, adsorption column packing, solution flow rate and temperature. The results showed that potato peel had high sorption of phenol at low concentrations and the adsorption efficiency was inversely proportional to acidity, initial concentration and flow rate, whereas other variables were directly proportional to phenol adsorption efficiency from aqueous solutions. The highest percentage of removal was 95.37% and 41.15% at 1 and 100 ppm of phenol respectively. The residues of the adsorption process were collected, sorted, dried outdoors and studied as rodenticides. The results showed that laboratory rats died after 102 and 7 hours when fed with phenolic residues of 0.1 and 1 wt% respectively, indicating that they could be used as an effective rodent according to high toxicity of this hazardous compound in adsorption residues. The extracted PPO enzyme was loaded on type Y-zeolite pre-prepared from rice husks and the adsorption experiments were carried out at high concentrations of phenol (50-100) ppm at a flow rate of 5 ml/min, neutral acidic function, laboratory temperature and using the same continuous unit. The results indicated that the enzyme was capable of dismantling phenol with high efficiency of 99% and 86% for concentrations 50 and 100 ppm respectively. By this method potato peel, which considered as a large proportion of agricultural and municipal waste and toxic and polluted phenol, was eliminated, in the same time useful materials were prepared in a beneficial, economical and environmentally friendly manner reaching to zero residue level (ZRL).

The concept of zero residue level (ZRL) has been applied in a new way by (Abbas, 2014a), through the exploitation of waste in general and agricultural in particular to obtain the greatest benefit before and after use. This method involved extracting useful materials from these wastes before using them first and then using them and trying to produce useful materials with a longer service life and not just safe disposal. This principle was applied to exploit the remaining used tea leaves (UTL) in five steps. The first stage was extraction of the peroxide enzyme from UTL and then the use of UTL (after extraction) in the adsorption of zinc heavy metal from the contaminated solutions in the next step. In the third step the adsorption residue were converted to promoted activated carbon catalyst, which was used in the fourth step as a media for thiophenol adsorption. The final step was used the activated carbon, loaded with toxic thiophenol, as a rodenticide. The results from the previous steps showed that the application of the concept of zero residue level in this way would be of greater benefit and greater economic cost and lead to the disposal of several wastes combined simultaneously and in the same unit without the need for additional costs, materials or further preparations.

The concept of zero residue level developed by banana peels has been applied by (Abbas, 2014b). This type of agricultural waste is considered one of the richest species with its useful materials. PPO enzyme was extracted from banana peels in the first step and the results showed that the enzyme productivity reached about 15% which represents a good productivity compared to the extraction methods used. In the second step, banana peels (after PPO extraction from them) was used as a media for adsorption of hexavalent chromium ions from aqueous solutions in a unit of continuous mode and at different operational conditions of column packing height, acidity, contact time, temperature, flow rate and initial concentration of hexavalent chromium ions. The results showed that the banana peels had high adsorption efficiency of chromium reached 93.75%. In the third step, the residues of the adsorption process were utilized in the preparation of varnish, and when exhausted, it was finally converted into a rodenticide.

By the same previous principle, raw potato peel was transacted by (Abbas, 2014c) where it was exploited (after extracting the PPO enzyme) to adsorb nine kinds of dark dyes and bright colors then converted into writing ink. The orange residues were also exploited by (Abbas,

2014d) to extract pectin methylesterase (PME) enzyme from them, then to extract the limonene acid (D-limonene acid) and in the next step the remaining cellulosic residues were used as a raw material in the production of bio-ethanol with the help of bakery yeast (*Saccharomyces cerevisiae*). In the last step, the remaining residues were used as fertilizer for a broad bean crop. Similarly, pomegranate peels were used by (Abbas, 2014e) as a source of anti-oxidants firstly then the peels were used as a fluorine adsorption media in the second step. In the third step, the residue is used as a raw material for the preparation of cheap and effective toothpaste. Thus, no residue was left, but it was converted into fully useful materials, *i.e.* the ZRL concept was completely and perfectly applied.

The concept of zero residue level was not limited to the treatment of contaminated water, but also the remediation of contaminated soils with pesticides. (Abbas and Al-Madhhachi, 2015) studied the removal of two types of pesticides which were pirimicarb and imidacloprid by regular water washing method from three types of soils namely sandy, silty loam, and clayey that were laboratory contaminated and then tested the treatment of these contaminated aqueous solutions by adsorption using two adsorbents watermelon peel (WP) and used tea leaves (UTL). The results indicated that the least soil contaminated with pesticides was sandy soils and the washing method was effective in removing pesticides from all soils with efficiency ranging from 71% to 99% for different pesticides. Pesticide-contaminated water was treated by adsorption in a continuous unit with packed column and at different operational factors of flow rate, column packing height and treatment time. The results showed that the WP was highly efficient in removing pirimicarb pesticide and reached the ideal efficiency while the lowest efficiency was achieved using UTL in removing imidacloprid and was 90%. The residue was collected after ended of adsorption process then sorted, dried and tested for using as rodenticides. The results showed that the applicability of both types of residues (WP and UTL) as a pesticide was based on the calculated lethal half dose that was identical to the values in literature.

Radioactive elements were not far from exploiting their contaminated residues within the concept of zero residue level (ZRL), where (Alalwan *et al.,* 2018) studied the possibility of removing thallium (Tl^{+3}) element by adsorption technique using rice husks as a adsorption media from aqueous solutions of laboratory preparations to simulate contaminated wastewater. The unit used in this study was of continuous type with packed column and at different design parameters of acid function, temperature, elevation of packing in the bed, flow rate, initial concentration of thallium. The results showed from the breakthrough curve that the percentage of thallium removal increased by increasing the height of the packing, acid function and temperature before 298 K and decreased initial concentration of thallium, flow rate and temperature after 298 K. The dynamics of the adsorption process were represented by three models: Bed Depth Service, Yoon – Nelson and Thomas then compared with the practical results obtained. The waste of rice husks after the adsorption process is collected, dried, sorted and currently is tested by the researchers for converting it to promoted activated carbon and this research is about to be completed in the near future. By the same way, cesium ions were adsorbed using rice husks by (Abbas, 2014f) and utilized from the residues in the preparation of a promoted catalyst for the catalytic thermal cracking process of heptane. The results showed the high ability of cesium adsorption with 95.7% efficiency at 1 ppm concentration and capability of prepared promoted catalyst to convert heptane to beneficial ingredients, propane and butane, with better productivity and selectivity than ordinary catalyst. In the same way, unit and the residues, kinetics and isotherm have been studied to remove rhenium from aqueous solutions by (Abudi *et al.,* 2018). The results showed the efficiency of rice husks in the adsorption process of rhenium and that the adsorption kinetics followed the pseudo-second-order with a correlation coefficient of 0.98.

In the field of petroleum purification, (Abbas and Alalwan, 2019) studied the possibility of treating crude oil by combining desulfurization and adsorption technologies together for removing harmful and undesirable sulfur compounds from the heavy naphtha fraction. The treatment process was tested using white eggshell (WES) and granular activated carbon (GAC) as catalysts in a batch unit, and at several important operational conditions, which were (water/heavy naphtha), quantity of adsorbent, temperature, contact time, agitation speed and acidic function. The obtained results showed that the efficiency of the sulfur removal process is inversely proportional to the acidic function and directly with other variables, while the removal percentage of sulfur compounds from crude oil reached to 86% and 65% using activated carbon and white eggshells respectively, according to the difference in surface area value of the two catalysts. The same method has been applied by (Abbas and Ibrahim, 2019), on light naphtha fraction, where the removal of sulfur compounds from them by catalytic adsorptive-desulfurization technique and

comparing the results obtained with the thermal method of treatment. The results showed that the removal percentage of sulfur compounds was in the following order *granular activated carbon> white eggshell> heat treatment* by a value of 81.73%, 56.78% and 23.71%, respectively.

Copper-loaded rice husk residues have been used as a concrete reinforcement material by (Abbas *et al.,* 2019a). The behavior and characterization of concrete as a result of the addition of rice husks and copper-loaded rice husks were studied. The concrete mixture was prepared according to the British standard using 4: 2: 1 ratio (1: cement, 2: sand, 3: gravel). The rice husks were mixed with both types of raw and loaded with copper at ratios ranging between (0.5 - 3)%. The concrete mixture above used to prepare cubes of 150 x 150 mm and their compressive strength were measured at 7 and 28 days. The obtained results showed that the concrete compressive strength were in the following order: *concrete mixture of copper-loaded rice husk> concrete mixture of ordinary rice husks> reference concrete mixture*.

Aluminum waste is a very slow degradation in nature and is discharged in large quantities to the environment, thus causes significant pollution. To identify the disposal possibility of these metal waste up to the level of zero residue (ZRL), one kind of this waste type, which was the kitchen waste represented by aluminum foil, was used by (Ghulam et al. 2019 a,b) as a raw material for preparation of alumina (Al_2O_3) by precipitation method. The prepared alumina was tested for purity using X-ray diffraction (XRD), its components were determined using X-ray fluorescence (XRF), the surface area was detected by BET and the functional groups was identified by Fourier-transform infrared spectroscopy (FTIR). The preparation process was carried out in vitro and at different operational conditions of digestion acid concentration, calcination temperature and acidity of the precipitation solution. The results showed that the resulting alumina powder was of ã type with a purity of 97% and its surface area was 246 m^2/g. The prepared alumina was tested as an adsorption agent for RG-19 dye from aqueous solutions contaminated in a batch mode unit at various values of the initial dye concentration, acidity function, temperature, contact time, amount of alumina and agitation speed. The results showed that the prepared alumina was effective in adsorption of RG-19 dye with an efficiency of 98.634%.

Adsorption materials of biological origin are among the most important materials used in the adsorption technique and the most attractive to researchers. These materials are not limited to agricultural residues, but biomass materials also have important and their role as an effective adsorption media in dealing with pollution problems, including algae. The susceptibility of biomass prepared from sea lettuce (*Ulva lactuca*) as a biosorption media of phenol was tested by (Abbas *et al.,* 2019b) from contaminated aqueous solutions at different operating conditions of biomass weight, temperature, acidity, contact time, initial concentration of phenol, agitation speed. The results showed that the adsorption efficiency ranged from 25.446% for the concentration of 100 ppm to 90.125% for the concentration of 1 ppm and that the efficiency is inversely proportional to the acidic function, the initial concentration and temperature and directly to a certain extent with other variables. The results also showed that the adsorption process is spontaneous, exothermic and tends towards regularity. In addition, the Langmuir isotherm model for adsorption is better than Freundlich isotherm model, while the adsorption kinetics follows the pseudo second order with a correlation factor of 0.92.

Conclusions

The observation of previous research shows that the concept of zero residue level is a modern concept dealing with the application of new manners to protect the environment from pollution and at the same time allows the development of human activities in all fields. Through this new concept, the traditional view of waste as harmful and causing problems for both the environment and the human being can be changed. Instead of treating waste as harmful substances to be disposed of, they can be used to treat pollution or produce cheap and low-cost useful materials. It also tries to put the idea of eliminating more than one type of pollutant at the same time and equipment without the need for additional effort or further costs. The review article presents many examples of how the ZRL concept could be applied efficiently, despite the simplicity of the possibilities. From the exploitation of agricultural waste to the purification of water through the production of biofuels and the end of the preparation of active organic fertilizers or cheap pesticides are all useful applications that can be benefited and developed instead of the subject only to remove a material from the water using waste. Here it should be noted that this concept presented a clear and useful solution to the issue of accumulation of toxic residues after the end of the adsorption process which remained for a period not less than a subject of research by researchers and concerned with the field of environmental pollution. The problems that can be dealt with by this concept are not limited to adsorption technology only or agricultural waste only, as mentioned earlier; the concept of ZRL is applied in all engineering and scientific fields. The most important

aspect of this concept is that it is a subject that does not stop at a certain extent or a dedicated area, being a modern idea, despite its close association with the environmental aspect, which makes it scalable with highly efficient. In summary, any applied research that involves treatment of an environmental problem with maximum efficiency, and greater benefit, in the same time lower cost and negligible residues can fall under the concept of zero residue level (ZRL).

Acknowledgment

The authors would like to thank Mustansiriyah University (www.uomustansiriyah.edu.iq) Baghdad – Iraq and Diyala University (http://www.uodiyala.edu.iq), Diyala – Iraq for their support in the present work.

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