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REVIEW PAPER

Utilization of low cost adsorbents for the adsorption process of lead ions

Mohammed Jaafar Ali Alatabe[1*] Zainab T Al-Sharify[2]

[1]Lecturer,Department of Environmental Engineering, College of Engineering, University of Al-Mustansiriya, P.O. Box 14150, Bab-al-Mu'adhem, Baghdad, Iraq

[2]Academic visitor,School of Chemical Engineering, University of Birmingham, Edgbaston B15 2TT, Birmingham, United Kingdom.

ABSTRACT: This study is aimed on exploring the possibilities of recovering Pb^{+2} ions using several low cost adsorbents through wastewater processing. In the past, several traditional methods were employed for removing Pb^{+2} ions. These included precipitation, evaporation, electroplating and ion exchange. However, these processes were associated to various limitations, which included the treatments to be restricted to a certain concentration of the Pb^{+2} ions. In addition, drawbacks involved the production of huge amounts of harmful waste while fixed costs were also very high, hence making these processes very expensive. Therefore, the process of using low cost adsorbents can be deemed as an eco-friendly one. At the moment, an enormous amount of natural materials and agricultural waste is produced, which is extremely harmful to the environment. Thus, adsorption is an alternate process for removing Pb^{+2} ions. Based on the enhanced characteristics of the process of adsorption, such as cost-effectiveness, improved adsorptive properties and increased availability, the process is definitely an economical one for removing Pb^{+2} ions. This study provides a brief appraisal of the relevant literature which exists on the low cost adsorption for removing Pb^{+2} ions from polluted wastewaters.

KEYWORDS:Adsorption; Conventional methods; Lead(II) ions; Low cost adsorbent.

I. INTRODUCTION

Nowadays, there is an increasing amount of concern regarding wastewater contamination. This is mainly because water is a necessity of life, hence being vital to all living organisms. Due to progressive development all over the world, several industries are now producing vast amounts of contaminants, which are very harmful to the ecological system [1],[2]. Such industries include the metal mining, fertilisation, paper and pesticides. Several impurities are present in discharges produced by industries and homes, which involve wastes related to mining, agriculture, and seepage. These contaminants are disposed in the water system, which then affects the overall ecological system, as the harmful effects of these pollutants are well known. In terms of Lead(II) ions, these are known to contaminate water ways more seriously as compared to other toxins, when exposed to the natural ecology. The term “heavy metal ions” is used for elements, whose atomic masses are in the range of 63.5 to 200.6 with a specific gravity being higher than 5 g/cm^3. Some cases of heavy metals involve Cadmium, Zinc, Copper, Nickel, Lead, Mercury and Chromium. These are mainly present in processes involving metal plating, mining, battery manufacturing, petroleum refining and paint manufacturing[3],[4].

Lead(II) ions are non-biodegradable impurities which are not only hard to remove from the ecological system but are also extremely poisonous if concentrations exceed the permissible limits. Increased concentrations of these Lead(II) ions may also accumulate in human bodies if they enter the food chains. Consequently, these may also lead to serious health issues. Lead also has an impact on the environment because of its harmfulness, which occurs due to its presence in industrial wastes produced from manufacturing sites. These include storage-battery manufacturing, printing, fuel combustion cookware, some Mexican potter glazes and also photographic materials[5][6],. In addition, lead appears to be one of the major risk factors for several deadly diseases if the concentrations of lead go above the permissible limits, as recommended by the World Health Organization (WHO). To elaborate, concentrations greater than 3-10 μg/l in drinking water can lead to serious harmful effects on human bodies. Also, lead is a harmful metal which can also have serious health effects on humans including children. Children are more prone to absorb increased quantities as compared to grown-ups due to their developing and growing bodies. While lower concentrations of lead ions in the blood can lead to some not very detrimental effects such as anaemia, diarrhoea, and headaches, higher concentration (>10 μg/l) on the contrary can lead to harmful effects on the liver, kidneys, neurological and reproductive systems. The presence of Lead(II) ions in waterways produced by industries can also affect water bodies, which further presents an unsafe effect on the marine and extra-terrestrial bodies. Amongst the exhaustive list of issues related to lead poisoning, one most common issue led by the exposure of lead is the occurrence of miscarriages and neonatal deaths[3],[5][7].

Lead exists naturally in an insoluble form and in other harmless forms as well[8]. Several processes are used for treating wastes produced from industries which consist of lead(II) ions. Chemical precipitation, ion-exchange, electro dialysis and carbon adsorption are a few vital processes which have been employed for treating wastewaters. Furthermore, other progressive practices are also used for removing Pb^{+2} ions. These include increased expenditures, which may not be reasonable for the small-scale productions that discharge lower amounts of wastewaters. Many treatments for wastewater polluted with lead ions have been proposed, including an adsorption process, which does not have high effectiveness, unless the adsorbent material shows certain physicochemical and mechanical properties. In the recent years, some physical, chemical, and biological treatments on natural raw minerals have been performed in order to modify their structure, thus increasing the adsorption capacity or the selectivity[9],[10]. Overall, adsorption is known as an efficient process for purifying contaminated waters. Also, treating wastes containing lead is an increasing concern for the industries and hence an effective solution needs to be found for the successful elimination of harmful metals from wastewaters. One solution is also to use activated granular carbon[11].

Over the last few years, several investigative works have been in order to explore an alternate to the expensive methods for treating wastewaters. Several kinds of materials have been used for the adsorption process to test their adsorption abilities. Based on the results of these studies, it appears that elimination of Pb^{+2} ions with the use of low cost adsorbents is increasingly favourable, especially in long term[12]. This is because several materials are **(**natural, sustainably,economically, viable and environmental friendly for Lead ions removal)readily available, i.e. these exist naturally or are found in agricultural waste and manufacturing by-products, and can be used as low-cost adsorbents. Previous researches show that there is a growing interest in searching for a variety of materials, which can serve as low cost adsorbents. These include: sawdust[13], cocoa shell[14], rice husk ash [15], modified sawdust of walnut[16], Cane papyrus[3], papaya wood[17], maize leaf[18], rice husk[19], Water Hyacinth

(EichhorniaCrassipes)[20], Gamma Irradiated Minerals[21], Tree Fern[22], manganoxide minerals[23], banana (Musa paradisaca) stalk[24],banana peel[25], peat[26], Indonesian Peat [27],Cocoa pod husk[28], Coconut (Cocos nucifera L.) Shell[29],[30], peat collected from Brunei Darussalam[31], rice straw/Fe_3O_4nano-composite[32], Sugarcane Bagasse Derived activated carbon[33], agroforestry waste derived activated carbons[34], fly ash[35],[36], tea waste[37], Dried Olive Stone[12], Thorns[38], Sun Flower Husks[39], Pin Cone activated carbon [10], activated carbon from Militia ferruginea plant leaves[40], granular activated carbon[41], pomegranate peel[42], maize stalks[43], activated carbon derived from waste biomass[44], chemically modified orange peel [45], modified orange peel[46], maize (Zea mays) stalk spong[47], olive mill solid residue[48], petiole and fiber of palm tree[49],cladophorarivularis (Linnaeus) Hoek[50], flamboyant flower (DelonixRegia)[51], common edible fruit wastes[52], Watermelon rind: agrowaste or superior biosorbent[53], shewanellaoneidensis[54], chemically modified moringaoleifera tree leaves[55], zeolite A4 supported on natural carbon[56], Rosa bourbonia[57], grape stalk waste[58],spirodelapolyrhiza[59], crop milling waste (black gram husk)[60], arborvitae leaves[61], African breadfruit (treculiaafricana) seed hull[62], potato peels[63], acid modified and unmodified gmelinaarborea (verbenaceae) Leaves[64], waste chestnut shell[65], ailanthus excelsa tree bark[66], Lemon Peel[67],EDTA-modified cocoa (The obroma cacao) Pod husk residue, Iranica[68] and biological activated dates stems[69].

Therefore, the utilisation of these materials as low cost adsorbents is acknowledged as a possible and economical application for wastewater treatment. This is reflected in the increasing numbers of periodicals, which have appeared in the literature on the usage of low-cost adsorbents[70]. These mainly conclude the immense interest in finding appropriate adsorbents for the process of adsorption [71],[72].

This review aims to provide an outline on the adsorption processes utilising low-cost adsorbents for eliminating Pb^{+2} ions from different sources. This will be achieved by underlining the characteristics of the adsorbents, their optimum parameters and their adsorption capacity.

The main objective of this paper is to offer a review on the off acts which are related to the adsorption processes using low cost materials as adsorbents for the elimination of Lead(II) ions. This study has been carried out in Baghdad at University of Mustansiriyah in 2019.

Lead ions

Sources and toxicity

Lead(II) ions are commonly found on earth and are well known for their characteristics which include perseverance, increased harmfulness along with their ability to serve as non-biodegradable impurities if gather in the ecological system. Several industries are still making use of lead. These include the autonomous, battery, recycling, refining, smelting and various more manufacturing industries. Lead is known to be a toxic metal, which has the ability to affect organs in a human body [73],[74]. It is also known to have the most severe affect on the nervous system in humans of all ages. However, lead is more harmful in children as children tend to have softer internal and external tissues as compared to adults. Thus, they are more prone to being severely impacted by lead toxicity[75],[76]. In terms of negative effects of lead poisoning in adults, it has been found that long term exposure to lead can cause a decrease in the cognitive ability, which means that the nervous system is affected mainly.

In addition, toddlers and younger children may also be sensitive to lower levels of lead. These may lead to developmental and behaviour issues, which may further cause issues with learning and overall intellectual abilities[74]. In terms of older people, it is often found that long term contact with lead can result in anaemia and increased blood pressure issues[77],[78],[79]. Moreover, serious damage to valuable organs such as brain and kidneys is also plausible due to lead exposure, which may also result in deaths. Additionally, for pregnant couples, exposures to lead may cause miscarriages in women while leading to a decreased fertility in males[80]. Table 1 presents a summary of the different sources which may produce Lead(II) ions, which exist in the environment[81],[82], along with providing the limit of the concentration of these ions that can be present in wastewaters in MCL (Maximum Contaminant Level), as recommended by USEPA[83],[84],[5].

Table 1 : Various sources of Lead(II) ions into the environment

Sources of Toxicities	Lead(II)	MCL (mg/l)
Paint, smoking, automobile emission, mining, burning of coal.	Damages the foetal brain, circulatory system and nervous system	0.06

The emission of Lead(II) ions into the environment from industrial processes and car exhaust will pollute the surface and also underground waterways[85]. This can result in pollution of soil while enhancing the overall pollution rate, especially when ores from mining processes are disposed in landfill sites. In addition, agricultural wastes in soils can consist of metals, which would then be consumed by plants thus resulting in the accumulation of such harmful substances in their tissues. It is expected that animals, which feed on the aquatic and plant life may also be poisoned due to the presence of harmful Lead (II) ions[86]. Hence, it is vital that strict wastewater regulations are laid to reduce the environmental risks of dangerous substances[87].

Removal of lead(II) ions

Traditional processes

Several processes have been used for eliminating Lead(II) ions from polluted waters. These consist of the biological, chemical and physical treatments. It is worth mentioning that usually these processes are mainly based on the physical and chemical treatments[88],[89]. The overall traditional method to remove Lead (II) ions involves the chemical precipitation, membrane filtration, ion exchange, reverse osmosis, electro-dialysis, solvent-extraction, evaporation, oxidation and activated carbon adsorption[90],[91]. Chemical precipitation is the commonly used process for Lead(II) ions removal from inorganic effluents depending on the pH alteration in a basic solution[92]. Nevertheless, the disadvantages of chemical precipitation are manifold. To elaborate, the discharge of too much sludge produced needs additional treatments, which slows the metal precipitation, leads to inadequate settling and the aggregation of metal precipitates.

In addition, there are several long term ecological concerns with the disposal of sludge[93],[94]. Coagulation-flocculation is also used to process wastewaters with Lead(II) ions by adding a coagulant in the coagulation process. However, this treatment has the possibility of destabilizing colloidal particles and thus resulting in sedimentation[95]. The several advantages and disadvantages of the conventional method are provided below in Table 2.In spite of these approaches being expensive, these are mostly the ones which can have a positive impact on the commonly occurring discharge issues.

Additionally, these methods are also feasible for treating polluted waters containing Lead(II) ions. It is known that issues usually are found in the traditional methods where there is an increased usage of the reagent and energy, a low selectivity, increased operational costs and production of secondary pollutants taking place. Asides the traditional methods, it is vital now to explore alternatives for replacing these traditional approaches of eliminating Lead(II) ions from polluted water sources[96],[1].

Table 2: Traditional approaches for the elimination of heavy metals.

Traditional treatments	Benefits	Limitations
Ion-exchange	Metal-selective Increased regeneration of materials	Increased initial capital and maintenance costs
Chemical precipitation	Simple operation Non-metal selective Cheap	Increased production of sludge Increased costs of disposal sludge
Membrane filtration	Reduced production of solid waste Reduced chemical consumption	Increased initial capital and maintenance cost Low flow rate
Electro-chemical treatment	Metal-selective Potential for treating effluent >2000 mg dm^3	Increased initial capital cost

Adsoprtion

Over the past few years, the process of adsorption has attracted great interests, as it appears to be a favorable methodology for long-term effective treatments along with being an economical approach for the removal of Pb^{+2}ions.Depending on the flexible design and simplicity of operation, adsorption is an important process nowadays. The term “adsorption” refers to the mass transfer from a liquid phase to the surface of adsorbent[97],[82]. Advantages of the adsorption approach in removing or minimizing the Lead(II) ions, even at low concentrations, involve the enhancement of the application of adsorption as a useful and practical approach. The effectiveness of the adsorption processes is mainly categorized depending on the nature of the solution in which the pollutants are spread, the molecule sizes and the polarity of the contaminant along with the type of adsorbent used. Adsorption also occurs based on the interactions between surfaces and species being adsorbed at certain molecular levels [98],[99].

Adsorption can be categorised in two methods; physical adsorption and chemi-sorption. Physical adsorption is a reversible phenomenon which results due to intermolecular forces of attraction that take place in molecules of the adsorbent and the adsorbate. Meanwhile, chemi-sorption occurs because of the chemical interactions amongst solid and adsorbed substances. Chemi-soprtion is an irreversible method, which is also known by activated adsorption. Increased physical adsorption occurs at a temperature in the range of the critical temperature of a known gas while chemi-sorption takes place at a temperature higher than the critical temperature.

Moreover, depending on the situation, it is probable that both processes take place either separately or at the same time. It is important to ensure that various variables are monitored in the adsorption processes occurring between adsorbent and adsorbate[100]. This includes the physical and chemical characteristics of the adsorbent and adsorbate, the concentration of adsorbate in liquid solution, temperatures, pH and also contact times. In terms of pH, this accounts for the most important factor as compared to other parameters due to its ability to regulate the charge distribution on the adsorbent surface among the adsorbate ion. However, in most related studies, the zero charge point (pHzpc) must be take into consideration in order to perform comparison with pH as pHzpc regulates the limits of the pH of the adsorbent. pHzpc is the charge an adsorbent's surface carries and can be known by the protonation and de-protonation of the adsorbate ion. Also, the surface charge density is dependent on the specific metal ions that respond in a direct manner with the adsorbent surface. For instance, in cases of the pH values of the solutions being more than pHzpc, the adsorbent's surface charge will be negative. Or else, the pH rise within a certain range can result in increasing the rate of adsorption rate[101].

However, any additional increase in pH can result in the reduction of the adsorption rate. This is due to some adsorbate ions being unaltered by pH changes. As an alternative to pH, the adsorbent dosage is an additional feature, which influences the adsorption process. Moreover, with a rise in the adsorbent's dosage, the adsorption rate also tends to increase. Nevertheless, the adsorption rates can reduce if the adsorbent's dosage rises more[101],[102],[103]. This is because of the availability of a larger number of occupied active sites, while the concentration gradients of the adsorbate are maintained constant. Higher adsorption rate can be obtained when the temperature increases with the growth of the surface area and pore volume of adsorbent[101].

Initial metal concentration can be the mainspring to avoid mass transfers between the surface of adsorbent and the solution. The initial metal concentration has an influence on the adsorption rate depending on the presence of the explicit surface functional groups and the capability of the surface functional groups to bind metal ions (specially at increased concentrations). Thus, any parameters influencing the adsorptive capacity of adsorbent should be considered during the adsorption process [104].

Adsorption mechanism

Adsorption mechanisms are complex due to the non-existence of any simplified theory on the adsorption of Lead(II) ions on the adsorbent surface. Earlier works have been observed to report on the several models, which describe the mechanism between the adsorbate and the adsorbent[105]. The Langmuir and Freundlich models, both, are often employed for describing the sorption isotherms. In regards to kinetics, the pseudo first-order and pseudo second-order kinetic models can be employed for describing the sorption kinetics. The thermodynamics of the metal ion sorption can be explained based on thermodynamic factors, for example free energy ($\Delta\mathbf{G}°$), enthalpy ($\Delta\mathbf{H}°$) and entropy changes ($\Delta\boldsymbol{S}°$) based on the endothermal and exothermal sorption processes. Table 3 lists some of the empirical models of equation[3].

Adsorption isotherm

Sorption isotherm can be referred to the process of the interaction of adsorbate ions on the adsorbent's surface. In the literature, various isotherm equations exist, which can be used to analyse the relevant experimental parameters. However, one of the well-known adsorption isotherm models, which is commonly employed for the single solute system, is the Langmuir[106] and Freundlich isotherm[107]. These models are more feasible in explaining the association between the quantity of adsorbed material at equilibrium, q, in mg/g and the concentrations of the remaining adsorbate in the bulk solution at equilibrium, C, in mg/l.

Table 3 : Adsorption models of the Lead(II) ions system

Types of mechanism	Equations	Nomenclature	References
a) Adsorption Isotherm i) Langmuir Isotherms	$\frac{\mathrm{l}}{qe} = \frac{\mathrm{l}}{qmax} + \left\{\frac{\mathrm{l}}{bqmax}\right\}\frac{\mathrm{l}}{Ce}$	q_e is equilibrium metal sorption capacity, Ce is equilibrium solute concentration in solution, q_{max} and b are Langmuir constants linked to highest sorption capacity (monolayer capacity) and bonding energy of adsorption	[106]
ii) Freundlich isotherms	$q_e= K_f C e^{l/n}$	K_F is a bio-sorption equilibrium constant, q_e is the sorption capacity, n is a constant indicative of bio-sorption strength	[107]
b) Adsorption kinetics i) Pseudo first-order pseudo-second	$(qe - qt) = logqe - \{\frac{Kt}{2.303}\}$	q_e and qt are the sorption capacity at equilibrium and at time t, k_1 is the rate constant	[108]
ii) Pseudo second-order	$\frac{t}{qt} = \frac{1}{K2qt2} + \left\{\frac{1}{qe}\right\}$	$q_e$andqt are the sorption tcapacity at equilibrium and at time t, k is the rate constant of pseudo-second order sorption	[109]
c) Thermodynamics	$K_C=C_A /Ce$	Kc is the equilibrium constant, CA is the solid phase concentration C_e is the at equilibrium, K_c equilibrium concentration	[110]
	$\mathbf{\Delta G°} = \mathbf{\Delta H°} - \mathbf{T\Delta S°}$	**ΔG°**is the Gibbs free energy, **ΔH°** is the entalphy change, **ΔS°**is the entropy change	[111],[112]
	$\Delta G° = -RTlinKc$	T(K) is the absolute temperature, R is the gas constant (8.314 J/mol K) ,	[111],[112]

Langmuir isotherms

Depending on the Langmuir adsorption theory, particles tend to adsorb at known well-defined sites, that are consistently dispersed over the adsorbent's surface. These sites also have similar affinities for adsorption of a mono-molecular layer along with no interactions existing between adsorbed molecules[106]. For Langmuir equation, it is written as Eqs. 1 and 2.

$$\frac{l}{qe} = \frac{l}{q\max} + \{\frac{l}{bq\max}\}\frac{l}{C_e} \qquad (1)$$

$$q_e = \frac{q_{\max}\ bC_e}{1+bC_e} \qquad (2)$$

where qe is the metal adsorption capacity of adsorbent and is based on the physical and chemical characteristics of adsorbate and adsorbent. Langmuir isotherms can be described depending on the assumption that the adsorption process is only limited to mono-layer adsorption and reversible process, when no interaction takes place between the molecules adsorbed on the active site and the adjacent sites. This isotherm is suitable for representing chemisorptions on fixed sets of localised adsorption sites.

Freundlich isotherm

Freundlich isotherm models are used for the interpretation of the adsorption on heterogeneous surfaces with interactions taking place among the adsorbed molecules. This process is not limited to the production of a mono-layer This isotherm is usually utilised to define the adsorption of organic and inorganic compounds on a wide spread diversity of adsorbents. For Freundlich equation[107], it is written as Eqs. 3 and 4:

$$q_e = K_f {C_e}^{1/n} \qquad (3)$$

$$\log q_e = \log K_1 + \frac{l}{n} \log C_e \qquad (4)$$

Where, K_f is the adsorption equilibrium constant, 1/nis the heterogeneity factor, which is associated to the capacity and intensity of the adsorption and *C* is the equilibrium concentration (mg/l). This model makes use of the assumption that with an increase in the adsorbate concentration, the concentration of adsorbate on the adsorbent surface also increases and, consistently, the sorption energy reduces in an exponential manner with the achievement of the adsorbent's sorption center. Langmuir and Freundlich isotherm models are usually employed to define the short term and mono component adsorption of metal ions through varying materials[110].

Adsorption thermodynamic

Temperature is significant factor for the sorption of metal ions related with the thermodynamics of the adsorption procedure. Usually, two general types, which exist are endo-thermal and exothermal sorption processes. These are determined depending on the rise or reduction in the temperature during the process of adsorption. The term endo-thermal is applicable when the sorption rate increases due to the rise in temperatures. On the contrary, the term exothermal refers to the decrease in sorption as the temperature increases. The equilibrium constant achieved from the Langmuir equation at several different temperatures can be used to control the various thermodynamic variables. These include, enthalpy ($\Delta H°$), free energy change ($\Delta G°$) and entropy change ($\Delta S°$)[111],[112]. The free energy of adsorption ($\Delta G°$) can be associated to the Langmuir adsorption constant through Eqs. 5 and 6.

$$\Delta G° = -RT \ln Kc \qquad (5)$$

$$\ln Kc = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (6)$$

The value obtained from the thermodynamic parameters was numerically analyzed to forecast the characteristics of the sorption process. The adsorption of various heavy metal ions on different adsorbents is a complex process where the thermodynamic variables of the metal ion sorption are influenced by the type of metal ion, type of sorbents, solution conditions, ionic strength and experimental circumstances.

Adsorption kinetics

The contact time based on the experimental parameters can be considered for studying the rate-limiting step in the adsorption process, relating to the kinetic energy.

The overall adsorption processes can be regulated through steps such as pore diffusion, surface diffusion or a mix of more steps. Lagergen's first-order equation[108] and Ho's second-order equation[109] (Ho, 1998) are instances of kinetic models, which are often used to describe these adsorption kinetic models. The pseudo first order kinetic equation of Lagergen's model is given as Eq. 7[108].

$$\frac{\mathrm{d}q_t}{\mathrm{d}_t} = k_1(q_e - q_t)(7)$$

Where, *q*e and *q*t are quantities of adsorbed waste (mg/g) at an equilibrium and at any instant of time *t* (min), correspondingly. k_1 is the rate constant of pseudo first order adsorption operation (min). Pseudo first order equation refers to the assumption of the rate of change of solute's uptake with time which is in a direct relation to the change in the saturation concentration and the amounts of solid uptake overtime[109]. The pseudo second order kinetic is given as Eq. 8.

$$\frac{\mathrm{d}q_t}{\mathrm{d}_t} = k(q_e - q_t)^2(8)$$

The pseudo second-order model is dependent on the proposition that the rate-limiting step may arise from the chemical adsorption, which involves the valences forces that take place due to the distribution or exchanging of electrons in the adsorbent and adsorbate[109]. In regard to removing Pb^{+2}ions, researchers in the past have also considered the wastes of tea in wastewaters. This was carried out at various optimal conditions for the initial metal concentrations, adsorbent doses, the solution's pH and particle's sizes. It was revealed that the ratio of adsorbent to solution along with the metal ion concentration can have an effect on the quality of the metal ions removed.

The most adsorption of Pb^{+2}ions was about 96%, as the doses of the adsorbent were increased from 0.25 g to 1.5 g per 200 ml at various concentrations of the ions, i.e., 200 mg/l and 100 mg/l. An increase in the adsorption takes place with an increase in the electrolyte concentration. It was noticed that the most metal uptake in tea waste took place at 48 mg/g and 65 mg/g for Pb^{+2}ions, for pH ranging from 5-6, correspondingly. Analysing the isotherm for the adsorption data achieved at 22°C demonstrated that the equilibrium data for Pb^{+2}ions fits well with both, the Langmuir and Freundlich isotherms. Also, Pb^{+2}ions were seen to have an increased affinity and adsorption rates at all experimental circumstances. Moreover, the study of kinetics revealed that Pb^{+2}ions uptake was faster with a 90% or even a higher percentage of adsorption taking place within the first 15 – 20 minutes of contact times. In addition, the kinetics data was able to fit well with the pseudo second order model, where correlation coefficients were found to be higher than 0.999. The rise in the overall adsorption rate and capacity of Pb^{+2} was observed when smaller adsorbent particles were used.

In addition, investigative research was performed with varying pH (i.e. pH of 2.5, 6.6 and 7.2), varying temperatures (i.e.30°C,40°C, 50°C and 60°C) and adsorbent doses (i.e. 1 to 10g).The outcomes of this investigative study showed that adsorption capacities of clays for removing lead increase with a rise in the solution's temperature. It was also revealed that the maximum adsorption capacity was 117 mg/g at a temperature of 60°C. Also, the adsorption process exhibited a Langmuir and Freundlich behavior, which was shown by the coefficient (i.e. R2 > 0.99). Increased percentage of Lead(II)removal at low solution pH is possible due to the decreased content of Lead (II) ions. On modeling, the kinetic data fit the pseudo first-order model well as compared to the pseudo second-order model. The works on the adsorption of Lead(II) by the durian shell waste in terms of isotherms, kinetics and thermodynamics have verified the process, which has endothermic (H°>0), spontaneous (

G°<0) and irreversible (S°>0) characteristics.

Moreover, the peel of a banana was also considered for removing Lead (II) from water (Gonzalez et al., 2006). The works were performed as a function of: pH (i.e. with pH values in the range of 1.18 to 13.5), particle sizes (i.e. with sizes of 600, 420, 300, 150, 75 and <75 ìm), doses (of 0.05, 0.1, 0.2, 0.5 and 1 g), contact time (of 3hr) and temperature (in the range of 30-70°C). The findings revealed that the optimum conditions for adsorption are achieved at a pH of 6.5, at a size of particle less than 75 ìm, a dosage of 0.5g/100ml and a 1-hour contact time.

The adsorption capacities of banana peels for removing Lead(II)reduces with a rise in the solution temperature, which shows that the adsorption process is impulsive. The type of adsorbent is an important factor. Adsorption capacity depends on activated carbons, which is not feasible for use, currently, based on its highly expensive cost of production and operations. Activated carbon also needs a somewhat complicated mix of agents for improving the removal process for inorganic matters. Due to the problems mentioned earlier, latest researches have looked into an alternative adsorbent with high regeneration capability, obtainability and cost-effectiveness to substitute the expensive activated carbons. Up to the present time, several works have investigated the usage of low-cost adsorbents. Agricultural wastes along with natural materials all were investigated as potentially low-cost adsorbents for treating wastewaters, plagued with Lead(II) ions.

Low cost adsorbents

Recently, quite a significant amount of research has been carried out for obtaining materials, which could be used as low-cost adsorbents. These consist of natural materials, agricultural waste and wastes produced from industries. Low cost adsorbents refer to those materials, which are found abundantly in the environment or are byproducts or wastes from industries. Moreover, adsorbents are known as low-costs if they have reduced processing requirements. Previous adsorption works concentrated on plant wastes such as the maize leaf[18], rice husk ash[15], Cane papyrus[3], coconut husk[28]and tea waste leaves[37], which can be utilised either in their natural form or after some physical or chemical alterations. Converting these materials into adsorbents is an effective way of reducing the costs of waste disposals and for providing alternate treatments for replacing the commercially activated carbons[33]. Table 4 provides a summary of the outcomes of different works on adsorption, utilizing several adsorbents. Several features may have an impact or dominate the adsorption capacities of different adsorbents[113]. Earlier works in the relevant fields made use of the assumption that the competence of an adsorbent is heavily dominated by the physio-chemical properties of solutions. These properties include factors like pH, initial concentrations, temperature, contact times and adsorbent doses. To understand the association of these parameters, several investigative researchers have been carried out in the relevant areas[114].

Effects of pH

The adsoprtion of metal ions from wastewaters is usually dominated by the solution’s pH. It is worth mentioning that pH of the solution influences the surface charges on the adsorbent, the extent of ionization along with the class of adsorbents. Over known pH range, mostly metal sorption is improved with pH. However, this is valid for a known increase in pH, after which an additional rise in pH can lead to a reduction in the metal sorption. The dependency of Pb^{+2} ions approval on pH is related to the surface functional groups on the biomass cell walls and also the metal chemistry in the solution. The pH value of the medium influences the system equilibrium, as the pH correlation can be expressed as Eq. 9.

$\mathrm{pH} = \mathrm{pk_a} - \log \frac{[\mathrm{AH}]}{[\mathrm{A}]}$(9)

Where, [A] and [AH], refer to the concentrations of deprotonated and protonated surface groups. The equilibrium constant, pKa, resembles the carboxyl groups. The effects of pH on the Pb^{+2}ion uptake are also investigated for removing Pb^{+2} ions in utilising the Cane Papyrus[3]. The pH values used were in the range of 2 to 8. It was seen that the highest bio-sorption occurs when the pH value was in the range of 2.5 to 5. This is probably due to the fact that a low pH value leads to the detachment of carboxylic acids, which further results in the production of carboxylate groups plus H^{+}. A further rise in the pH results in an increase in the metallic ion bio-sorbed. Moreover, for pH more than 5, a strong reduction is observed in the metal uptake. This is mainly because of the hydrolysis of the metal ion. Effects of pH on banana peels has also been looked into[115].

Furthermore, in terms of the Pb^{+2} ions, the pH effects were also monitored and it was observed that the adsorption abilities rose from 0.5 mg/g to around 2.88 mg/g with a rise in pH from 2 to 6. This can be based on the availability of the free ion, which exists at pH lower than 6. Nevertheless, the adsorption capacities decrease after a further rise in pH (i.e. from a pH of 6 to 12). To elaborate, at lower pH values, the adsorption abilities are lesser than Pb^{+2} ions, which are competing with hydrogen ions for the binding site on the surfaces of the adsorbent. On the contrary, at increased pH values, the Pb^{+2} ions tend to precipitate in the solutions.

Effects of temperature

Based on the adsorbent utilised, the relative temperatures can have an influence on the adsorption capacities. To elaborate, the thermal value is able to alter the adsorptive equilibrium based on the type of the procedure (i.e. whether it is exo or endo-thermic). Hence, it is vital to determine factors such as enthalpies, entropies and Gibbs free energies, prior to the conclusion of the procedure. Gibbs free energy ($\Delta G°$) is measured as the impulsiveness pointer of a chemical response[109],[116]. The connection between Gibbs free energy change, ($\Delta G°$), temperature and equilibrium constant, Ka, is expressed by Eq. 5.

The enthalpy, $\Delta H°$and entropy, $\Delta S°$ changes on the adsorption procedure can be found from equilibrium constants as functions of temperature through the Van't Hoff equation, as can be referred in Eq. 6. The percentage of Pb^{+2} ions adsorption by dried Gamma plant that increases with the rising temperatures from 25 to 40°C have been investigated. Negative free energy change ($\Delta G°$) values designate the impulsive characteristics of the adsorption process. Whereas, positive values of the enthalpy change ($\Delta \mathbf{H}°$) suggest the endothermic characteristics of the adsorption procedure. These findings are also reported due to a rise in the uptake capacities of the adsorbent with an increase in temperature. It has been found that the rising sorption capacities of the sorbent with temperature are due to the increase of pores and/or the activation of the sorbent surface [117]. Additionally, positive values of entropy ($\Delta \boldsymbol{S}°$) show the increased extents of free active sites at the solid–liquid interface during the adsorption of Pb^{+2}ions on dried plants[109].

Table 4: Adsorption capacities of Lead(II) ions utilizing several different adsorbents

Type of adsorbent	pH	Contact time (min)	Temperature (°C)	qmax(mg/g)	References
Banana peel	7	80	25	1.25	[115]
Cocoa shells	2	< 120	22	26.2	[14]
Rice husk	4	< 120	25	102.96	[19]
Thorns	6	90	25	154.76	[38]
Gamma Irradiated Minerals		60	40	9.91	[21]
Mangan oxide minera		60		6.8	[23]
peat		60		82.31	[112]
Peat (Indonesian)	6	60		79.6	[27]
Tree fern	6	60		40	[22]
Hyacinth roots	6	60		16.35	[20]
Coconut shell	6	60		24.24	[29],[30]
Peat (Bruneian)	5.5	60		14.97	[31]
Rice straw	6	90	25	35.17	[32]
cane papyrus	6.5	60	25	45.5	[3]
Sugarcane bagasse	5	90	25	23.4	[33]
Natural Clay	6	120	25	49.5	[82]

Effects of contact time

Adsorption of Pb^{+2} ions adsorbent also is dependent on the connections of functional groups concerning the solution and the surface of adsorbent. Adsorptions can be considered to conclude when an equilibrium stage is obtained with the solute of the solution and the adsorbent. Nevertheless, a certain period of time is required for maintain the equilibrium connections to confirm that the adsorption process has been completed. The effects of contact times on rice husk ash for the adsorption lamination of Pb^{+2}ions from aqueous solutions is observed[19].

The experiment measures the effects of contact times under the initial concentrations of the batch adsorption as 20 mg/l and a pH of 5 for Pb^{+2}. The increased contact time improved the adsorption of Pb^{+2} ions. Conversely, the quick adsorption had an initial effect on the overall required time to obtain an equilibrium. For rice husk ash, the equilibrium time was 2.5hr, for Pb^{+2} adsorption while for Cane papyrus, 2hr were required to attain an equilibrium for the adsorption of Pb^{+2} ions. Hence, a 3hrcontact time was maintained as an optimal time for future studies. The adsorption of Pb^{+2}ions on Cane Papyrus is observed to have taken 120 min as the optimal time for future studies[3].

The ranges of contact times ranged from a minute to 3 hr. However, the significant removal of Pb^{+2}ions occurred during the first 30 minutes where no considerable variations in terms of the removal were observed after 2 hr. The adsorption of Pb^{+2}ions is originally higher mainly because of the existence of increased surface areas of cane Papyrus for adsorption. All further experimental works maintained an equilibrium time of 2 hr for removingPb^{+2}ions onto Cane Papyrus.

Effects of adsorbent dose

Adsorbent dosage is a useful variable in determining the adsorbent’s capacities at known concentrations of the adsorbate. Effects of adsorbent doses on Cane Papyrus powder for adsorbing Pb^{+2} ions from aqueous solutions is examined. At room temperature, the adsorbent dosages were changed from 5 to 30 mg/l along with an initial concentration of 10 mg/l [119].

Results achieved from this work describe the adsorption of Pb^{+2} ions, which improves and advances when doses of Cane Papyrus powder are amplified from 5 to 20 mg/l. This explains the increased accessibility of surface areas at increased adsorbent concentrations. Additional increases in the adsorbents will not have any effect on the adsorption because of the overlying adsorbent particles' sites[3].

Effects of initial concentration

Initial concentrations of Lead(II) ions can modify the effectiveness in terms of removing metals based on a mix of features. These include the existence of a specific surface functional groups in addition to the capability of these groups to bind Lead(II) ions. Moreover, this initial solution concentration can act as a vital factor in overcoming the mass transfer resistances of Pb^{+2}ionsconcerning the aqueous and solid phases[120].

The rapid adsorption of Lead(II) using Cane papyrus after 30 minutes before it continues at a faster rate and achieves saturation has been examined[3]. As the initial concentration of Lead(II) rises from 10, 20 and 30 ppm, the adsorption removal decreased, which was mainly because of the lower concentrations, where almost all Lead(II) ions were adsorbed rapidly on the outer surface. Nevertheless, further rise in the initial concentration of Pb^{+2}ions resulted into the rapid saturation of adsorbent [115].

CONCLUSION

Several industries produce vast amounts of contaminants and impurities in their waste discharges. Lead (II) ions are commonly found on earth and are known to have several harmful effects on the overall ecological system. They are vastly present in the water ways and are very harmful to the environment. This is due to their non-biodegradable characteristics, which makes them hard to be removed from the ecological system. In fact, they can accumulate and thus become part of the human food chains as well leading to serious health issues. Lead also appears to be one of the major risk factors for several deadly diseases in cases where its concentration exceeds the permissible limits.

Due to the multiple issues associated with lead poisoning, several processes are used for treating wastes produced from industries which are rich of lead (II) ions. These include chemical precipitation, ion-exchange, electro dialysis and carbon adsorption. Over the last few years, several investigative works have been carried out in order to explore an alternate to the expensive methods for treating wastewaters. Several kinds of materials have been used for the adsorption process to test their adsorption abilities. Based on the results of these studies, it appears that elimination of lead (II) ions with the use of low cost adsorbents is increasingly favourable, especially in long term. Low cost adsorbents can be obtained from various materials, which are thoroughly mentioned in this study.

This study explores the possibilities and potentials of recovering lead (II) ions using several low cost adsorbents through wastewater processing. The study provides a review of the relevant literature on this subject. The review highlights the specific features of lead (II) ions, which includes its sources, toxicity and methods for its removal including the traditional processes. Further, this review reveals the efficiency and scope of using low cost adsorbents. It is known that the adsorptive capacity is dependent on the nature of the absorbent utilised and the type of wastewaters under treatment. The review thus mentions an analysis on the adsorption mechanisms and the theory behind these processes. Effects of various parameters such as pH, temperatures, contact times, adsorbent doses and initial concentrations on the adsorption capacities are also mentioned in this study.

The use of commercially activated carbon can be replaced by the inexpensive and effective low cost adsorbents. There is need for more studies to understand better process of low-cost adsorbents and to demonstrate the technology effectively. Various low cost adsorbents show a high degree of removal efficiency for Lead ions. If low cost adsorbents perform well in removing Lead ions complexes at low cost, they can be adopted and used widely in industries, not only to minimize cost but also to improve profit. In addition to this, the living organisms and the surrounding environment will also be benefited from the decrease or elimination of the potential toxicity due to the Lead ions.

Further investigative works need to be performed in order to develop an improved understanding on the adsorption processes of low-cost adsorbents as an alternative of endorsing the use of non-conventional adsorbents on a large scale. These works could involve structured works on adsorbents, batch investigations on the parameters that influence adsorption, adsorption modeling such as isotherm, kinetics and thermodynamics, the recovery of lead (II) ions and the improvement of adsorption capacities through the alteration of adsorbents.

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CONFLICT OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

ABBREVIATIONS

%	Percent
AAS	Atomic Absorption Spectrometer
b	Langmuir constants
C_A	Solid phase concentration
Ce	Equilibrium solute concentration in solution(mg/l)
C_i	Initial Concentration of Metal Ions(mg/l)
C_f	Final Concentration of Metal Ions(mg/l)
DDW	Double Distilled Water
Eq.	Equation
Fig.	Figure
K2	Pseudo-Second-Order Adsorption Rate Constant in (g/ mg.min)
Kc	equilibrium constant
K_F	abio-sorption equilibrium constant
MCL	Maximum Contaminant Level
q_e	equilibrium metal sorption capacity
q_{max}	highest sorption capacity
q_t	sorption capacity at time t
R	gas constant (8.314 J/mol K)
T	absolute temperature in (^oK)

W	Adsorbent Weight
ΔH°	Standard Enthalpy Change(KJ/mol.)
ΔG°	Free Energy Change (KJ/mol.)
ΔS°	Standard Entropy Change (KJ/mol. °K)

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