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Eco-Friendly Method for Removal of Some Heavy Metals in Water; Physical and Analytical Study

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Abstract

This study sought to examine the removal of some heavy metal ions from an aqueous media utilizing an adsorbent made from waste materials Cyperus papyrus and nano Cyperus papyrus. Because of their abundance of (OH) groups, Cyperus papyrus biomaterials are promising adsorbents for removing heavy metals. Therefore, this study proposed removing Al, Fe, Pb, and Cd from aqueous solutions using dried Cyperus papyrus. The effectiveness of removal was determined to be in this sequence Fe >Pb> Cd>Al. In another method, some of the cyperus papyrus was converted to nanopowder and used to investigate the elimination of Pb and Cd from aqueous solutions, and the results showed that the nano cyperus papyrus is more effective than normal cyperus papyrus. Normal cyperus papyrus was applied into two samples; the first was a sewage water sample, and the other was ground water. The Freundlich isothermal adsorption method worked better for the adsorption of Al, Fe, Pb, and Cd using Cyperus papyrus, and it also demonstrated an ion exchange process that took place in the adsorption surface layer that is uneven. Cyperus papyrus had a high affinity for adsorbing heavy metals Al, Fe, Pb, and Cd without additional chemicals. The results revealed that the used adsorbent had been a promising material for treating some contaminants and was eco-friendly.

Keywords: Adsorption, Agricultural waste, Adsorption isotherm , Cyperus papyrus, Heavy metals, Nano adsorbent..

Introduction

Due to the health issues it causes, water supply pollution is a global issue. Heavy metal pollution of water is an environmental issue due to industrial processes such as mining, smelting, metal plating, and fertilizer manufacturing [1]. There are many sources through which heavy metals can enter the environment directly or indirectly for aquatic species and human life, and they are poisonous or carcinogenic [2]. Even though some heavy metals, such as iron (Fe), zinc (Zn), cobalt (Co), and manganese (Mn), are necessary for human health, they are extremely dangerous when introduced in ion form or as compounds. They are also easily absorbed by living things, plants, and animals since they are soluble in water. Several treatment methods have been used to remove heavy metals from wastewater and water, including membrane filtration, ion exchange, coagulation - floculation, precipitation, and adsorption [3]. These techniques have some limitations, such as a high cost of energy, ineffective removal, the creation of hazardous sludge, and the fouling of metal ions [4]. However, due to their ease to use and low cost, adsorption-based methods have the efficiency in eliminating heavy metal ions [5]. Until now, adsorption-based technologies require the exploration of low-cost, eco-friendly alternatives to sorbents, such as biosorbents made from agricultural waste. With or without chemical changes, biosorbents from natural agricultural wastes have been employed, including rice husk [6], coconut coir [7], maize straw [8], orange peel [9], and water hyacinth plant [10]. The enormous herb Cyperus papyrus, also known as Bardi in Egypt, is found in northern (Egypt, Sudan) and central (Cameroon, Guinea, Nigeria) Africa [11]. The environmentally friendly technology used to purify water employs a built wetland planted with Typhalatifolia and Cyperus papyrus supported by a zeolite substrate. Cyperus papyrus primarily comprises cellulose (53.29-62.04%) and lignin (22.42-32.77%) [12, 13]. The Cyperaceae family includes the rhizomatous perennial plant known as papyrus (Cyperus papyrus L.). The plant thrives in tropical and subtropical climates and is indigenous to eastern, central, and southern African wetlands. Papyrus can grow up to 5 meters above the ground in monotypic floating stands of plant culms topped by an umbel that acts as the primary photosynthetic surface [14, 15]. Papyrus is mainly used to create fences, roofs, mats, white paper, fiberboard, and briquette production is also rising [16]. In the past, the Ancient Egyptians had grown papyrus and utilized it to make papyri, a kind of paper manufactured from slices of the stem pith [17]. Papyrus is a lignocellulosic substance that can also be utilized to make biomaterials and biofuels. A thorough examination of the nature and content of their principal constituents is necessary for this aim. However, investigations on the specific chemical makeup of the plant's constituents are relatively rare, despite a large number of researches on the production of papyrus sedge as a significant resource of biomass, and there is just one prior publication that described the lignin content in lignified cell walls of papyrus flowering stems. [18]. Papyrus is made of fibrous substances [19], which include only 3% proteinaceous components and 97% cellulose, hemicellulose, and lignin [20]. The percentage of lignin varies from 12% to 34% [21]. Papyrus is prepared by removing the outer shell and using a portion of the papyrus stem [22]; the stem is cut into water-moistened slices and laid on a board [23,24]. Then, another layer of slices is put on top at suitable angles . They are compressed by being wrapped in a cylinder and then dried [25]. Papyrus sheets may pick up salt or dirt during production and handling, which has a negative impact when the combined substances are deposited and mainly affects the mechanical strength . This research examines the removal of metal ions from an aqueous media utilizing the waste biomass adsorbent Cyperus papyrus.

Materials and Methods

Instruments

The pH values of various solutions were monitored by a digital pH meter (Thermo-Scientific USA instruments). Atomic absorption (A.A.S) (Thermo Scientific, ICE 3000 Series, U.K) was used to measure Pb and Cd ions concentrations. (Cecil 7400 Double Beam UV/Vis spectrophotometer) was used to measure Al and Fe ions concentrations, shaking of samples was performed using an (orbital shaker, Thermo-Scientific, UK), and (Ball mill model PM400, U.K) was used to ground Cyperus papyrus powder and converted to nano size. (Sensitive balance, Sartorius, Germany), was used to weigh materials.

Materials

The reagents used in all experiments were of analytical grade and used without further purification. Aluminum Nitrate, Cadmium Sulfate octa hydrate, Lead acetate tri hydrate, Eriochrome cyanine R, Acetic acid, and 1,10-phenanthroline were purchased from Sigma-Aldrich, USA. Nitric acid, Ammonium acetate, and Sodium acetate were purchased from Panreac Quimica S.LU. Ferric Chloride hexahydrate was purchased from POCh Gliwice, Poland. Hydrochloric acid was purchased from J.T. Baker, USA. Sodium hydroxide was purchased from Fluka.

Solutions

Aluminum (III) standard solution: Al (III) solution 10 mg/L was prepared in a measuring flask by taking 10 mL of 1000 mg/L ready standard solution from Sigma-Aldrich and completing it to 1000 mL with distilled water.Ferric (III) standard solution: Fe (III) solution 1000 mg/L was made by dissolving 2.42 g from Ferric Chloride Hexahydrate ($FeCl_3 .6H_2O$) in 500 mL of distilled water. Lead (II) standard solution: Pb (II) solution 1000 mg/L was made by dissolving 0.9153 g from Lead acetate tri hydrate $Pb(CH_3COO)_2.3H_2O$ in 500 mL of distilled water. Cadmium (II) standard solution: Cd (II) solution 1000 mg/L was made by dissolving (1.571 g) from Cadmium Sulfate octa hydrate ($CdSO_4.8H_2O$) in 500 mL of distilled water. Phenanthroline solution: 100 mg of 1, 10-phenanthroline monohydrate dissolved

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in 100 mL distilled water. Eriochrome cyanine R solution: In 50 mL of water, dissolve 150 mg Eriochrome cyanine R then 1 + 1 acetic acid was used to reduce the pH from 9 to 2.9 and completed to 100 mL with distilled water [26]. Sodium acetate buffer solution: 136 g sodium acetate was dissolved in distilled water; 40 mL of 1N acetic acid was added and then completed to 1 L with distilled water. Ammonium acetate buffer solution: Dissolve 250 g CH_3COONH_4 in 150 mL distilled water. Add 700 mL Glacial acetic acid 99.5%, and complete to 1 L with distilled water, then pH values were detected using pH meter [27].

Preparation of Cyperus papyrus adsorbent

One Kg of Cyperus papyrus was collected from Sharkia, Egypt. Rinsed many times using distilled water, dried at room temperature 25 ^{0}C for one week using a desiccator, crushed with a blender, sieved through 150 mesh sieved, and kept in 100 mL plastic bottle. Then Cyperus papyrus was divided into five parts, four dried at different temperatures (85, 105, 150, and 170)^{0}C for two hours to form Cyperus papyrus powder sorbent, and the fifth part was converted to nanopowder.

General procedures

In five conical flasks, 0.5 g of Cyperus papyrus powder was placed in each one and mixed with 50 mL (6 mg/L) of metal ions solutions which were studied and shaken for 30 minutes. The metal ions solutions were filtrated using filter paper. The concentration of each ion was measured by spectrophotometer using the Eriochrome cyanine R method for Al, the Phenanthroline method for Fe according to Rice et al. [26], and an Atomic Absorption spectrometer for (Pb, Cd).

Factors affecting the elimination of Al (III), Fe (III), Pb (II), and Cd (II) from different water samples

Effect of quantity of adsorbent

The impact of the quantity of sorbent on the efficiency of absorption of Al (III), Fe (III), Pb (II), and Cd (II) was studied. (0.1, 0.25, 0.5, 1.0, 1.5 g) Cyperus papyrus powder was placed in five conical flasks containing 50 mL of 6 mg/L metal ions solutions, which were studied and shaken for 30 minutes. The metal ions solutions were filtrated using filter paper. The concentration of each ion was detected by spectrophotometer for (Al, Fe) and Atomic Absorption spectrometer for (Pb, Cd).

The Effect of pH

50 mL of the metal ion solution of Al (III), Fe (III), Pb (II), and Cd (II) were contacted with 0.5 g of the adsorbent in five conical flasks, and the pH of the solution was adjusted with 0.1M HCl and 0.1M NaOH to obtain pH of 1, 3, 5, 7 and 9. The solution was equilibrated for 30 min, and the metal ions solutions were filtrated using filter paper. The concentration of each ion was measured by spectrophotometer for (Al, Fe) and Atomic Absorption spectrometer for (Pb, Cd).

The Effect of initial ions concentration

The impact of initial ions concentration was studied. Different concentrations of the metal ions were prepared by serial dilution of the stock metal ion solution(2, 4, 6,8, and 10 mg/L) and then contacted with a fixed dosage(0.5 g) of the adsorbent and 50 mL of the metal ion solution for Al(III), Fe (III), Pb (II) and Cd (II) in a conical flask, and shake for 30 minutes after time ended the mixtures were filtered and analyzed using a spectrophotometer for (Al, Fe) and Atomic Absorption spectrophotometer for (Pb, Cd).

The Effect of contact time

The reaction time is one of the most important variables affecting eliminating heavy metals from a medium. The effect of contact time on the elimination of Al(III), Fe (III), Pb (II), and Cd (II) onto cyperus papyrus powder was studied. Procedures were done to investigate the effect of different contact times (5, 15, 30, 60, and 120 minutes) on the elimination of Al (III), Fe (III), Pb (II), and Cd (II). 50 mL of 6 mg. l^{-1} of the metal ion solution for Al (III), Fe (III), Pb (II), and Cd (II) were contacted with 0.5 gm of the adsorbent in a flask and shaken for 30 minutes then filtered using filter paper. Furthermore, concentration was measured using a spectrophotometer for (Al, Fe) and Atomic Absorption spectrophotometer for (Pb, Cd).

The Effect of interfering ions

The effect of interfering ions was studied by mixing 0.5 g cyperus papyrus powder with 50 mL from a series of solutions containing 6 mg/L Al(III) and 6 mg/L of [Na^+, k^+, Ca^{2+}, SO_4^{2-}, CO_3^{2-}, I^-] separately for Al(III), and Fe(III)adsorbent mixed with 50 mL from series of solutions contain 6 mg/L Fe(III) and 6 mg/L of [Na^+, K^+, Ca^{2+}, SO_4^{2-}, CO_3^{2-}, I^-] separately, and for Pb(II) adsorbent mixed with 50 mL from series of solutions contain 6 mg/l Pb(II) and 6 mg/l of [Na^+, K^+, Ca^{2+}, SO_4^{2-}, CO_3^{2-}, I^-] separately, and for Cd(II) adsorbent mixed with 50 mL from series of solutions contain 6 mg/l Cd(II) and 6 mg/L of [Na^+, K^+, Ca^{2+}, SO_4^{2-}, CO_3^{2-}, I^-] separately, in a flask, and shake for 30 minutes then filtered using filter paper. Moreover, concentration was measured using a spectrophotometer for (Al, Fe) and Atomic Absorption spectrophotometer for (Pb, Cd).

Applications

Using normal Cyperus papyrus as an adsorbent removes Pb(II) and Cd(II) from water samples obtained from Bahr Elbaqer (a water bank) and a certain common groundwater. Separately, two liters of wastewater and two liters of groundwater were gathered and boiled for four hours till the volume was reduced to about 250 mL. Then 50 mL of each sample was added to 0.5 gm of Cyperus papyrus stalks to powder and shaken for 30 minutes; then, The metal ions solutions were filtrated using filter paper. Furthermore, an atomic absorption spectrometer determined the concentration of Pb (II) and Cd (II).

Nano Cyperus papyrus powder

Conversion of Cyperus papyrus powder into Cyperus papyrus nano powder.

The fifth part of Cyperus papyrus powder was dried at 170 ° for 2 hours using an electric drier oven. Then 10 grams of Cyperus papyrus powder was ground several times in a Ball mill device to convert Cyperus papyrus powder to a nanoparticle size.

General procedures using nano ash

0.1 g of Cyperus papyrus nano powder was placed in five conical flasks, mixed with 50 mL metal ions solutions under consideration, and shaken for 30 minutes. Then the formed solution was filtered using Whatman filter paper. The concentration of each ion was measured by Atomic Absorption spectroscopy.

Results and Discussion

FTIR spectrum of Cyperus papyrus

Fourier-transform infrared spectra of cyperus papyrus were presented in Fig. 1, denoting many extreme peaks on the sorbent surface, specific to various important functional groups. It is noted that the peak at 3381 cm^{-1} is due to the O–H stretching vibration. The peak at 2902 cm^{-1} was linked to the C–H stretching in methyl and methylene groups, while the band at 1639 cm^{-1} refers to the existence of a C=C bond. The band at 1430 cm^{-1} may be due to COO– groups. The peak at 1375 cm^{-1} may attribute to the oxygen functional groups as C=O carboxylic stretching group. The band at 1061 cm^{-1} was assigned to the C–O of the cellulose. The band at 668 cm^{-1} may attribute to functional group C–O–C of esters, phenol, or ether [28], as shown in Table 1.

Table 1. FTIR functional groups presented in cyperus papyrus and nano cyperus papyrus ash.

Functional group	**O–H stretching**	**C–H stretching**	**C=C bond**	**COO–**	**C=O**	**C–O**	**C–O–C**
Frequency	3381	2902	1639	1430	1375	1061	668
Functional group	O-H stretching	S-H stretching	C=O stretching	C-H bending	O-H bending	C-Br stretching	C≡N stretching
Frequency	2931	2519 2600 2654	1701 1739	1458 1906 879	1334	678	2245

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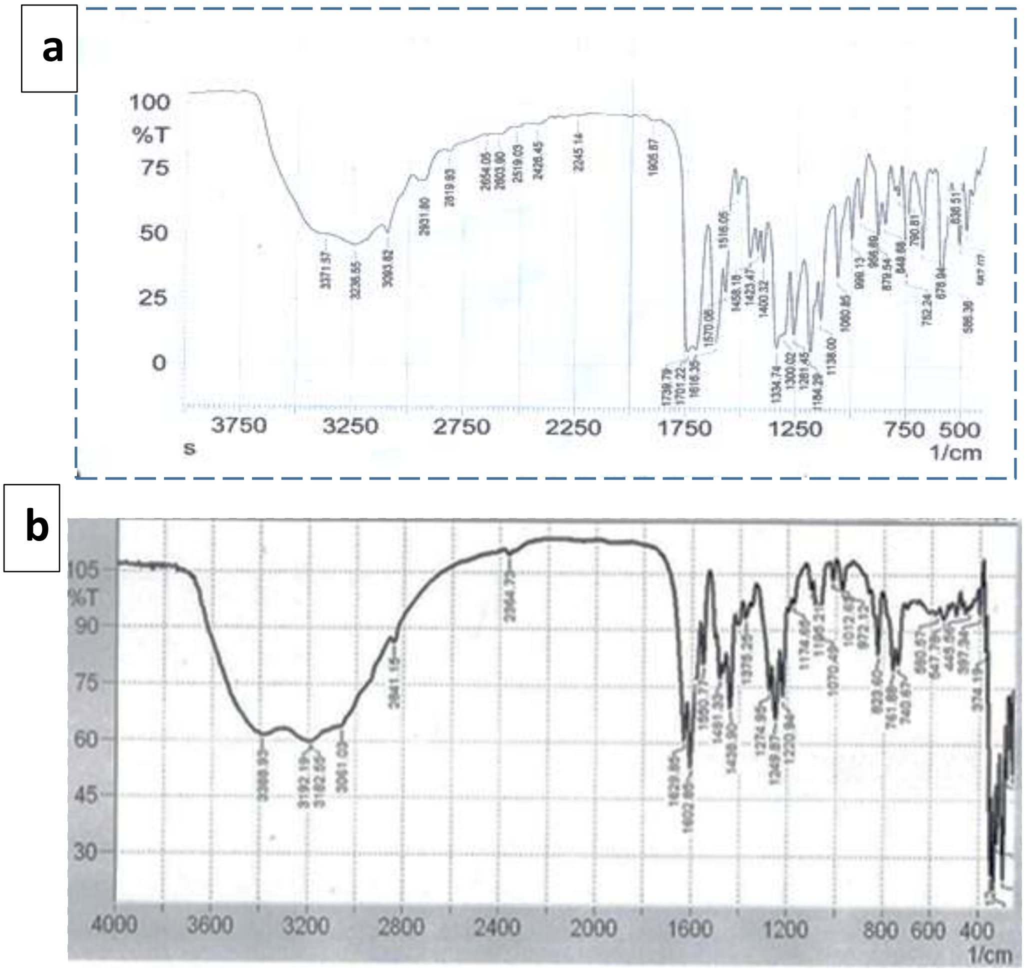

Figure 1. FTIR spectrum (a) normal cyperus papyrus, (b) nano cyperus papyrus.

Parameters affecting the adsorption process

Adsorption is preferred for removing metal from wastewater due to its ease of use, non-toxicity, high effectiveness, reasonable pricing, cheap investment, and quickness. The adsorption process was performed using cyperus papyrus and nano cyperus papyrus adsorbent under several factors such as drying temperature, amount of cyperus papyrus, initial ions concentration, contact time, and interfering ions will be discussed in the following section.

The Effect of drying temperature

The drying temperature of cyperus papyrus was evaluated as one of the most important factors affecting the adsorption efficiency. As shown in Fig. 2, it was founded that the best drying temperature is 85°C, 85°C, 150°C and 170°C for Al (III), Fe (III), Pb (II), and Cd (II), respectively.

The Effect of amount of cyperus papyrus

The impact of sorbent dose on Al (III), Fe (III), Pb (II), and Cd (II) adsorption was studied in Cyperus papyrus. As shown in Fig. 3, it was founded that the best amount of cyperus papyrus is 1 g, 0.25 g, 1 g, and 0.5 g for Al (III), Fe (III), Pb (II), and Cd (II), respectively.

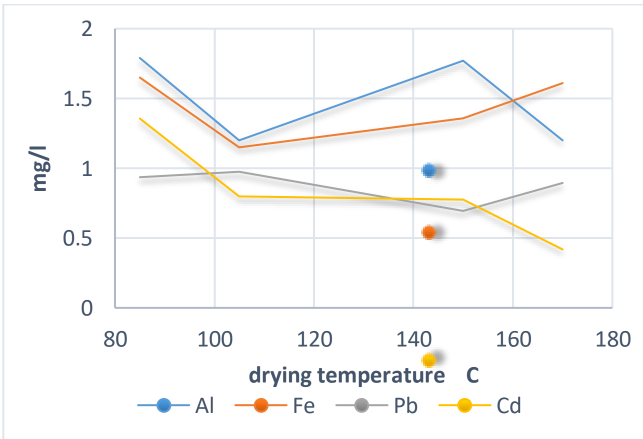

Figure 2. Effect drying temperature

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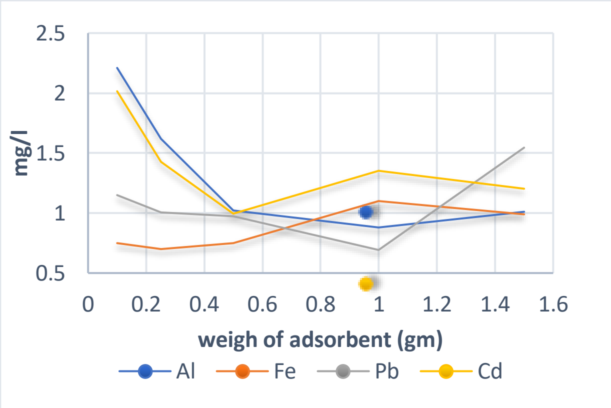

Figure 3. Effect amount of cyperus papyrus.

The Effect of pH

One of the most crucial elements determining the sorption of metal ions is pH. Hydrogen ions' capacity to compete against heavy metals for adsorption active sites on the sorbent surface is directly related to initial pH variations [13]. The impact of pH on the sorption of Al (III), Fe (III), Pb (II), and Cd (II) ions onto Cyperus papyrus was examined at pH (1, 3, 5, 7, and 9). As shown in Fig. 4, it was founded that the best pH value is 9 Al (III), Fe (III), Pb (II), and Cd (II).

The Effect of initial ions concentration

The study examined how initial concentrations affected the elimination of Al (III), Fe (III), Pb (II), and Cd (II) ions by Cyperus papyrus. As shown in Fig. 5. it was founded that the best initial concentration was 6 mg/L, 6 mg/L, 2 mg/L, and 8 mg/L for Al (III), Fe (III), Pb (II), and Cd (II), respectively.

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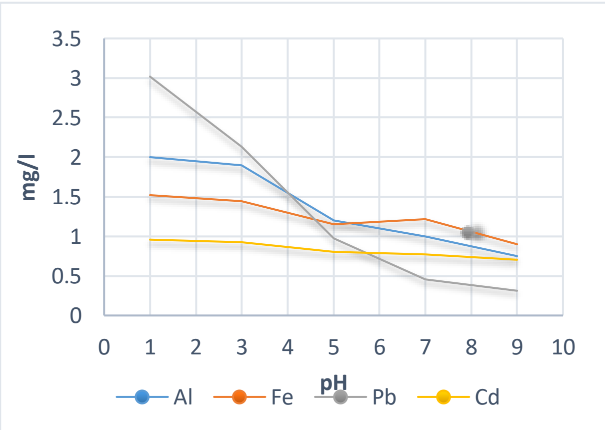

Figure 4. Effect of pH.

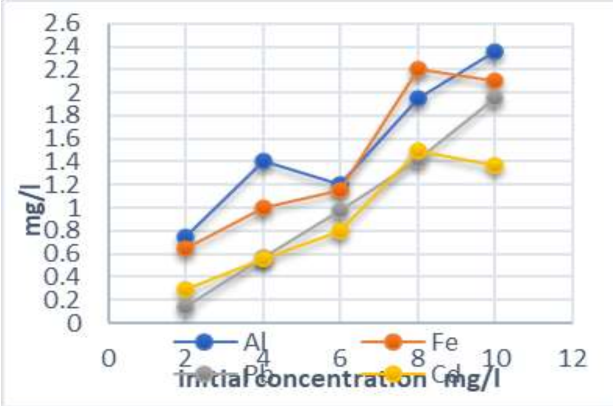

Figure 5. Effect of initial concentration.

The Effect of contact time

The equilibrium point was established by analyzing how time affected the adsorption process. The studies were conducted to examine the impact of reaction time on the elimination of Al(III), Fe(III), Pb(II), and Cd(II) ions. As shown in Fig. 6, it was founded that the best contact time was 30 minutes, 120 minutes, 120 minutes, and 60 minutes for Al (III), Fe (III), Pb (II), and Cd (II), respectively.

The Effect of interfering ions

The effect of interfering ions on adsorption Al (III), Fe (III), Pb (II), and Cd (II) by Cyperus papyrus shown in Fig. 7 the presence of interfering ions (cations and anions) effect on the percent of removal of Al (III), Fe (III), Pb (II), and Cd (II) was founded that the presence of (Na^+, k^+, Ca^{2+}, SO_4^{2-}, CO_3^{2-}, I^-) ions the percent of removal of Al (III) decreased by (27.5 %, 23.67 %, 21.83 %, 15.67 %, 17.50 %, and 15.83 %) respectively, the percent of removal of Fe (III) decreased by (11.7 %, 12.2 %, 11.3 %, 13.2 %, 10.3 %, and 13.8 %) respectively, the percent of removal of Pb (II) decreased by (4.9 %, 6.1 %, 5.4 %, 6.5 %, 5.3 %, and 4.5 %) respectively and the percent of removal of Cd (II) decreased by (19.97 %, 12.51 %, 4.91 %, 5.90 %, 19.18 %, and 18.06%) respectively.

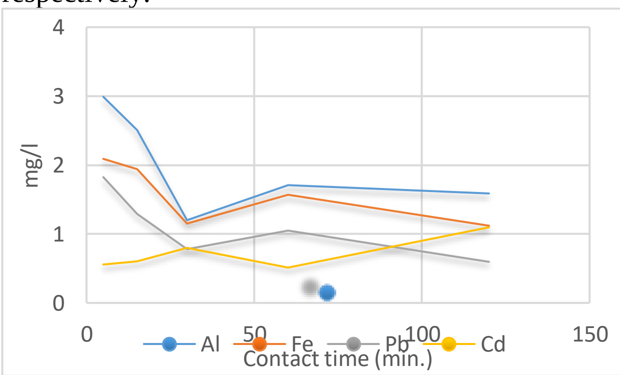

Figure 6. Effect of contact time.

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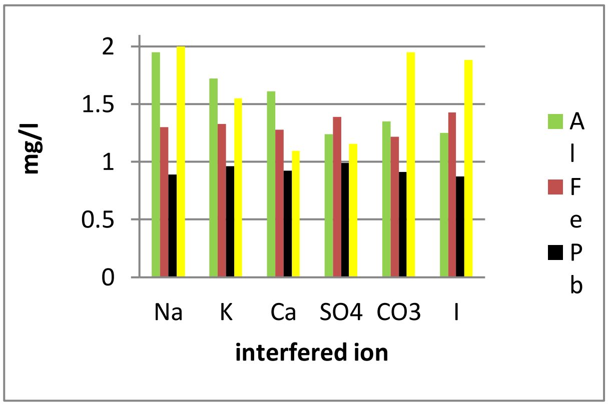

Figure 7. Effect of interfering ions.

Nano cyperus papyrus powder results

The adsorption process was performed by using nano cyperus papyrus adsorbent under several factors, such as the amount of cyperus papyrus, initial ions concentration, and contact time will be discussed in the following section.

Characterization of the cyperus papyrus nanopowder nanoparticle

Fourier-transform infrared spectroscopy (FTIR)

Identification of the cyperus papyrus nanopowder by FTIR is represented in Fig.1b, which showed the differences in all functional group peaks compared to that of the cyperus papyrus ash it was noted that disappear many peaks like the peak at 2931 cm^{-1} is due to the O–H stretching. The peaks at 2519,2600 cm^{-1} was linked to the S–H stretching, the band at 1701,1739 cm^{-1} refers to the existence of a C=O stretching. The band at 1334 cm^{-1} may be due to O-H bending. The peak at 879 cm^{-1} may attribute to C-H bending, and The peak at 678 cm^{-1} may attribute to C-Br bending [28].

X-ray diffraction characterization (XRD)

The cyperus papyrus nanoparticles particle size is proved by the XRD technique and the XRD patterns for cyperus papyrus powder. The XRD pattern affects the particle sizes to smaller sizes which can be calculated by Scherer's Equation.

Scherer's equation: $D=K\lambda/\beta\cos\theta$

Where: λ is the wavelength of the X-Ray (0.1540 nm), β is FWHM (full width at half maximum), and θ is the diffraction angle[29]. As shown in Fig. 8, the particles were found to be in the range of between 20-25 nm at the more intense x-ray beaks at 25.1^o, 47.8.0^o and 55 ^{o} .

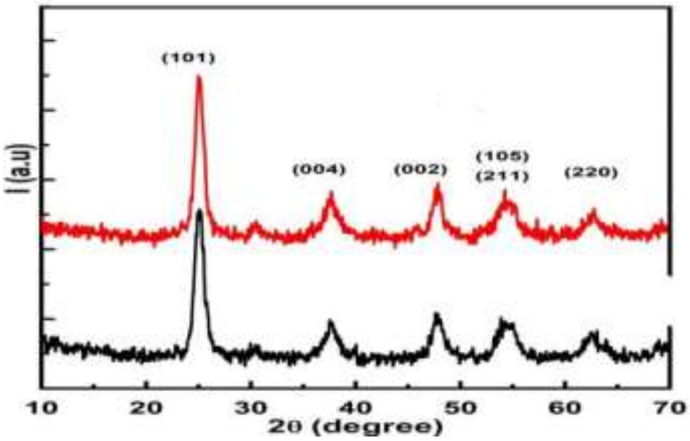

Figure 8. XRD patterns for nano cyperus papyrus.

Morphological and characterization studies:

Each transmission and scanning electron microscope provided with (DLS) gives valuable feedback and sufficient study about the material's surface and the morphology of the prepared nanoparticles and their shape.[30] The resultant synthesized modified nanomaterial by Ball mill with different species was examined by (EDX) as shown in Figs. 9, 10.

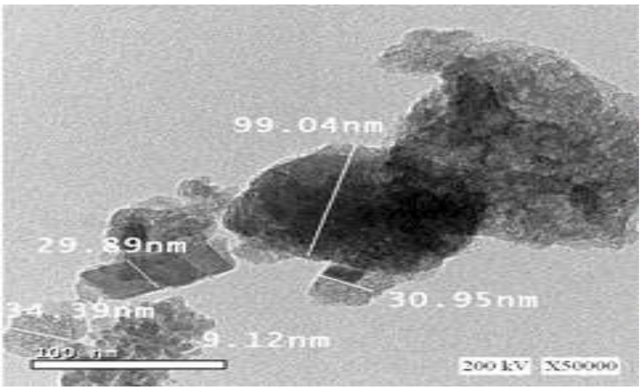

Figure 9. TEM image for nano cyperus papyrus.

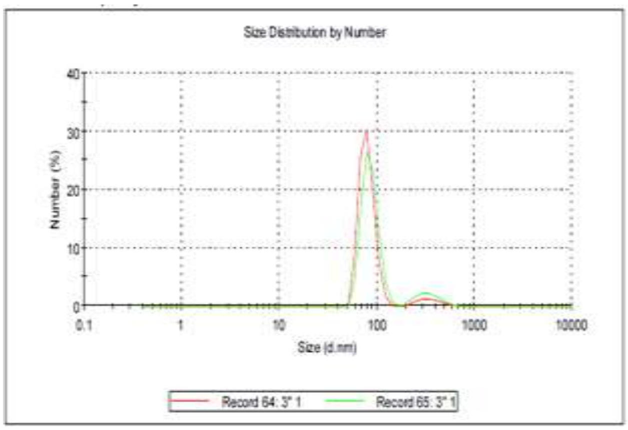

Figure 10. DLS for sample nano cyperus papyrus.

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Factors affecting adsorption of Pb(ii) and Cd(II) on nano cyperus papyrus powder:

The Effect of quantity of nano cyperus papyrus powder

The quantity of nano cyperus papyrus powder's effect on the efficient absorption of Pb (II) and Cd (II) was studied. (0.05, 0.075, 0.1, 0.125, 0.15 g) of cyperus papyrus stalks powder placed in five conical flasks containing 50 mL of 6 mg/L metal ions solutions, which were studied and shaken for 30 minutes, then filtered by filter paper. An Atomic Absorption spectrometer measured the concentration of each ion. As shown in Fig. 11, it was founded that the best amount of cyperus papyrus is 0.15 g and 0.125 g for Pb (II) and Cd (II), respectively.

The Effect of contact time

The effect of retention time on the uptake of Pb (II) and Cd (II) ions onto nano cyperus papyrus powder was studied. Procedures were performed to investigate the impact of several contact times (5, 15, 30, 60, and 120 minutes) on the removal of Pb (II) and Cd (II), 50 mL of the metal ion media for Pb (II) and Cd (II) were contacted with 0.1g of the adsorbent in a flask, and shake for 30 minutes then filtered with filter paper then Pb (II) and Cd (II)concentration were measured by using Atomic Absorption spectrometer. As shown in Fig. 12, it was founded that the best contact time was 60 minutes and 30 minutes for Pb (II) and Cd (II), respectively.

The Effect of initial ions concentration

In this factor, we investigated how initial ions concentration affected removal percent. Serial dilution of the stock solution produced different concentrations of the metal ions (2, 4, 6,8, and 10 mg/L) and then contacted with a fixed dosage of the adsorbent and 50 mL of the metal ion solution for both Pb (II) and Cd (II)a flask, and shake for 30 minutes then filtered with filter paper. The mixture was eventually filtered and examined by employing an Atomic Absorption Spectrophotometer. As shown in Fig. 13, it was founded that the best initial concentration was 4 mg/L and 10 mg/L for Pb (II) and Cd (II), respectively.

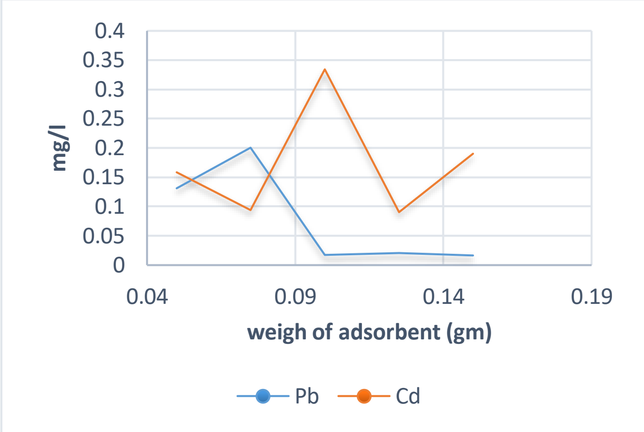

Figure 11. Effect of amount of nano Cyperus papyrus.

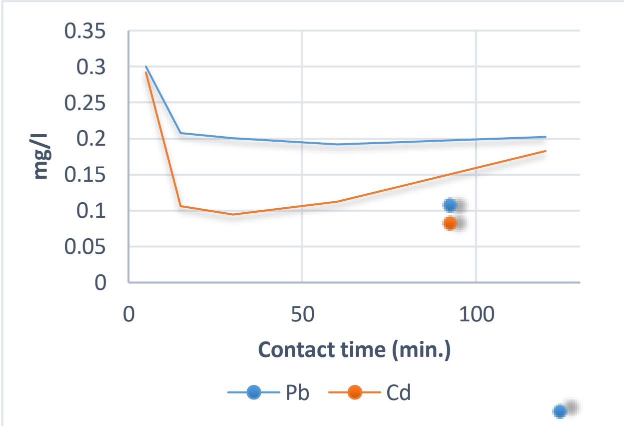

Figure 12. Effect of contact time of nano Cyperus papyrus.

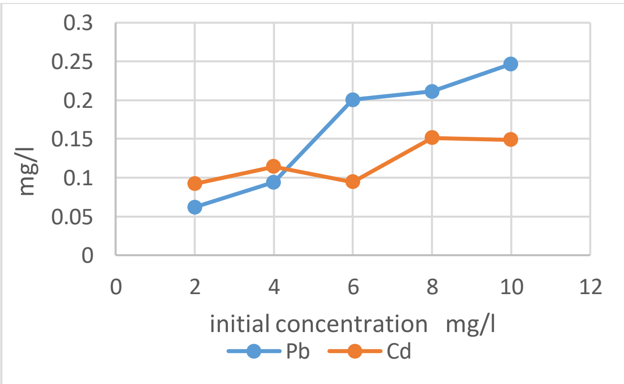

Figure 13. Effect of initial concentration of nano Cyperus papyrus.

Adsorption isotherm for adsorption Al (III), Fe (III), Pb (II), and Cd (II) using normal cyperus papyrus powder.

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Isotherm of Langmuir Adsorption

Langmuir Isotherm quantitatively describes creating a monolayer sorbate on the sorbent's outer surface [31]. Langmuir presented the subsequent Eq.1:

$$q_e = \frac{Q_o K_l C_e}{1+K_l C_e} \quad \text{...............1}$$

Where: C_e = equilibrium concentration of adsorbate (mg/L), q_e = the ratio of metal adsorbed to adsorbent in milligrams per gram at equilibrium (mg/g), Q_o = capacity for maximal monolayer coverage (mg/g), and $K_{L.}$ = Langmuir constant (L/mg). The values of q_{max} and $K_{L.}$ were calculated using the intercept and slope of the Langmuir plot of $\frac{1}{qe}$ against $\frac{1}{Ce}$ [31]. It is possible to express the main characteristics of the Langmuir isotherm in terms of the equilibrium parameter R $_L$; this is a dimensionless constant known as the equilibrium parameter or the separation factor [32]. As shown in Figs. 14, 15, 16, and 17

$$RL = \frac{1}{1(1+K_l C_0)} \quad \text{...............2}$$

Where: C_0 indicates the starting amount of concentration, and K = (Langmuir Constant) **.**

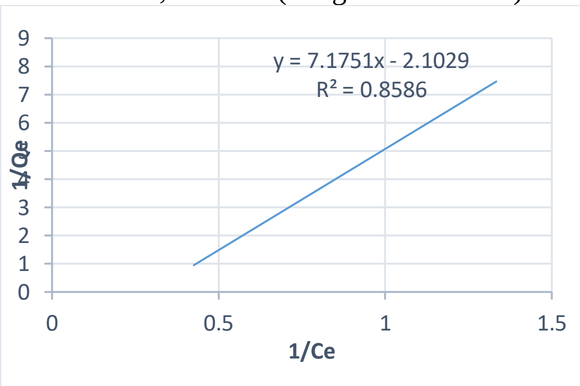

Figure 14. Langmuir isotherm for Al(III)

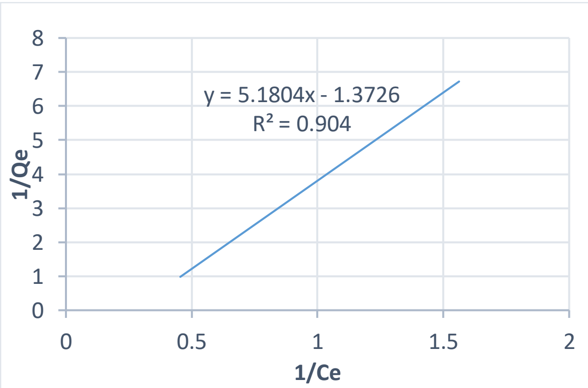

Figure 15. Langmuir isotherm for Fe (III)

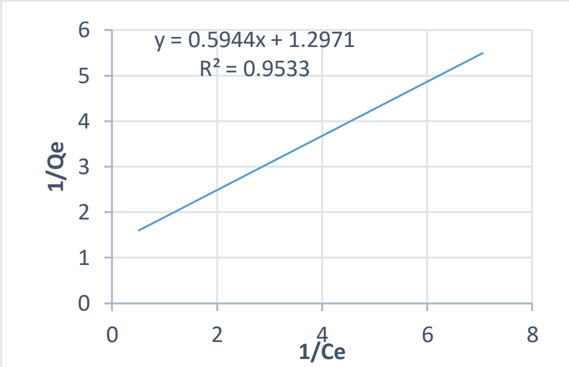

Figure 16. Langmuir isotherm for Pb (II)

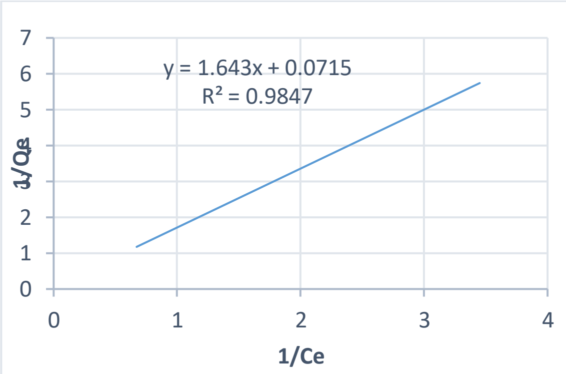

Figure 17. Langmuir isotherm for Cd (II)Isotherm of Freundlich Adsorption

Freundlich Isotherm is a usual way to describe how the heterogeneous surface adsorbs substances [33]. These data frequently match the empirical formula suggested by Freundlich: $Q_e = K_f C_e^{\frac{1}{n}}$ …3

Where K_f = Freundlich constant (mg/g), n is the sorption intensity, Ce= the amount of sorbate that can be sorbed in equilibrium (mg/L), and Q_e= the ratio of metal sorbed to sorbent in milligrams per gram at equilibrium (mg/g), given linear Eq. 3,

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{......4}$$

As shown in Figs. 18, 19, 20, and 21.

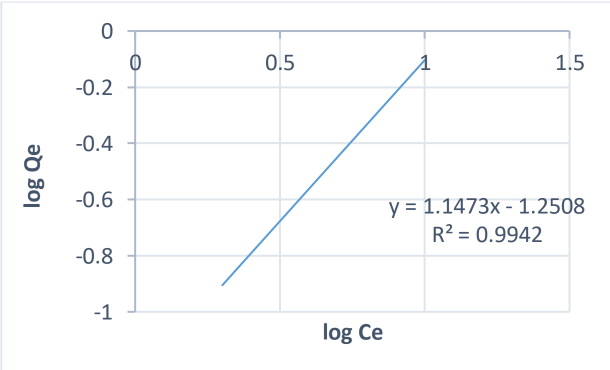

Figure 18. Freundlich isotherm for Al (III)

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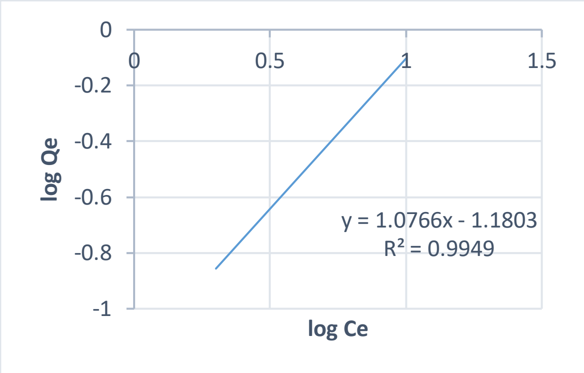

Figure 19. Freundlich isotherm for Fe (III)

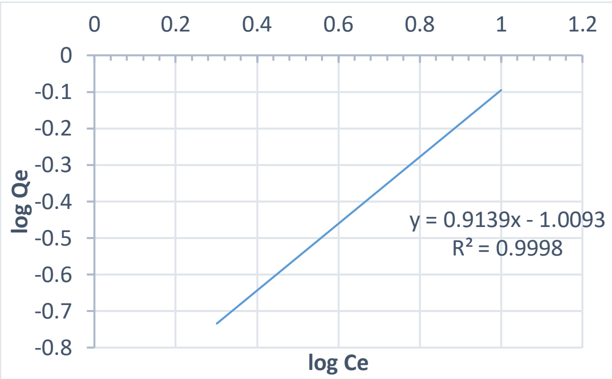

Figure 20. Freundlich isotherm for Pb(II)

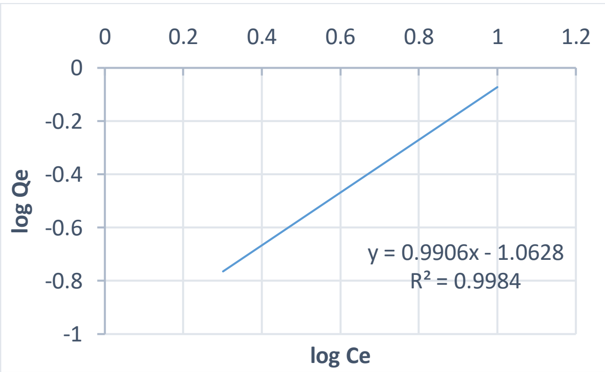

Figure 21. Freundlich isotherm for Cd (II)

It is observed from Figs. 14- 21 the value of R^2 in Freundlich isotherm for Al, Fe, Pb, and Cd were higher than that produced from Langmuir isotherm; also, it is closer to the unit assumed that the adsorption process is fitted to Freundlich isotherm

Temkin Isotherm

This isotherm has a component that evidence accounts for interactions between sorbent and sorbate. The model assumes that all molecules in the layer's heat of adsorption—a function of temperature—would drop linearly rather than logarithmically with coverage by neglecting low and high concentrations [34]. the variable sorbed qe was plotted against Ln Ce, and the constants were obtained from the slope and intercept. As the equation indicates, its derivation is identified by a regular distribution of binding energies (up to some maximal binding energy). The model is given using the following Eq. 5-7 [35].

$$q_e = \frac{RT}{b} \ln(A_T C_e) \qquad \text{..........5}$$

$$q_e = \frac{RT}{b_T} \ln A_T \left(\frac{RT}{b}\right) \ln C_e \qquad \text{...............6}$$

$$B = \frac{RT}{b_T} \qquad q_e = B \ln A_T + B \ln C_e \qquad 7$$

A_T =Binding constant for Temkin isotherm equilibrium (L/g), b_T = Temkin constant, R= constant of universal gas (8.314J/mol/K), T= Temperature at 298K. , and B = Heat of sorption constant (J/mol). As shown in Figs. 22, 23,24, and 25.

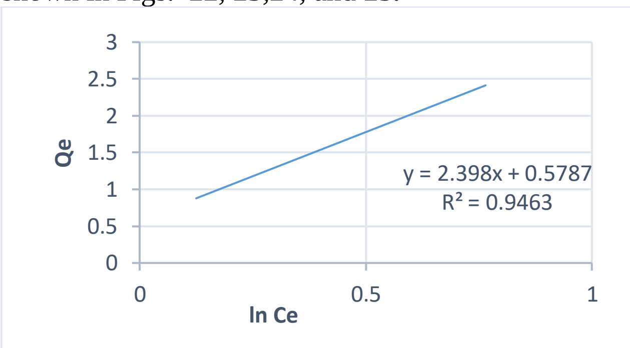

Figure 22. Temkin isotherm for Al (III)

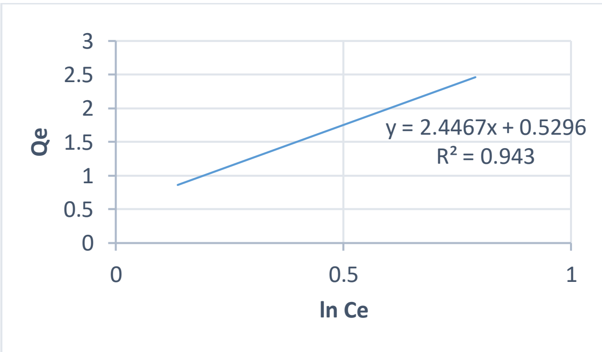

Figure 23. Temkin isotherm for Fe (III)

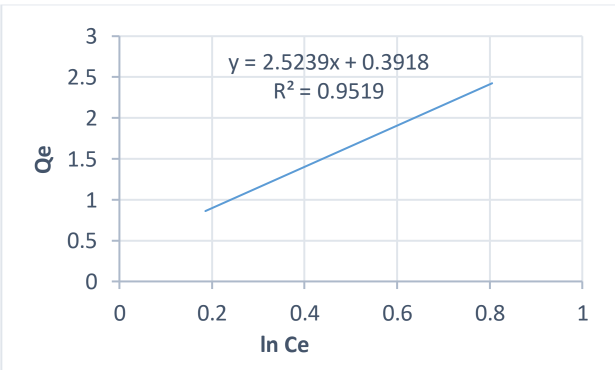

Figure 24. Temkin isotherm for Pb (II)

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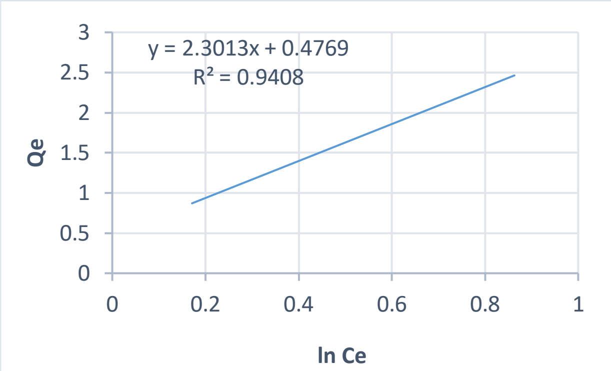

Figure 25. Temkin isotherm for Cd (II)

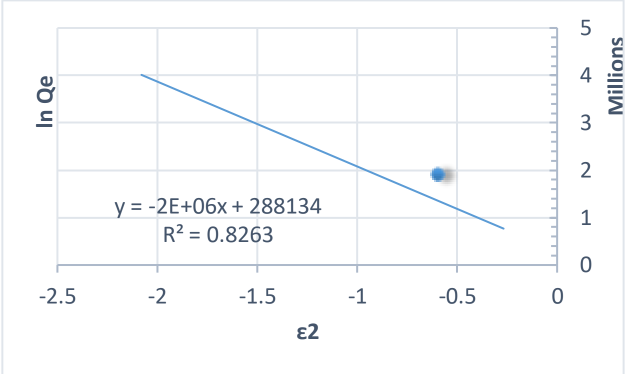

Figure 26. Dubinin isotherm for Al (III)

Dubinin–Radushkevich isotherm model

The adsorption process with a Gaussian energy distribution onto an uneven surface is represented by the Dubinin-Radushkevich isotherm [36]. High solute activities and data from the middle range of concentrations have frequently been well-fit by the model.

$$q_e = (q_s)exp(-K_{ad}\varepsilon^2) \quad \text{..................8}$$

$$\ln q_e = \ln(q_s) - (K_{ad}\varepsilon^2) \quad \text{..................9}$$

q_e = amount of adsorbate in the adsorbent at equilibrium(mg/g), qs= theoretical isotherm saturation capacity (mg/g); K_{ad} = Dubinin–Radushkevich, isotherm constant (mol^2/kJ^2) and ε=Dubinin–Radushkevich isotherm constant.The strategy was frequently used to differentiate between the physical and chemical adsorption of metal ions with their mean free energy, E per molecule of adsorbate (for eliminating a molecule from its position in the adsorption space to infinity), can be calculated by the relationship

$$E = \left[\frac{1}{\sqrt{2B_{DR}}}\right] \quad \text{.........................10}$$

Where the isotherm constant is represented by B_{DR} Meanwhile, the variable ε can be computed as

$$\varepsilon = RT\ln\left[1 + \frac{1}{C_e}\right] \quad \text{.........................11}$$

where R is the gas constant (8.314 J/mol K), T is the temperature (K), and C_e represents adsorbate equilibrium concentration (mg/L); the dependency on the temperature of the Dubinin-Radushkevich (DRK) isotherm model is one of its distinguishing features, in which data on adsorption at various temperatures are displayed as a function of the logarithm of the quantity adsorbed ($\ln q_e$) vs ε^2 the square of potential energy. As shown in Figs. 26,27,28 and 29.

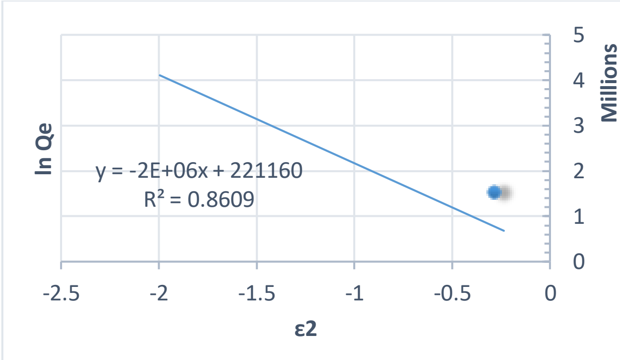

Figure 27. Dubinin isotherm for Fe (III)

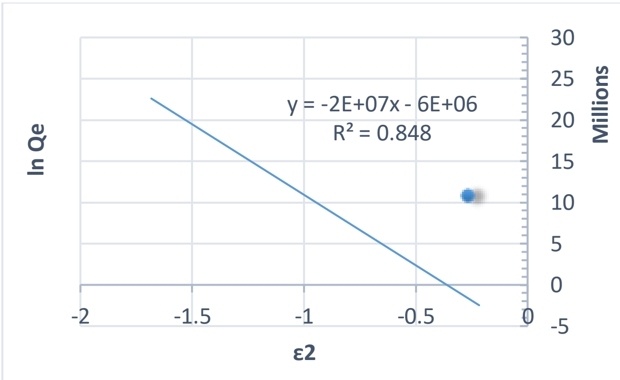

Figure 29. Dubinin isotherm for Cd (II)

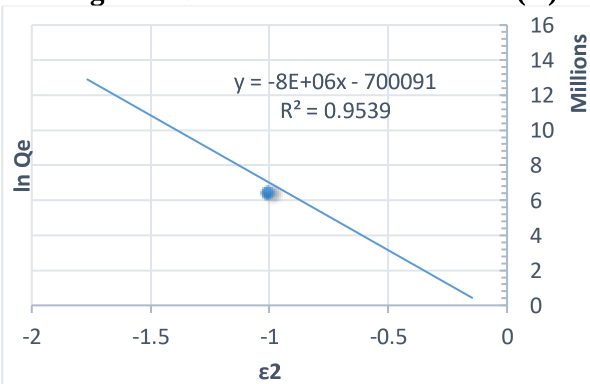

Figure 28. Dubinin isotherm for Pb (II)

It is observed from Figs. 22- 29 the value of R^2 in Temkin isotherm for Al, Fe, Pb, and Cd were higher than that produced from Dubinin–Radushkevich isotherm; also, it is closer to the unit assumed that the adsorption process is fitted to Temkin isotherm

Statistical treatment

The Statistical studies were represented in Table 2

.

Table 2. Statistical analysis of cyperus papyrus on Al^{3+}, Fe^{3+}, Pb^{2+}, and Cd^{2+}.

Parameter	Mathematical formula	Results			
		Al^{3+}	Fe^{3+}	Pb^{2+}	Cd^{2+}
Mean Value ($\bar{X}$)	$\bar{X} = \Sigma (Xi / n)$	1.012	0.755	0.893	0.992
Standard deviation (SD)	$SD = \sqrt{\frac{\Sigma(Xi-\bar{X})}{n-1}}$	0.019321	0.01715	0.01767	0.01619
Relative Standard deviation (RSD %)	$RSD \% = (SD/\bar{X}) \times 100$	1.909272	2.27276	1.97870	1.63238
Standard error of the mean (SEM)	$SEM = SD/\sqrt{n}$	0.006110	0.00542	0.00558	0.00512
Student t-test	$t\text{-test} = ((\bar{X}-\mu)\sqrt{n})/SD)$	1.964	2.766	-3.042	-1.563

Where $\bar{X}$ is the mean, SD is the standard deviation, and n is the sample size.

Conclusion

Al, Fe, Pb, and Cd were adsorbed and removed from an aqueous solution in batch testing using Cyperus papyrus powder and nano Cyperus papyrus powder. Heavy metals are removed by the many hydroxyl groups (-OH) present in Cyperus papyrus. Furthermore, the organic functional groups carboxylic, C=O carbonyl, C-H stretching, and carboxylic groups in the structure of Cyperus papyrus made it simpler for heavy metals to be adsorbed to the material. Additionally, nano cyperus papyrus is more efficient than regular cyperus papyrus. The adsorption procedure matched the Temkin and Freundlich isotherms. According to the results of the research, Cyperus papyrus is a novel, environmentally friendly adsorbent that is inexpensive, efficient, and practical for removing heavy metal ions from contaminated water. Cyperus papyrus may be a less expensive option for removing heavy metal ions from wastewater than commercially available activated carbon.

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Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at Zagazig University.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.

Authors' Contribution Statement

K. E designed the study, wrote, revised and proofreading the paper.A. N. M. performed the experiments and wrote the paper. M. Z. and A.A. analyzed the data and revised the paper.

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طريقة صديقة للبيئة لازالة بعض العناصر الثقيلة من المياه: دراسة فيزيائية وتحليلية

خالد الجندي، منير زكي، عاطف عامر، عبد الناصر محمد

قسم الكيمياء، كلية العلوم، جامعة الزقازيق، الزقازيق، مصر.

الخلاصة

تهدف هذه الدراسة الي التحقق من امكانية ازالة بعض ايونات العناصر الفلزية من بعض المحاليل المائية باستخدام مادة ممتزة مصنوعة من مخلفات نبات البردي و مسحوق البردي في حجم جزيئات النانو, وبسبب تواجد العديد من مجموعة الهيدروكسيل فإن مسحوق البردي يعتبر مادة ممتزة واعدة لإزالة العناصر الثقيلة. تم التحقق من امكانية ازالة ايونات الالمنيوم والحديد والرصاص والكادميوم من محاليل مائية باستخدام نبات البردي. وكانت كفاءة الازالة بالترتيب الاتي ايونات الحديد > الرصاص > الكادميوم > الالمنيوم ..وفي طريقة اخري تم تحويل مسحوق نبات البردي الي مسحوق نانوي وتم دراسة تأثيرة علي ازالة ايونات الرصاص والكادميوم من محاليل مائية. وكانت كفاءة المسحوق النانوي افضل بكثير من مسحوق نبات البردي المجفف العادي.

وتم تطبيق استخدام مسحوق البردي المجفف العادي علي عينتين واحدة من مياه صرف صحي والاخري من مياه جوفية.حيث وجد ان تطبيق معادلة فريندليش مناسب لامتزاز العناصر المذكورة بواسطة البردي العادي واوضحت حدوث تبادل ايوني في طبقة الامتزاز السطحية.

ومن هنا كان لاستخدام مسحوق نبات البردي له قدرة علي ازالة بعض ايونات الالمنيوم والحديد والرصاص والكادميوم من محاليل مائية وبدون استخدام مواد كيميائية اضافية مما يوحي ان هذه الطريقة صديقة للبيئة.

الكلمات المفتاحية: الامتزاز، النفايات الزراعية، منحنيات الامتزاز الحرارية ، نبات البردي، المعادن الثقيلة، المواد الماصة النانوية.