Biosorption to removing heavy metals from wastewater

S A. Hussain¹, N K Hasan² and E E Al-Abodi³*

¹Directorate General of Education Karkh, Ministry of Education, Iraq
²Directorate General of Education Diyala, Ministry of Education, Iraq
³Chemistry Department, College of Education for Pure Science/Ibn Al-Haitham, University of Baghdad, Iraq

*Corresponding: entisaree2020@gmail.com

Abstract. In this research, the efficacy of walnuts shell as bio adsorbent surface has been evaluated in the process of heavy elements removing from aqueous solution. Heavy metals concentrations are determined using X-ray fluorescence (XRF) techniques in walnuts shell and using the atomic absorption spectrometer to determined heavy elements concentrations in wastewater from the southern Rustumiya station, as Chromium (Cr), Nickel (Ni), Copper (Cu), Mercury (Hg), Cadmium (Cd) and Lead (Pb). XRF technique is a viable and precise for analyzing a variety of harm materials and environmental samples with different advantages compared with conventional laboratory analysis ways.

Keywords: Biosorption, walnuts shell, XRF, heavy elements removing.

1. Introduction

Toxic heavy metals are major pollutants of wastewater which is very hazardous (Mouhamad et al., 2019; 2020). The important toxic metals, as Chromium (Cr); Nickel (Ni); Copper (Cu); Zinc (Zn); Mercury (Hg); Lead (Pb); and Cadmium (Cd), finds its way to the water bodies through wastewaters (Nasser et al, 2019). Many physicochemical ways using for the removal of heavy metals as liquid extraction, chemical oxidation, Electro precipitation, ion exchange, reductions, Electrodialysis, and ultrafiltration. These ways are costly and not completely removing the toxic pollutants. Biosorption is potentially an attractive application for the treating of water for reduction heavy metal concentration. (Mouhamad et al., 2019; 2017). It has been suggested as more effective, minimization of chemical and biological sludge as well as cheaper. There are many bio adsorbents is present in the environment which have the ability to removing the heavy metals from wastewater (Nandal et al, 2014; Musab and Al-Abodi, 2019). It is necessary in order to decrease the associated risks, to make the land resources available for agricultural production, to improve food security, as well as to decrease land tenure problems appearing from change in the pattern of water uses.

Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments (Bentahar et al, 2015). The application of activated carbon for wastewater treatment is not feasible due to its high price and cost associated with the regeneration as a result of high degree of losses in real process. Therefore, it will be much logical and cost effective to use the abundant agricultural and industrial wastes as adsorbents since they are already posing disposal problems. More studies have been carried out on the feasibility of using agricultural adsorbents such as sawdust (Ismadji et al., 2005), rice husk (Kumar and Bandyopadhyay, 2006), and walnut shell (Altun and pehlivan, 2007).
Walnuts shell is characterized as a plant use in soil and water treatment, including the use of plant roots capable of displacing, bioaccumulating and deconstituting contaminants (Dhir, 2013). Walnut shell manufacturing is one of the cases in which heavy metals utilizing plants have to be decontaminated (Gardea Torresdey, 2003). Walnut shell treatments are focused on the application of the origin of plant dynamics in the soil and aquatic system in deposition, storage and removal of heavy elements (Mandakini, 2016). It is recognized as renewable manufacturing or green technology because all processing activities require the use of solar energy (Dietz 2001).

Due to the high capacity of walnut shell to extract and accumulate numerous toxins, minerals, and heavy elements (Hossein A. et al. 2014). In this research, the efficacy of walnuts shell as adsorbent surface has been determined in the process of heavy metal removing from aqueous solution in a batch adsorption.

2. Experimental part

A. Adsorbent

The walnuts shells were properly washed in tap water and then rinsed in distilled water. Then are dried in an oven at a temperature of (35-40°C) for 72 hours. The dried walnuts shell are pulverized, by using a sterile electric blender, to obtain a powdered form, which is stored in airtight glass containers, and protected from sunlight until required for use (Mouhamad et al., 2017).

B. Instrumentals

The equipment used for the experiments was, X-ray Fluorescence (XRF) spectroscopy (SPECTRO XPOS Ametek cloth analysis division, Germany), shaker incubator (Heidolph, No.549-59000-0, Korea), Atomic Absorption Spectrometer: AAS (GBC 933 plus, Australia), electrical balance (TE 2145, Sartorius Germany) and filter paper (Whatman 40 mm).

C. Reagents

The wastewater requirements from the southern Rustumiya station after treated the crushed sow cloth was instantly analyzed because of the content material of trace metals through the Energy Dispersive X-ray Fluorescence (XRF) spectroscopy. The valuation was once instantly led abroad near the Department of Geology, Ministry of Science and Technology (MSOT), Baghdad, Iraq. The fundamental contract was evaluated via the usage concerning SPECTRO XPOS (Ametek cloth analysis division, Germany) with silicon weft detector with a high resolution. Analysis for the solution of single metal system, stock solution of a fixed volume of wastewater in a conical flask were mixed vigorously with different concentration of bio adsorbent dose at 200 revolutions/minute (rpm) for 30min at room temperature. For sorption experiment a contact period of another 150min is given to ensure the equilibrium. The solutions will be separated from the biomass by filtration at the end of the experiment by using whatman filter paper. By using Flame Atomic Adsorption Spectrometer(AAS) the filtrates of single metal system SMS will be diluted to 10 to 0.2 g/L with deionized DI water and analyzed for heavy metals concentration. In triplicates, all tests and analyses were performed. Using IBM SPSS software, data was analyzed using the Tukey test. At a P < 0.05 probability level (Mouhamad et al., 2018).

3. Results and Discussion

3.1 Metals Composition

Heavy elements, generally existent in little amounts in natural water systems, their occurrence in surface water can be due to natural sources, or human activities like fuels, mining, smelting of ores and improper disposal of industrial rubbishes in Diyala river. Logartim Mean concentration of major ions in the walnut shell samples in the two sampling periods (2018-2019) are presented in figure 1. Mean concentrations of heavy metals are found to be higher in the adsorbed after 2 week compared with treated one week, while the higher in the untreated. For Diyala river, the concentration of major metals such as Na and Cl are increased with quality and quantity discharge of the plant. Walnut shell tissue absorbs Cl>Na>Cr>Ni>Co>Pb>Cd>Hg from water treated. This is because of the fact that most of the heavy
elements released from the wastewater treatment plant and industrial plants near the Diyala River were reduced as a result of renewed.

![Logarithm adsorption of Walnuts shell tissue of heavy metals detected by X-ray Fluorescence (XRF) spectroscopy (mean ± SD) in the analyzed samples.](image)

**Figure 1.** Logarithm adsorption of Walnuts shell tissue of heavy metals detected by X-ray Fluorescence (XRF) spectroscopy (mean ± SD) in the analyzed samples.

Wastewater samples were analyzed after treatment for elements and their results were tabulated in Table 1 along with WHO (2008) and Iraqi standards (2009) for surface water standards. No clear variation in the concentration of these elements in the study periods can be seen. Concentrations of Cl, Na,Cr,Ni,Co,Pb,Cd and Hg ions were found to be higher than the permissible limits for drinking water, whereas, the remaining elements are within the permissible limits, the highest absorption in Na reached more than 30% and Cl reached more than 50% after 2 week from treatment, maybe its occurrence in natural water can be attributed to landfill leaches, sewage effluent and salinity-related industries in Diyala river. Mean concentration of Hg absorbed between 1.5-1.1 mgL\(^{-1}\) (after 1, 2 week) and Cr also lowest more than 60% ranged from 61.4-27.2 mgL\(^{-1}\) after two week, most of the surface samples showed concentration of trace elements higher than the acceptable limits. Pb, Co and Ni revealed the highest reduced in concentration reached more than 50%, ranges from 11.9-7.2 mgL\(^{-1}\) for Pb and 20.7-10.5 mgL\(^{-1}\) for Co and 41.5 to 15 mgL\(^{-1}\) for Ni, respectively the lowest absorbed was in Cd 6.1-5.1 mgL\(^{-1}\). which was highest than the Iraqi standard limits and within the WHO limits, This is due to the fact that most of the trace elements released from the industrial plants and wastewater treatment plant near the Diyala river were decreased because of renewed.

**Table 1.** Mean water samples before and after treated compared with IQS(Iraqi), 2009 and WHO, 2008 standards detected by By Flame Atomic Adsorption Spectrometer (AAS).

| Parameter (mgL\(^{-1}\)) | Samples Treated | IQS (mgL\(^{-1}\)) | WHO (mgL\(^{-1}\)) |
|--------------------------|----------------|------------------|------------------|
|                          | Before | After 1 Week | After 2 Week | |
| Na                       | 1800   | 1600           | 1587            | 200   | 200 |
| Cl                       | 4876   | 2813           | 2789            | 350   | 250 |
| Hg                       | 1.5    | 1.1            | 1.1             | 0.03  | 0.002 |
| Cr                       | 61.4   | 47.2           | 27.2            | 0.05  | 0.05 |
| Pb                       | 11.9   | 7.9            | 7.2             | 0.01  | 0.01 |
Co  20.7  17.1  10.5  0.02  0.02
Cd  6.1   5.6   5.1  0.003 0.003
Ni  41.5  24.1  15   0.02  0.07

**Figure 2.** Impact percentage on the separation of heavy elements from waste water of Walnuts Shell remedying technologies.

Waste-water movement and lines rises equal in Al-Rustameia plant and high line equal less than two notches from the Dyalia and Tigris River as the stream water movement towards the east and southeast, which gives the advantage to the site that may be Effect of contaminated soil and groundwater surrounding it over contaminated groundwater under the Tigris River (Hussain and Hussain, 2011).

As Figure 2 showed that the green treatment for wastewater from heavy metal and alkalinity. The whole heavy meals have highest reduced at 1 week more than after two week from treated. The pollutant in wastewater have more than the heavy metals polluted that have also organic pollutant and clay particiles, where the river is only 2 km from the site can be considered the most dangerous sites that pose a serious environmental threat to groundwater and surface water of the Tigris River and the surrounding areas (Abdullah, 2010).

4. Conclusion.

As the contaminated areas spread throughout the region with clear heavy contamination in the local soil, the heavy contamination status of Diyala river water is worrying. However, under pollution conditions, the regional plants have managed to retain their major heavy composition without the normal ranges. In addition, the results of XRF spectroscopy showed that many of the watersheds contain various important functional adsorpseds that increase their significance in sustainability of the river ecosystem. In order to provide a better understanding of the situation and to introduce effective remediation solutions, more studies should be carried out to evaluate chemical pollution in the region. Furthermore, more expanded studies should be carried out on the phytochemical potential of green chemistry under polluted conditions.

Reference

[1] Abdul-Hussain, F. M., 2007 Hydrochemical and environmental study of the infiltrated water in Baghdad City, Ph.D. thesis, College of Science, University of Baghdad, 128,(in Arabic).

[2] Abdul-Karim, J., 1996; The effects of Al-Rusafa landfill on local surface and groundwater quality, M.Sc. thesis, College of Engineering, University of Baghdad, 69.
[3] Abdullah, E. J., 2010; Environmental factors affecting diabetic patients in Baghdad City, a specific study in medical geochemistry, Ph.D. thesis, College of Science, University of Baghdad, 195.

[4] Al-Hiti, B.M., 1985; Groundwater quality within Baghdad area, M.Sc. thesis, College of Science, University of Baghdad, 235,(in Arabic).

[5] Bentahar S., Lacheral A., Dbik A., El messaoudi N., and El khomri M., (2015). Equilibrium, Isotherm, Kinetic and Thermodynamic Studies of Removal of Crystal Violet by Adsorption onto a Natural Clay, *Iranica Journal of Energy and Environment* 6 (4) 260.

[6] Doneen, L. D. 1964. Water quality for Agriculture, Department of Irrigation, University of California, Davis, 48.

[7] Gibbs R.J. 1970 Mechanisms controlling world’s water chemistry. *Science* 170, 1088.

[8] Hussain, S. and Hussain, S.Y., 2011  Study of hydrochemical parameters of groundwater around Ethanol plant, Bellur.(v.) TQ. Dharmabad dist., Nanded, Maharashtra, *archives to applied science research*, 3(2) 606.

[9] Kannan, N. and Sabu J. 2010 Quality of Groundwater in the Shallow Aquifers of a Paddy Dominated Agricultural River Basin, Kerala, India. *International Journal of Civil and Environmental Engineering* 2 160.

[10] Latha S. and Rao N. 2012 An integrated approach to assess the quality of groundwater in a coastal aquifer of Andhra Pradesh, India. *Carpathian Journal of Earth and Environmental Sciences* 66, 2143.

[11] Mouhamad R.S. , Al-Gburi H.F., Rasheed A.G., Razaaq I. and Al-Lafta H.S. 2019 Bioaccumulation and Biomegnecification study of AlChibayish marsh, plants, southern Iraq. *Iraqi J. Sci* 60(6):1.

[12] Mouhamad R.S., Hussein A.A., Alsaedi S. A., Nasif N. S. and Joda S. O. 2017 Detect of human fecal contamination in water and soil of multiple sanitary landfills in Baghdad city. *Microbiol Res Int*, 5(4): 43.

[13] Mouhamad RS, Hussein, A., Jafaar, M. 2020 Bacteriological contamination status and phytochemical characteristics of Al-Chibayish marsh regional plants. *DYSONA - Life Science* 1(1): 36. doi: 10.30493/dls.2020.220731

[14] Mouhamad RS, Iqbal M, Nazir A. 2018 Physicochemical characteristics and irrigation suitability of groundwater in the landfill site, Baghdad, Iraq. *Waste Management*, 76, 3.

[15] Mouhamad RS, Khalel S, Ali M., Joda S., Nazir A, Iqbal S., Nasif NS. 2017 Geochemical properties and agricultural suitability of groundwater at landfill site, Baghdad, Iraq. *Int J Ecol Ecosolution* 4(2): 17.

[16] Mouhamad RS, Munawar I. and Arif N. 2018 Physicochemical characteristics and irrigation suitability of groundwater in the landfill site, Baghdad, Iraq. *WASTE MANAGEMENT* 76, III-IV.

[17] Musab L., Al-Abodi E. E. 2019 " Preparation and Characterization Composites Contain of Magnetic Iron Oxide Nanoparticles with Different Weight Ratios of Dextrin , and Using it to Removal of Heavy Metals from Aqueous Solutions", *Energy Procedia* 157, 752.

[18] Nandal , Hooda R. and Dhania G. 2014 Tea Wastes as a Sorbent for Removal of Heavy Metals from wastewater . *International Journal of Current Engineering and Technology* 4 (1) 243.

[19] Nasser A. A., Adnan Sh. F. and Mouhamad RS 2019 Effect of mineral fertilizers application on accumulation of heavy metals in soils and tomato plant. *Agri. Rech. J*. 6(2): 20.

[20] Ramesh K. and Elango L. 2012 Groundwater quality and its suitability for domestic and agricultural use in Tondiar River Basin, Tamil Nadu, India. *Environmental Monitoring and Assessment*. 184, 3887.

[21] Ramkumar T., Venkatramanan S., Anithamary I., and Ibrahim S.M.S. (2012) Evaluation of hydrogeochemical parameters and quality assessment of the groundwater in Kottur blocks, Tiruvarur district, Tamilnadu, India. *Arabian Journal of Geosciences*. 6, 101.
[22] Richards L.A. 1954 Diagnosis and Improvement of Saline and Alkali Soils. pp.160. U.S. Department of Agriculture Handbook 60, Washington.
[23] ALI S. M., (2012). Hydrochemical environmental assessment of Baghdad area, Ph.D. thesis, College of Science, University of Baghdad, (in English).
[24] Schoeller H. (1965) Qualitative evaluation of groundwater resources. In Methods and Techniques of Groundwater Investigations and Development. pp.54–83. UNESCO, Paris.
[25] Srinivas Y., Hudson Oliver D., Stanley Raj A., and Chandrasekar N. (2014) Quality assessment and hydrogeochemical characteristics of groundwater in Agastheeswaram taluk, Kanyakumari district, Tamil Nadu, India. Chin.J.Geochem. 33, 221.
[26] Todd D.K. (1980) Groundwater Hydrology (2nd edition). Wiley, New York.
[27] USGS (US Geological Survey) (2000) Classification of Natural Ponds and Lakes. Department of the Interior, Washington DC.
[28] USRSL (US Regional Salinity Laboratory) (1954) Diagnosis and Improvement of Saline and Alkali Soils [Z]. pp.1–160.
[29] Valdman, E., Erijman, L., Pessoa, F. L. P., and Leite, S. G. F. (2001). Continuous biosorption of Cu and Zn by immobilized waste biomass Sargassum sp. Process Biochemistry, 36(8–9), 869.
[30] Wilcox L.V. (1955) Classification and Use of Irrigation waters. USDA, Circular 969, Washington DC, USA.
[31] Gaofeng Z., Yonghong S., Chunlin H., Feng Q., and Zhiguang L. (2010) Hydrogeochemical processes in the groundwater environment of Heihe River Basin, Northwest China [J]. Environmental Earth Sciences. 60, 139.