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Using of Iron Oxide Nanoparticles and Application in the Removing of Heavy Metals from Sewage Water

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Abstract:
This study investigated the applicability of iron oxide (Fe_2O_3) nanoparticles for the removal of cadmium metal from sewage water by using batch scale experiments. The iron oxide nanoparticles of 27.7nm were synthesized using a biological method and characterized by Atomic Force Microscope (AFM). The Box-Wilson design was used to conduct experiments with three parameters such as pH (2-6), time of adsorption (6-120min) and adsorbent dosage (5-25mg/L). The best conditions occurred at pH: 5.5; contact time: 95.8 min; and iron oxide nanoparticle dosage: 20.77 mg/L for maximum cadmium removal of (96.9%).

Keywords: Iron Oxide Nanoparticles, Adsorption, Bow-Wilson design.

استخدام دقائق أكسيد الحديد النانوية والتطبيق في إزالة المعادن الثقيلة من مياه الصرف الصحي

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الخلاصة
بحثت هذه الدراسة في امكانية تطبيق دقائق اكسيد الحديد النانوية لإزالة عنصر الكادميوم من مياه الصرف الصحي باستخدام تجارب النمط الدفعي (Batch experiment). تم تصنيع الدقائق النانوية بقطر 27.7 نانومتر لأكسيد الحديد باستخدام طريقة بيولوجية وتم تحديد صفاتها باستخدام جهاز مجهر القوة الذرية. اجريت التجارب وفقا للتصميم (Box–Wilson) مع ثلاثة عوامل كمدخلات مثل قيم الاس الهيدروجيني (4–6), زمن التلامس (6–120 دقيقة) وتركيز الدقائق النانوية (5–25 ملغم/لتر). وافيد ان الظروف المثلى لتكون 5.5 قيمة الاس الهيدروجيني مع تركيز 20.77 ملغم/لتر و زمن 95.8 دقيقة وكانت الازالة في هذه الظروف 96.9%.

Introduction

Water is a vital source to sustain life, and a satisfactory must be of adequate, safe and accessible, and available to all population [1]. Approximately, 20% of the world's population lacks safe drinking water, including developing countries, which discharge an estimated 95% of their untreated urban sewage directly into surface waters, Iraq is one of nine countries in the Middle East that has insufficient fresh water [2]. Sewage water generated from hospitals usually contains human wastes and fluids, pathogens, pharmaceuticals, substances with genotoxic properties, chemical substances and heavy metals such as cadmium, lead and Zinc [3]. Some of these pollutants are frequently discharged through sewage plants after having undergone little degradation [4].

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To become the heavy metal contamination, one of the most severe environmental problems, and various methods during the past decades have been extensively studied for heavy metal removal from sewage water, such as electro chemical techniques, chemical precipitation, ion exchange, membrane filtration, and adsorption [5].

In the absence of efficient methods of physical, chemical or high cost treatment of wastewater, it would be necessary to find other methods through the use of biological efficient systems, such as remove pollutants from the environment via nanoparticles [6]. In the fields of water treatment Nanomaterials may provide solutions to technological and environmental problems [7]. Among various metal nanoparticles, iron oxide nanoparticles have widely explored during the past decades because of their new chemical and physical properties, and their potential applications in separation and treatment of wastewater by removing heavy metals from water by adsorption process [8]. In theory, the adsorption process can offer flexibility in design and operation and in numerous cases will produce high-quality treated sewage. In addition, as the adsorption is sometimes reversible and adsorbent can be regenerated by suitable desorption process, many types of adsorbents have found application in the removal of heavy metals, including carbon nanotubes [9,10], activated carbon [11,12], metal oxides [13], polymeric adsorbents [14] and bioadsorbents [15]. Adsorption operation can be batch, semi-batch and continuous. Batch processes are generally conducted when small amounts of pollutants are to be treated [16].

The aim of this study is to use iron oxide nanoparticles for removal of cadmium from sewage water by using Box-Wilson design with three parameters such as of pH, contact time and Fe_2O_3 dose.

Materials and Methods:

Samples Collection:

Glass container used to collect a sample of sewage water from station represents Medical City hospital discharge into the river.

Determination of Various Environmental Parameters:

The sample of water is used to examine the physical and chemical parameters, including (Temperature, pH, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD_5), Electrical conductivity (EC) and Total hardness (T.H) **)** [17].

Isolation of Bacteria:

For the isolation of *E.coli* bacteria were collected from sewage water of Baghdad Medical City. Isolation of bacteria was carried from the (Serial Dilution Method). Then taken from 10^{-3}, 10^{-5} and 10^{-8} dilution 1 ml of diluted sample and the sample was spread on plat (EMB media) to isolate the bacteria *E. coli*. The plate was incubating overnight in the incubator at 37℃ [18].

Identification of *E.coli* bacteria:

The bacteria isolates were identified to the level of species using the traditional morphological and biochemical tests, according to the methods [19]. The identification of *E.coli* isolate was confirmed by vitek-2 system.

Production of Bacterial Biomass:

The bacterial strain *E.coli* were cultured in NB medium to produce the biomass for biosynthesis. The culture flask was agitated at 200 rpm by incubated on an orbital shaker at 37^0C. Harvested of growth the biomass after 24hrs by centrifuged at 10,000 rpm for 10 minutes [20].

Synthesis of Iron Oxide Nanoparticles by Biological Method:

Mixed 10 ml of supernatant bacteria *E.coli* were added to the reaction flasks, which contained 5 ml of 10^{-3} M (1%, v/v) of $FeCl_2$, the incubation conditions were at pH 5, 37˚C for 24h, control flasks contained the supernatant without $FeCl_2$, were incubated at the same conditions. The iron oxide nanoparticle was collected for 5 min twice by centrifugation at 10,000 rpm for purified, and for further characterization [20, 21].

Characterization of Fe_2O_3 NPs:

The surface morphology and diameter of the iron oxide NPs were visualized by Atomic Force Microscope (AFM) present in central laboratory of Chemical Department, Baghdad University and Scanning Electron Microscopy (SEM) available in the laboratories of environmental research center of the ministry of science and technology.

Experimental Design:

Box – Wilson composite rotatable design is a common type of statistical experiments, especially applicable in optimization analysis. In this design, a special series of tests are defined. The experimental results of these tests then serve a function to represent the relationship between the variable and the response, Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing problems where several independent variables influence dependent variable or response, and the goal is to optimize this response. For example, it is required to find the effect of pH values (X1), contact time (X2) and Fe_2O_3 dose (X3) that maximize the yield of a treatment process [22].

Batch Experiments:

"Single-dose" batch adsorption experiments with nanoparticle aggregates were conducted using different Concentration of iron oxide NPs (5, 9.23, 15, 20.77 and 25 mg/L) [23], add into 20ml of sewage water in 100ml glass vials. The adsorption on iron oxide investigated the effects of pH values on the cadmium metal adsorption was first studied at pH values from 4-6 [24]. With different contact time from 6-120min and 25±5℃ [25]. This parameter was done according to Box-Wilson design. separated the nanoparticle aggregates from the suspension by filtration through a 0.2 µm nylon membrane filter [23]. Atomic Absorption Spectrophotometer, (AAS) was used to measure the concentration of the Cd, the uptake of cd calculated by the following expression [26]:

$$\boldsymbol{Removal\ Efficiency\ R}\text{E \%} = \frac{C0 - Cr}{C0} \times 100\%$$

Where: C0 = the initial metal concentration (mg/L).
Cr = the final concentration (mg/L)

Results and Discussion:

Determination of Various Environmental Parameters:

The water temperature, pH, E.C, Salinity and T.H in this study were varied, the highest mean value was recorded in July and November, while the lowest mean value was recorded in April. The DO and BOD the lowest mean value was recorded in July and November, while the highest mean value was recorded in April.

Most of the results for physical and chemical finding there were the Seasonal changes played an important role in affecting the values of all studied. There were physical, chemical variables. The statistical analysis showed that there was a significant difference at probability level (P< 0.05) between data of water during the months as shown in Table-1.

Table 1- Mean (First Line), Standard Error (Second Line) for physical and chemical characteristics at study months 2017/2018.

NO	Parameters	Mean ± SE			LSD value
		November	April	July	
1	**Temperature ℃**	22 ± 1.69	19 ± 1.07	28 ± 2.62	4.844 *
2	**pH (mg/L)**	8.4 ± 0.49	6.7 ± 0.33	8.9 ± 0.52	1.092 *
3	**EC (µs/cm)**	1597 ± 96.25	585 ± 41.84	673 ± 48.63	327.53 *
4	**Salinity%**	1.0 ± 0.02	0.3 ± 0.05	0.4 ± 0.05	0.442 *
5	**DO mg/L**	2.4 ± 0.04	6.4 ± 0.11	3.2 ± 0.06	2.179 *
6	**BOD mg/L**	1.0 ± 0.02	2.0 ± 0.03	1.4 ± 0.02	0.883 *
7	**TH mg/L**	450 ± 28.87	240 ± 36.92	362 ± 31.07	128.64 *
Means having with the different letters in same row differed significantly * (P<0.05).					

PH: Hydrogen Ion
EC: Electrical Conductivity
DO: Dissolve Oxygen
BOD: Biological Oxygen Demand
TH: Total Hardness

Synthesis of Fe_2O_3 NPs:

The synthesis of Fe_2O_3 NPs by supernatant cultures is indicated by a change in color of the reaction mixture from yellow to brown within 24h of inoculation as shown in Figure-1.

The change in color of the solution is due to the excitation of surface Plasmon vibrations in the Fe_2O_3NPs, which is the characteristic property of the nanoparticles [27].

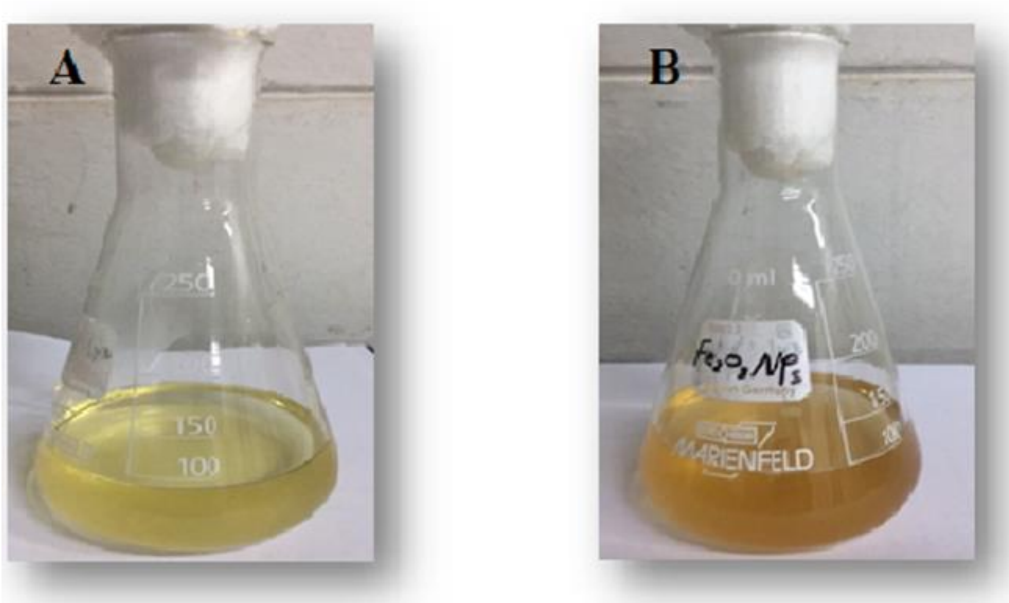

Figure 1- biosynthesized of iron oxide nanoparticles (A) Control flask. (B) Reaction mixture after biosynthesis of NPs.

Characterization of Iron Oxide Nanoparticles by *E.coli*:
Atomic Force Microscopy (AFM) analysis:

The results obtained from Atomic Force Microscopy showed that the biosynthesized iron oxide nanoparticles were almost spherical in shape with an average diameter of finding equal to 27.7 nm (Figure-2).

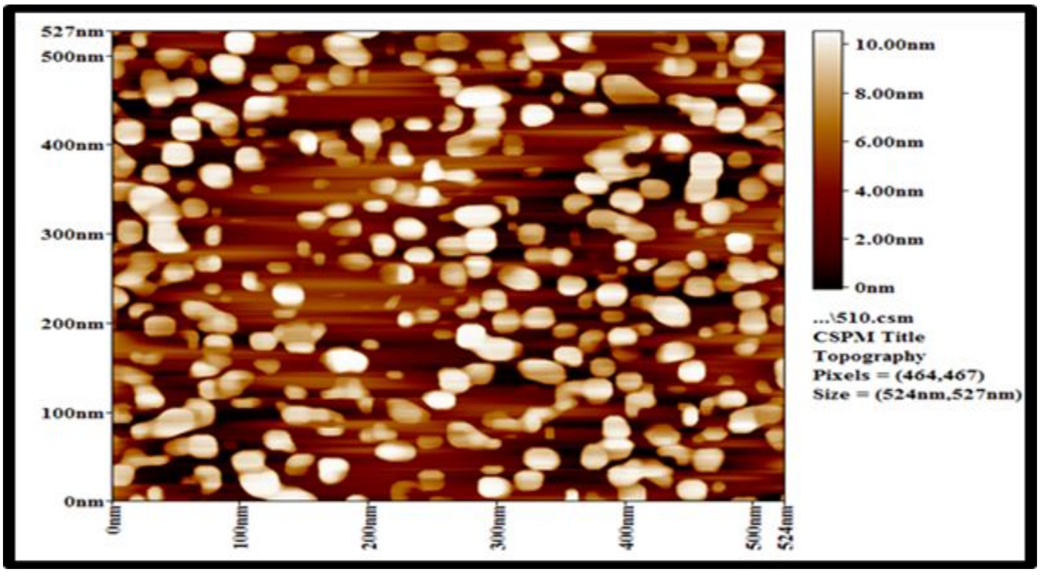

Figure 2- AFM of Fe_2O_3NPs at 37℃ and pH 5 (Avg. Diameter: 27.7 nm)

Scanning Electron Microscopy (SEM):

After being characterized by AFM analyses; the biosynthesized iron oxide nanoparticles were examined by the SEM to detect the morphology and the result confirmed the formation of iron oxide nanoparticles. It is observed that the biosynthesised Fe_2O_3 nanoparticles were roughly semi spherical and smooth spherical in shape (Figure-3).

The previous studies have come to agree with results of the current study [28] approved that the obtain Fe_2O_3NPs synthesis by Streptomyces are spherical in shape with a smooth surface

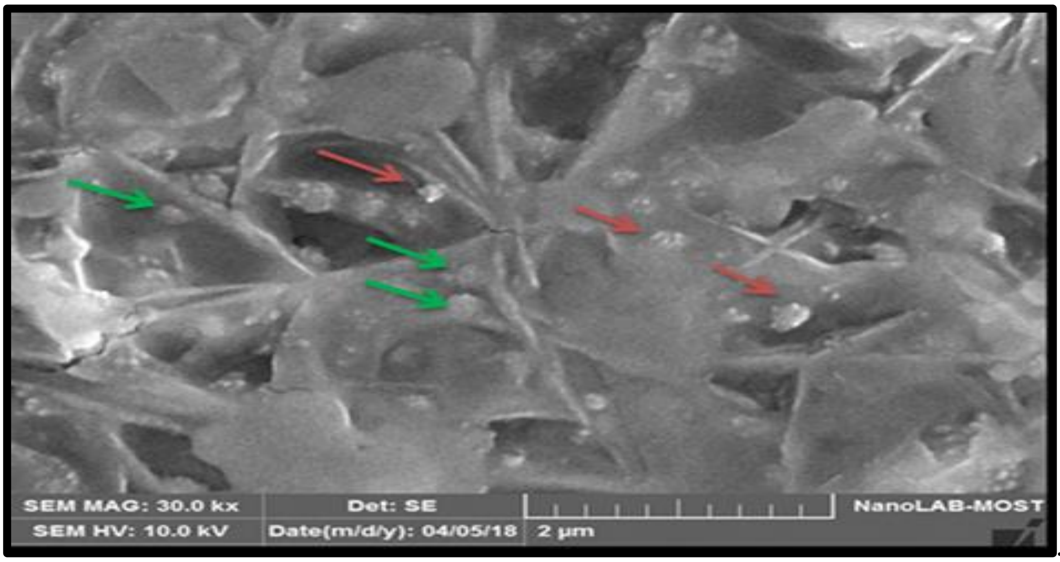

Figure 3- Biosynthesized of iron oxide nanoparticle by *E.coli* under SEM with a spherical shape. Red arrow (rough semi-spherical). Green arrow (smooth spherical).

Removal efficiency of (Cd) by Iron Oxide Nanoparticle from Sewage Water:

It is clear from Table-2 that when the pH value increase, the binding sites are starting to make different available functional groups for binding of metal [29], and increased the removal of Cd metal with the increase in the adsorbent dosage. This is to be expected because for a fixed initial solute concentration, increase in total adsorption doses provide adsorption sites or a greater surface area and increase the adsorption potential or iron oxide nanoparticle. Several researchers have reported similar results [30, 31]. However, after the dosage of 20.77 mg/L of iron oxide nanoparticle it is observed there was no change in percentage removal of heavy metals. It may be at higher dosage the overlapping of active sites. So, resulting due to the conglomeration of exchanger particles there was not any appreciable increase in the effective surface area [32]. Percentage removal of cd was increased with time. This might be due to the fact that the increased removal rate due to increased time allowed the particles to reach equilibrium state [33].

The current study is correlated with another study [16] that report the higher adsorption capacity was (95%) occurred at pH 5 of cadmium after 120min by *A.lebbeck* seed.

Table-2 shows the significant differences between the ability of adsorbent materials for sufficient removing of Cd metal ions from the sewage water depending on the heavy metals types and complete saturation of Cd binding sites on iron oxide at probability level ($P < 0.05$).

Table 2- The ability of adsorption for (Cd) metal by iron oxide nanoparticle at different pH value, contact time and dose concentration of NPs.

Exp. No.	Real Variables			Concentration of (Cd) after treatment	
	pH value	**Contact time (min.)**	**Concentration of NPs (mg/L)**	**Concentration of Cd (0.46ppm)**	**R.E ± SE (%)**
1	4.4	30	9.23	0.054	88.0 ± 3.62
2	5.5	30	9.23	0.051	88.9 ± 2.95
3	4.4	95.8	9.23	0.029	93.6 ± 3.81
4	4.4	30	20.77	0.13	71.0 ± 3.06
5	5.5	95.8	9.23	0.022	95.0 ± 2.77
6	5.5	30	20.77	0.05	89.0 ± 3.04
7	4.4	95.8	20.77	0.021	95.4 ± 2.37
8	5.5	95.8	20.77	0.014	96.9 ± 2.14
9	4	63	15	0.04	91.3 ± 3.68

10	6	63	15	0.020	95.6 ± 2.36
11	5	6	15	0.13	71.7 ± 3.52
12	5	120	15	0.022	95.0 ± 2.77
13	5	63	5	0.057	87.6 ± 3.82
14	5	63	25	0.3	34.7 ± 1.79
15	5	63	15	0.029	93.6 ± 3.54
LSD value	**--**	**--**	**--**	**--**	**10.036 ***
Means having with the different letters in the same column differed significantly * (P<0.05).					

Conclusion

The biosynthesized iron oxide nanoparticles by *E.coli* have a significant ability to remove cadmium from sewage water by use Box - Wilson design.

The experimental results showed, percentage Cd removal in permeate increased with the further increased in pH from value, also increased with time and concentrations.

The best conditions for maximum Cd removal (96.9%) were obtained at pH: 5.5; contact time: 95.8 min and Fe_2O_3 dosage: 20.7 mg/L.

References

1. WHO. (World Health Organization). **2006-c**. Guidelines for drinking water quality first addendum to third Edition, Recommendations.
2. Pimentel, D., Berger, B., Filiberto, D., Newton, M., Wolfe, B., Karabinakis, E., Clark, S., Poon, E., Abbett, E. and Nandagopal, S. **2004**. Water resources: agricultural and environmental issues. *BioScience*, **54**(10): 909-918.
3. Ma'alah, W.N. **2013**. Examining the Effects of Baghdad Medical City Waste Water on the Quality of Tigris River. M.Sc. thesis, department of biology, college of science, Baghdad University, Iraq.
4. Emmanuel, E., Pierre, M. G. and Perrodin, Y. **2009**. Groundwater contamination by microbiological and chemical substances released from hospital wastewater: Health risk assessment for drinking water consumers. *Environment international*, **35**(4): 718-726.
5. Majeed, N. S. and Naji, D. M. **2018**. Statistical analysis of the removal of Chromium (VI) by Iron Oxide Nanoparticle (Fe_3O_4). *Journal of Engineering*, **24**(2): 62-79.
6. Cheepi, P. **2012**. Musi River pollution its impact on health and economic conditions of downstream villages—A study. *IOSR Journal of Environmental Science, Toxicology and Food Technology*, **1**(4): 40-51.
7. Mezaal, D. KH. **2015**. Synthesis and Characterization of Silver Nanoparticles and their Antibacterial Activity in vitro. M.Sc Thesis. College of Science. Baghdad Univ. Iraq.
8. Lassoued, A., Dkhil, B., Gadri, A. and Ammar, S. **2017**. Control of the shape and size of iron oxide (α-Fe_2O_3) nanoparticles synthesized through the chemical precipitation method. *Results in physics*, **7**: 3007-3015.
9. Li, Y., Liu, F., Xia, B., Du, Q., Zhang, P., Wang, D. and Xia, Y. **2010**. Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites. *Journal of Hazardous Materials*, **177**(1-3): 876-880.
10. Kandah, M. I. and Meunier, J. L. **2007**. Removal of nickel ions from water by multi-walled carbon nanotubes. *Journal of hazardous materials*, **146**(1-2): 283-288.
11. Jusoh, A., Shiung, L. S. and Noor, M. J. M. M. **2007**. A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. *Desalination*, **206**(1-3): 9-16.
12. Kang, K. C., Kim, S. S., Choi, J. W. and Kwon, S. H. **2008**. Sorption of Cu2+ and Cd^{2+} onto acid- and base-pretreated granular activated carbon and activated carbon fiber samples. *Journal of Industrial and Engineering Chemistry*, **14**(1): 131-135.
13. Ai, Z., Cheng, Y., Zhang, L. and Qiu, J. **2008**. Efficient removal of Cr (VI) from aqueous solution with Fe@ Fe_2O_3 core− shell nanowires. *Environmental science & technology*, **42**(18): 6955-6960.

14. Dąbrowski, A., Hubicki, Z., Podkościelny, P. and Robens, E. **2004**. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *chemosphere*, **56**(2): 91-106.

15. Souiri, M., Gammoudi, I., Ouada, H. B., Mora, L., Jouenne, T., Jaffrezic-Renault, N. and Duncan, A. C. **2009**. Escherichia coli-functionalized magnetic nanobeads as an ultrasensitive biosensor for heavy metals. *Procedia Chemistry*, **1**(1): 1027-1030.

16. Khazaal, D. S .**2017**. Efficiency of *Albizzia lebbeck* pods and seeds in the removal of heavy metals (Lead, Cadmium and Cobalt) from aqueous solutions. M.sc, Thesis, Baghdad University, Iraq.

17. APHA (American Public Health Association). **1998**. Standard method for examination of water and waste water, APHA press. 20^{TH} ed

18. AOAC. Official Methods of Analysis **.2005**. 18th ed. edited by Horwitz, W. and G. W. Latimer, AOAC International.

19. Brenner, D. J., Staley, J. T. and Krieg, N. R. **2015**. Classification of Procaryotic Organisms and the Concept of Bacterial Speciation. *Bergey's Manual of Systematics of Archaea and Bacteria*, 1-9.

20. Kushwaha, A., Singh, V. K., Bhartariya, J., Singh, P. and Yasmeen, K. **2015**. Isolation and identification of *E. coli* bacteria for the synthesis of silver nanoparticles: characterization of the particles and study of antibacterial activity. *Eur J Exp Biol*, **5**(1): 65-70.

21. Divya, K., Kurian, L. C., Vijayan, S. and Manakulam Shaikmoideen, J. **2016**. Green synthesis of silver nanoparticles by Escherichia coli: Analysis of antibacterial activity. *Journal of Water and Environmental Nanotechnology*, **1**(1): 63-74.

22. Box GE, Hunter JC. **1998**. Conservation and Recycling, **21**: 227-245.

23. Hristovski, K., Baumgardner, A. and Westerhoff, P. **2007**. Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: from nanopowders to aggregated nanoparticle media. *Journal of Hazardous Materials*, **147**(1-2): 265-274.

24. Pavasant, P., Apiratikul, R., Sungkhum, V., Suthiparinyanont, P., Wattanachira, S. and Marhaba, T. F. **2006**. Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga Caulerpa lentillifera. *Bioresource Technology*, **97**(18): 2321-2329.

25. Arivoli, S., Nandhakumar, V., Saravanan, S. and Nagarajan, S. **2009**. Adsorption dynamics of copper ion by low cost activated carbon. *Arabian Journal of Science and Engineering*, **34**, 1-12.

26. Zhang, Y., Ghaly, A. E. and Li, B. **2012**. Physical properties of corn residues. *American Journal of Biochemistry and Biotechnology*, **8**(2): 44-53.

27. Hashim, M. H. **2018**. Study the Antibacterial Activity of Gold Nanoparticles against Some Clinical Isolates. M.Sc. thesis, department of biology, college of science, Baghdad University, Iraq.

28. Sherine, J., Sujatha, A. and Rathinam, M. **2016**. Biological synthesis of iron oxide nanoparticles using Streptomyces sp. and its antibacterial activity. *Journal of Chemical and Pharmaceutical Sciences* ISSN, **974**: 2115.

29. Esposito, A., Pagnanelli, F. and Veglio, F. I. **2002**. Plant proving their worth in toxic metal. *Chemical Engineering Sci*ence, **57**, 307-313.

30. Axtell, N. R., Sternberg, S. P. and Claussen, K. **2003**. Lead and nickel removal using Microspora and Lemna minor. *Bioresource technology*, **89**(1): 41-48.

31. Tokimoto, T., Kawasaki, N., Nakamura, T., Akutagawa, J. and Tanada, S. **2005**. Removal of lead ions in drinking water by coffee grounds as vegetable biomass. *Journal of Colloid and interface Science*, **281**(1): 56-61.

32. Tahir, H. **2005**. Comparative trace metal contents in sediments and liquid wastes from tanneries and the removal of chromium using Zeolite-5A. *Electronic Journal of Environmental, Agricultural and Food Chemistry*, **4**(4): 1021-1032.

33. Parsons, J. G., Hernandez, J., Gonzalez, C. M. and Gardea-Torresdey, J. L. **2014**. Sorption of Cr (III) and Cr (VI) to high and low pressure synthetic nano-magnetite (Fe_3O_4) particles. *Chemical Engineering Journal*, **254**, 171-180.