Marine Science Center-University of Basrah

Mesopotamian Journal of Marine Sciences
Print ISSN: 2073-6428
E- ISSN: 2708-6097
www.mjms.uobasrah.edu.iq/index.php/mms

Synthesis of new Adsorption System Contain Iron-Hay-Nano Product and their Application for Removing Some the heavy Metals from Polluted Waters

iD **Bassam.A. Al abdul Aziz[1]* and** iD **Zainab T. Alabdullah[2]**
1-Marine Science Centre, 2-Education collage for pure science, University of Basrah, Basrah-Iraq
*Corresponding Author: e-mail *bassam.rasheed@uobasrah.edu.iq*

Article info.
✓ *Received: 16January2022*
✓ *Accepted:24November2022*
✓ *Published:29December2022*

Key Words:
Adsorption,
Atomic absorption spectroscopy,
Iron nanoparticles,
TEM.

Abstract - Iron nanoparticles were synthesized by wet method. The reaction was done using iron salts as a source of iron, glucose was used as a reducing agent and trisodium citrate was used as a capping agent. The synthesized iron nanoparticles were added to hay powder in order to increase the desorption efficiency of hay. A new adsorption system contains iron nanoparticles–Hay was applied for removal of cadmium from polluted waters. The formation of iron nanoparticles was monitored using sevral instruments; UV-Vis spectra showed iron nanoparticles formation by exhibiting the characteristic surface plasmon absorption maximum at 350 nm. Transmission electron microscope (TEM) and scanning electron microscope (SEM) were used to identify the size and the morphology of iron nanoparticles. The images indicate that the synthesis of iron nanoparticles were in the range of 15-80 nm and were spherical in shape. The synthesized iron nanoparticles were applied for removal of heavy metals such as cadmium from polluted waters and flame atomic absorption spectroscopy (FAAS) was used for determination of the concentrations of cadmium before and after the addition of iron nanoparticles.

تركيب نظام امتزاز جديد يحتوي على حديد - تبن - منتج نانو وتطبيقه في إزالة بعض المعادن الثقيلة من المياه الملوثة

بسام عاشور رشيد العبد العزيز [1] وزينب طه ياسين العبد الله[2]
1- مركز علوم البحار، 2- كلية التربية للعلوم الصرفة، جامعة البصرة، البصرة – العراق

المستخلص - تم تصنيع جزيئات الحديد النانوية بالطريقة الرطبة. وإجراء التفاعل باستخدام أملاح الحديد كمصدر للحديد والكلوكوز المستخدم كعامل اختزال واستخدم ثلاثي سترات الصوديوم كعامل تغطية. تمت إضافة جزيئات الحديد المُصنَّعة إلى مسحوق القش لزيادة كفاءة امتصاص القش. يحتوي نظام الامتزاز الجديد على جسيمات الحديد النانوية – القش. تم تطبيق نظام الامتزاز الجديد لإزالة الكادميوم من المياه الملوثة. تمت مراقبة تكوين جزيئات الحديد النانوية باستخدام العديد من اجهزة التحليل الالية ، وأظهرت أطياف UV-Vis تكوين جزيئات الحديد النانوية من خلال إظهار امتصاص البلازمون السطحي المميز بحد أقصى (350نانومتر). تم استخدام المجهر الإلكتروني الناقل (TEM) والمجهر الإلكتروني الماسح (SEM) لتحديد حجم وتشكل جزيئات الحديد النانوية. تشير الصور إلى أن تخليق جزيئات الحديد النانوية في النطاق 15- 80 نانومتر كانت كروية الشكل: تم تطبيق واستخدام جزيئات الحديد النانوية لإزالة المعادن الثقيلة مثل الكادميوم من المياه الملوثة باستخدام مطياف الامتصاص الذري للهب (FAAS) لتقدير تركيز الكادميوم قبل إضافة جزيئات الحديد النانوية.وبعدها.

الكلمات المفتاحية: جزيئات الحديد النانوية ، الامتزاز ، مطيافية الامتصاص الذري ، المجهر الالكتروني النافذ.

Introduction

Currently, pollution of water has become a chief difficulty. Therefore, in order to produce a material lighter in weight and stronger, for replacing toxic chemicals, and for removing contaminants from groundwater nanoproducts were used (Morose, 2010). The exclusive properties of nanomaterials provide great potential to produce new breakthrough in technology,hence exploration of nanotechnology was necessary.

DOI: https://doi.org/10.58629/mjms.v37i2.314,

Quite a lot of studies documented nanoparticle synthesis using cost-effective, green, biocompatible methods excluding the use of material which are toxic. Many approaches such as chemical and biological methods have been used to synthesize metallic nanoparticles (Singh *et al*., 2008). Metallic nanoparticles are used increasingly in many fields, involving consumer, food, health care medical and industrial purposes, because of their new chemical and physical properties. These properties include high electrical conductivity, optical, electrical, thermal and biological properties (Gurunathan *et al*., 2015). Commonly, traditional chemical and physical methods are hazardous and expensive (Li *et al*., 2014; Gurav *et al*., 1994; Tao *et al*., 2006).

Overall, nanoparticle synthesis is being performed by three different methods, involving biological, physical and chemical approaches. From all these procedures chemical reduction is the most appropriate approach for nanoparticle fabrication. The formation of high yield metallic nanoparticles is performed via using chemical reduction method. This procedure is simple, economic and fast and can have an enhanced nanoparticle distribution by regulating parameters of the experiment (Dang *et al*., 2011). The presence of a large number of active sites within the nanoparticles is the main factor that results in cleaning the contamination sites and thus these materials display higher adsorption. If the size is further more minimized then the increased adsorption is correlated with an increased surface area of the adsorbent. This criteria play an essential role with increasing the capacity to eliminate the pollutants from organic compounds and wastewaters (Gupta *et al*., 2012; Mostafa *et al*., 2015; Auffan *et al*., 2009; Abdullah *et al*., 2020).

Previously, there is a preexisting method used frequently to remove inorganic and organic contaminants from wastewater. This includes adsorption by using various materials like alumina zeolites for elimination of metals from solutions (Martínez-Castañon *et al*., 2008). Moreover, hay is an agricultural byproduct it has important role. Hay can also be used to soak up oil spills and leave sanitary water behind. The current study establishes for the first time the use of iron nanoparticles-hay as a system of adsorption. The new system is mixed adsorption system from green chemistry and metal nanoparticles. The idea of this study is to enhance the adsorption value of hay by adding nanoproduct such as iron nanoparticles.

Materials and Methods

Adsorbents and Chemicals

Hay is a bio sorbent material, cheap and extremely offered lignocellulosic wastes in Iraq. Hay crushed to a size of 150 µm. The powdered materials have been carefully washed with deionized water to remove dirt and then dried up in the air for 24 hours.

Synthesis of Nanomaterials

Iron nanoparticles was synthesized using wet method (Della Gaspera, 2021), iron salt was used as a source of iron, glucose sugar was used as a reducing agent and trisodium citrate was used as a masking agent. Equal volume of this mixture was put on a hot plate stirrer for 1 hour at 100 °C. the black color appeared indicating the formation of iron nanoparticles.

Preparing of a new system (iron nanoparticles-hay)

The dry crashed hay was sieved to make a homogenized substance then mixed with synthesis iron nanoparticle, this system becomes ready to test the adsorption of cadmium as a pollutant, mechanical shaker was applied to ensure well mixing and penetration of the cadmium ions in the proposal system including a high surface area which was created by iron nanoparticles with the hay substances simultaneously. The new system for adsorption is forming from mixing iron nanoparticles-hay then the polluted solution of cadmium was added. Figure (1) shows this schematic diagram.

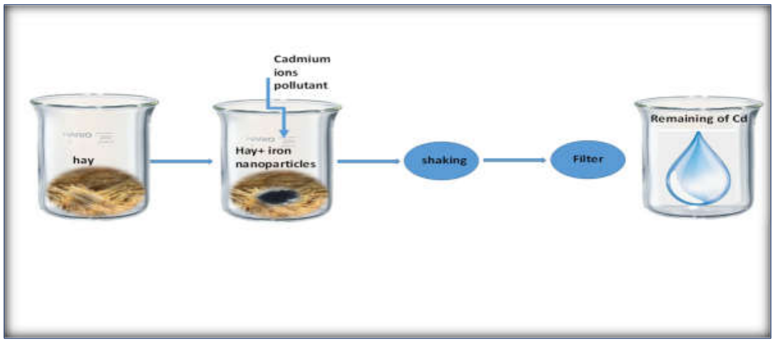

Figure 1. Schematic diagram showing the preparation of cadmium nanoparticles

Three stages of adsorption were done the first stage the adsorption was carried out using hay only the second stage was done using iron nanoparticles only, and the third stage the mixture of iron-hay were done. 0.1 g of hay was used as adsorption weight and 0.01 g of iron was used as an adsorption weight.

Results and Discussion

Characterization of iron nanoparticles

Transmission electron microscopy

Transmission electron microscope operated for imaging iron nanoparticles (Cac Centre, Baghdad, Iraq). Figure (2) shows the shape and size of the synthesized iron nanoparticles. The result indicates that the iron nanoparticles were just about spherical in shape, and with an average diameter of 15-80 nm.

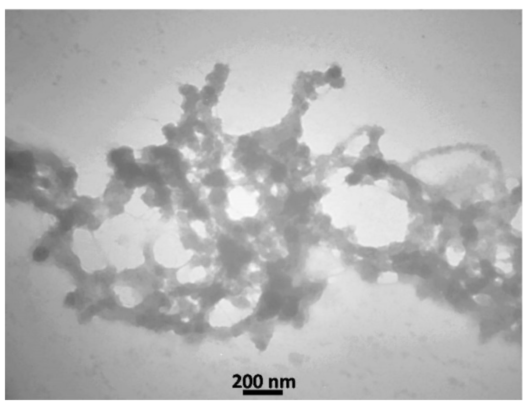

Figure 2. TEM image for synthesized iron nanoparticles

Scanning electron microscopy -energy dispersive x-ray

Scanning electron microscope (SEM-EDS) University of Basrah faculty of Pharmacy type ZELSS was used to examine the morphology of the surface. The image shows the shape is spherical and the size in the range of nanomaterials. Energy dispersive x-ray (EDX) shows the elementary analysis and the exist of iron on the surface (Figs. 3 a & b). The results from SEM are similar to the result from TEM.

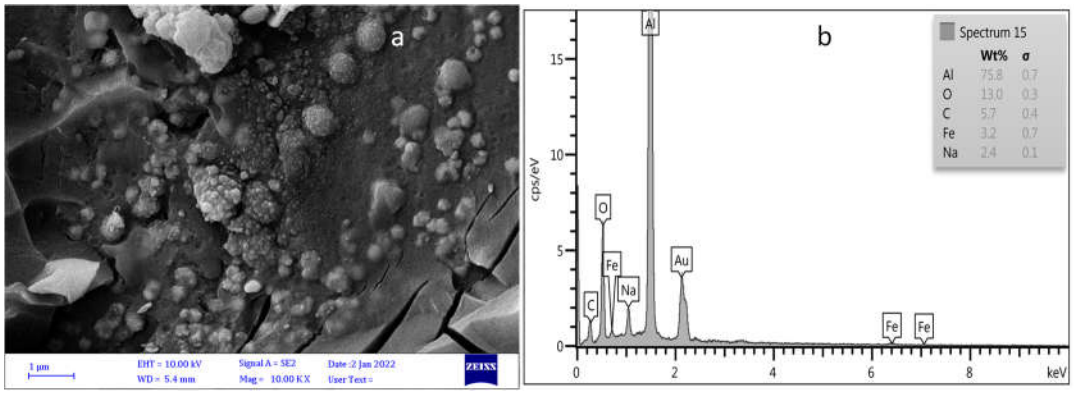

Figure 3. Shows (a) SEM images (b) illustrates the elementary micro analysis for EDX.

UV-Visible Spectrophotometery

The plasmon spectra is the main issue that can be examine by UV-Vis Spectrophotometer type U-1500 Spectrophotometer, Hitachi. Figure (4) shows the appearance of surface plasmon resonance peak (SPR) at 350 nm. This is in agreement with many studies (Dolci *et al*., 2020; Abdallah & Al-Haddad, 2021).

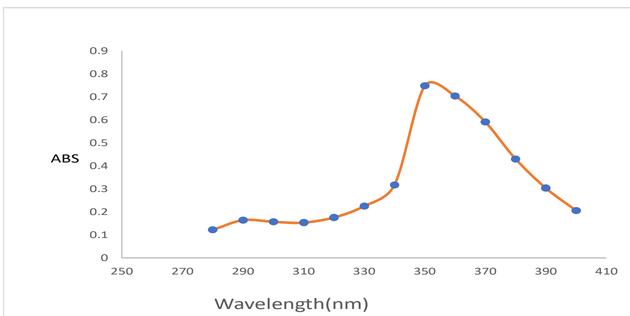

Figure 4. UV-Vis absorption spectrum of iron nanoparticles offer the plasmon peak at 350 nm.

Application of new adsorption system (iron nanoparticles-hay) for removing cadmium

The agricultural wastes metal adsorption and biosorption wastes reflected a complicated procedure affected by several factors (Roniboss *et al*., 2021). Moreover, metal oxide can be used for this purpose (Ramachandran *et al*., 2020). Here in hay was used for removal of cadimium from an aqueous solutions. Synthesize iron nanoparticles were applied for removing cadmium from an equeous solutions also. First of all standard calibratin curve of cadmium was done at the range of 0.05-2.5 ppm (Figure 5).

$$\% \text{ Removal} = \frac{(A^{\circ} - A_t)}{A_t} * 100 ----(1)$$

Where A° = initial absorbance, A_t = absorbance at time (t).

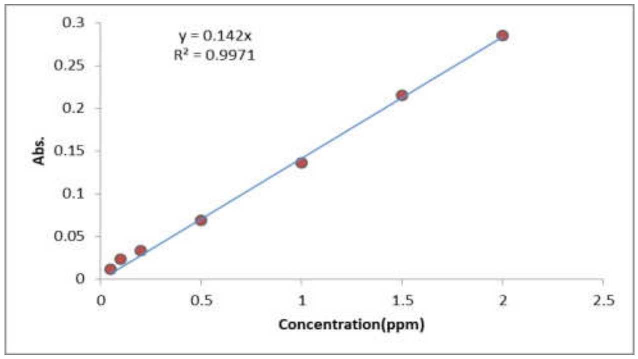

Figure 5. Calibration curve of Cadmium (II) ions.

Then the optimum conditions were done as follows:

The effect of contact time

The effect of contact time on the removal of cadmium ions by adsorption on hay was examined as a function of time at a fixed initial concentration (2 $mg.l^{-1}$) at different periods (15-60 min). Figure (6) presented that the rate of adsorption of metal on hay was fast at the beginning, then the adsorption slows down to a point of equilibrium which was at 15 min. This can be explained by the fact that the velocity is high at the onset of the adsorption on the surface of hay because the functional centers are empty but when these active centers are enclosed by the cations, the aforementioned, adsorption begins to slow down and optimum contact times was at 15 min. The removal percentage of metal on hay was found to be 96.3 %.

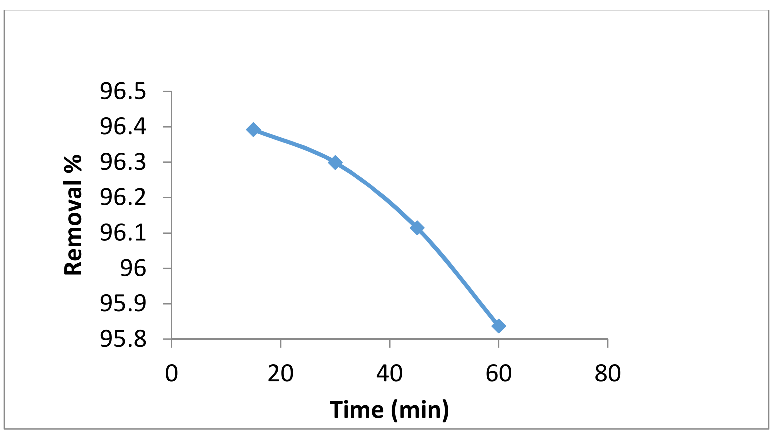

Figure 6. The effect of contact time on Cd(II) adsorption onto hay.

The effect of the dose of adsorbent

The effect of hay dosage on the adsorption was monitored at different weights of the adsorbent in the range of 0.1-1.5 at 25°C. As shown in Figure (6) the results indicated an increase the removal rate of cadmium ions with the increase in hay dosage from 0.1-1.5, the removal percentage of cadmium ions increased quickly to 95.6% as seen in Figure (7).

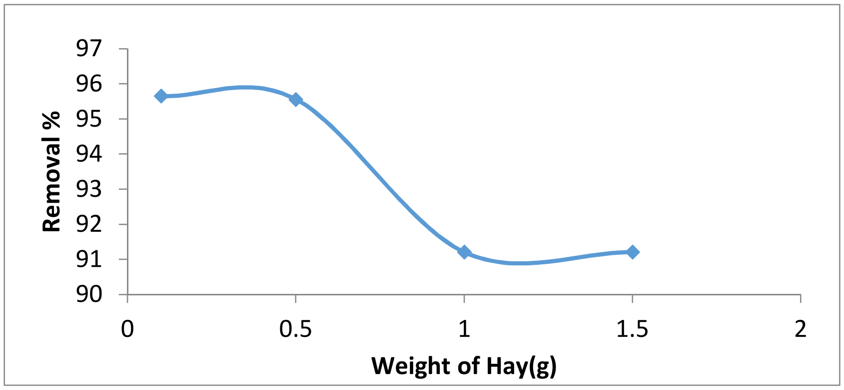

Figure 7. The influence of adsorbent dose on removal (%) of Cd.

The reason for such way might be ascribed to greater surface area and great number of vacant sites on the surface of adsorbent to correlate with cadmium ions.

Accordingly the adsorption procedure was done using the addition of iron nanoparticles to the hay in order to form a new adsorption system the concept of this addition is to increase the surface aria of the adsorbent because the high the surface area to the volume ratio of nano materials. Table 1 shows these results

Table 1.Adsorption (%) of cadmium on iron nanoparticles-hay using AAS at optimum conditions

Cd(ppm)	**Abs.**	**Abs.(Cd) Hay only**	**Adsorption %** $= \frac{(A^{\circ} - A_t)}{A_t} * 100$	**Abs.(Cd) After add Fe Nano only**	**Adsorption %** $= \frac{(A^{\circ} - A_t)}{A_t} * 100$	**Abs.(Cd) after add of Iron-hay**	**Adsorption %** $= \frac{(A^{\circ} - A_t)}{A_t} * 100$
0.05	0.016						
0.1	0.028						
0.2	0.034						
0.5	0.069						
1	0.136						
1.5	0.215	N.D	100	0.007	96.7	N.D	**100**
2	0.285	0.0114	96.0	0.04	85.9	N.D	**100**

Hence , only two concentrations ware examined before and after the addition of iron nanoparticles. The results showed that the iron nanoparticles-hay system had a high ability to adsorb the heavy elements, as the adsorption rate reached 100% of the original concentration of the solution (1.5 ppm) of Cd. And the adsorption rate reached 100 % of the original concentration of the 2 ppm Cd solution due to the high surface area and the ability of the hydrophilic iron nanoparticles to attract the largest amount of the aqueous Cd (II) solution.

Conclusion

The current study demonstrates for the first-time the use of metal nanomaterials to enhance the adsorption system. Synthesis of iron nanoparticles was done using wet chemistry which is simple, fast and economical method. The hay is very good adsorbent. The use of natural straw as a feedstock instead of chemicals is part of the green chemistry. The present study showed that hay is suitable for removing of the cadmium from the aqueous solution. However, adding nanomaterials on the hay surface make it more active as an adsorbent surface due to the increase in the surface area of adsorption.

New value provides a capable method to release inorganic polluted materials from polluted water by iron nano product-Hay. The ability of (iron nanoparticles-hay) to adsorb heavy metals such as Cd was studied, so the adsorption rate of concentration of 1.5 ppm was 96.7 % by iron nanoparticles, however, using iron nanoparticles-hay as a new adsorption system increase the rate of adsorption to 100%. The obtained results showed that adding the nanomaterials to the hay surface increase the percentage of adsorption and the use of iron increased the efficiency of the adsorption process.

According to the guidelines which provided by world health organization (WHO) the permitted concentration of Cd in the drinking water is 3ppb. In this study, the system used was able to absorb 2000 ppb of Cd resulting in fresh water with 100% efficiency of the system.

References

Abdallah, R. M. and Al-Haddad, R. M. S. 2021. Optical and Morphology Properties of the Magnetite (Fe3O4) Nanoparticles Prepared by Green Method. Journal of Physics: Conference Series, 1829(1), 12022. https://iopscience.iop.org/article/10.1088/1742-6596/1829/1/012022

Abdullah, Z., AL-SHAWI, A. A. A., Aboud, M. N., Al Abdul Aziz, B., QM Al-Furaiji, H. and Luaibi, I. N. 2020. Synthesis and Analytical Characterization of Gold Nanoparticles using Microwave-Assisted Extraction System and Study their Application in Degradation. Journal of Nanostructures, 10(4), 682–690.https://doi.org/10.22052/JNS.2020.04.001

Auffan, M., Rose, J., Bottero, J.-Y., Lowry, G. V, Jolivet, J.P. and Wiesner, M. R. 2009. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. Nature Nanotechnology, 4(10), 634–641.https://doi.org/10.1038/nnano.2009.242

Dang, T. M. D., Le, T. T. T., Fribourg-Blanc, E. and Dang, M. C. 2011. Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method. Advances in Natural Sciences: Nanoscience and Nanotechnology, 2(1), 15009.https://iopscience.iop.org/article/10.1088/2043-6262/2/1/015009/meta

Della Gaspera, E. 2021. Special Issue "Wet Chemical Synthesis of Functional Nanomaterials". In Nanomaterials (Vol. 11, Issue 4, p. 1044). MDPI.https://doi.org/10.3390/nano11041044

Dolci, M., Bryche, J.-F., Moreau, J., Leuvrey, C., Begin-Colin, S., Barbillon, G. and Pichon, B. P. 2020. Investigation of the structure of iron oxide nanoparticle assemblies in order to optimize the sensitivity of surface plasmon resonance-based sensors. Applied Surface Science, 527, 146773.https://doi.org/10.1016/j.apsusc.2020.146773

Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A. and Agarwal, S. 2012. Chemical treatment technologies for waste-water recycling—an overview. Rsc Advances, 2(16), 6380–6388.https://doi.org/10.1039/C2RA20340E

Gurav, A. S., Kodas, T. T., Wang, L.-M., Kauppinen, E. I. and Joutsensaari, J. (1994). Generation of nanometer-size fullerene particles via vapor condensation. Chemical Physics Letters, 218(4), 304–308.https://doi.org/10.1016/0009-2614(93)E1491-X

Gurunathan, S., Park, J. H., Han, J. W. and Kim, J. H. 2015. Comparative assessment of the apoptotic potential of silver nanoparticles synthesized by Bacillus tequilensis and Calocybe indica in MDA-MB-231 human breast cancer cells: targeting p53 for anticancer therapy. International Journal of Nanomedicine, 10, 4203.https://doi.org/10.2147%2FIJN.S83953

Li, C., Zhang, Y., Wang, M., Zhang, Y., Chen, G., Li, L., Wu, D. and Wang, Q. 2014. In vivo real-time visualization of tissue blood flow and angiogenesis using Ag2S quantum dots in the NIR-II window. Biomaterials, 35(1), 393–400.https://doi.org/10.1016/j.biomaterials.2013.10.010

Martínez-Castañon, G.-A., Nino-Martinez, N., Martinez-Gutierrez, F., Martínez-Mendoza, J. R., and Ruiz, F. 2008. Synthesis and antibacterial activity of silver nanoparticles with different sizes. Journal of Nanoparticle Research, 10, 1343–1348.https://doi.org/10.1007/s11051-008-9428-6

Morose, G. 2010. The 5 principles of "design for safer nanotechnology". Journal of Cleaner Production, 18(3), 285–289.https://doi.org/10.1016/j.jclepro.2009.10.001

Mostafa, A. A., Sayed, S. R. M., Solkamy, E. N., Khan, M., Shaik, M. R., Al-Warthan, A. and Adil, S. F. 2015. Evaluation of biological activities of chemically synthesized silver nanoparticles. Journal of Nanomaterials, 16(1), 443.https://doi.org/10.1155/2015/789178

Ramachandran, S., Dash, C. S., Thamilselvan, A., Kalpana, S. and Sundararajan, M. 2020. Rapid Synthesis and Characterization of Pure and Cobalt Doped Zinc Aluminate Nanoparticles via Microwave Assisted Combustion Method. Journal of Nanoscience and Nanotechnology, 20(4), 2382–2388.https://doi.org/10.1166/jnn.2020.17314

Roniboss, A., Subramani, A., Ramamoorthy, R., Yuvaraj, S., Sundararajan, M. and Dash, C. S. 2021. Investigation of structural, optical and magnetic behavior of MAl2O4 (M= Zn and Co) nanoparticles via microwave combustion technique. Materials Science in Semiconductor Processing, 123, 105507.https://doi.org/10.1016/j.mssp.2020.105507

Singh, M., Singh, S., Prasad, S. and Gambhir, I. S.(2008. Nanotechnology in medicine and antibacterial effect of silver nanoparticles. Digest Journal of Nanomaterials and Biostructures, 3(3), 115–122.URL

Tao, A., Sinsermsuksakul, P. and Yang, P. 2006. Polyhedral silver nanocrystals with distinct scattering signatures. Angewandte Chemie International Edition, 45(28), 4597–4601.https://doi.org/10.1002/anie.200601277