© IJCIRAS | ISSN (O) - 2581-5334
February 2020 | Vol. 2 Issue. 9

ADSORPTION OF LEAD IONS (PB2+) FROM AQUEOUS SOLUTION WITH TETRA-ETHYL ORTHOSILICATE MODIFIED SILICA-IRON OXIDE (SI-FE3O4) MAGNETIC NANO-ADSORBENT.

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Abstract

Lead as one of the toxic and dangerous heavy metals will always require an approach that is cost-effective, simple and environmentally benign to eliminate it from potable water sources especially. Tetra-ethyl orthosilicate was employed as a stabilizing and modifying agent on iron oxide magnetic nano-adsorbent from ferric and ferrous chlorides as precursors. Fourier transform infrared (FT-IR) and Transmission electron microscopy (TEM) was adopted in the characterization of this silica-coated magnetic iron oxide nano-adsorbent (Si-Fe3O4 Nanoparticles). FTIR clearly ascertained the relevant absorption peaks and affirmation of spheroidal Si-Fe3O4 nano-adsorbent at a 20nm nanometer scale with TEM and image J particle analysis software. The actual dimension of 82.54nm or 68.56nm was deduced from the absolute average area of (5756.144 ± 1055.833) nm2; standard error of 333.884nm2 with the silica-coated magnetic nano-adsorbent (Si-Fe3O4) and (77.5 ± 9.24) nm2 and standard error of 2.922nm2 with the uncoated nanoparticles (Fe3O4) were estimated. They (Si-Fe3O4 and Fe3O4) retained polydispersity indices of 2504.800 and 67.811 respectively, characterizing the nano-adsorbent as a polydispersed, randomly oriented nanoparticles. Si-Fe3O4 as a nano-adsorbent was then employed for the adsorption of lead (Pb2+) ions from the aqueous solution of 0.06M and 20mg of lead nitrate [Pb(NO3)2] under the influence of an external magnetic field. Qualitative determination of lead with a test kit was adopted as a direct signal in detecting the presence and absence of lead ions in aqueous solution. It was logically estimated that 20mg/g adsorption capacity of 5g and 100% removal efficiency of Si-Fe3O4 nano-adsorbent were achieved with lead ion.

***Keyword:** Magnetic nano-adsorbent, tetra-ethyl orthosilicate, iron oxide Nano-particles, lead, and magnetic field.*

1.INTRODUCTION

The growth in industrialization has thusly polluted streams and rivers through the release of toxic heavy metals, into the ecosystem [1]. Alongside the industrial pollution, local effluents, rural and urban overspills are of concern to the nature of the surface water [2]. Aquatic pollutants, for example, heavy metal particles and some synthetic dyes are destructive to the aquatic creatures as they influence the biological systems negatively. As the populace is expanding on a daily basis the water accessibility per capita is diminishing. So the test of the constrained measure of water quantities with its diminishing per capita accessibility is an issue of concern, while another significant factor is water contamination that has a natural effect on man's wellbeing. Statistically, 783 million individuals in the global scene lack access to safe and pure water [3]. Similarly, in Sub-Saharan Africa, 319 million populace are without access to improved dependable drinking water sources [3]. One of every nine individuals worldwide also lack access to sheltered and clean drinking water [4]. In evolving nations, as much as 80% of sicknesses are connected to poor water and sanitation conditions. Half of the world's emergency clinic beds are loaded up with individuals experiencing a water-related infection [5]. 2.6 billion individuals on the planet lack sufficient sanitation which results to about 10% of the worldwide sickness [6] Inorganic contaminants like, Hg(II), Pb(II), Cr(III), Cr(VI), Ni(II), Co(II), Cu(II), Cd(II), Ag(I), As(V) and As(III) are lethal Eco toxicologically[7].

Lead particularly emerges from various manufacturing and mining sources as the most commonly dispersed heavy and toxic metal [8]. The presence of Lead in water causes significant health issues like distortion of the central nervous system, kidney diseases and loss of red blood cells in man [9]. Placental transportation of lead in people influences infants as they retain 4–5 fold the amount of lead as grown-ups [10]. The lead toxicant amasses in the skeleton and causes unfavorable wellbeing impacts and interferes with calcium digestion and vitamin D metabolism [11]. Notwithstanding, the outcome of some studies on humans reveals serious neurotoxic impacts other than malignant cell growth occurring at exceptionally low centralizations of lead [12]. Consequently, there is a requirement for the elimination of lead from all drinking water. A viable strategy for wastewater treatment is the utilization of nanoparticles to sanitize the wastewater from various contaminants.

As nanotechnology is been considered for wastewater treatment and perceived to be one of the most developed, cheap and environmentally friendly procedures. In this regard, water treatment can be categorized into three methods: Nano-adsorbents, Nanocatalysts, and Nano-film [13]. Nano-adsorbents are nanoparticles made of natural or inorganic materials with a high attraction to adsorb substances, in another word, they have the capacity to evacuate numerous contaminations. These nanoparticles are synthesized and used to eliminate various sorts of contaminants with significant attributes such as potential catalyst, nanosized, high reactivity, and huge surface vigor [14]. They can be additionally arranged on the basis of their adsorption procedure, which incorporates metallic nanoparticle, nanostructured blended oxides, attractive nanoparticles, and metal oxide nanoparticles. Wastewater treatment that utilizes nanoparticles is one of the aspects of nanotechnology among other different applications like fuel cells, hydrogen conservation, and different clinical antibacterial applications. As of late, materials that are chemically magnetic have been utilized for the elimination of water contaminants, especially natural contaminants like, dyes, chlorinated hydrocarbons, aromatics, pesticides and metals [15]. There is an enormous number of procedures accessible for water treatment for safe drinking water including adsorption, precipitation, solvent extraction, ion exchange, reverse osmosis, membrane separation, evaporation, and photocatalysis.

The progression and improvement of nanoscience and nanotechnology show their probability of eliminating pollutants from water bodies with a viable and enhanced water treatment process. The techniques and advancement of nanomaterial with the size dimension of 1–100 nm give exceptional properties in the sectors such as manufacturing, health, electronics, and environmental remediation. The magnetic nanomaterial (paramagnetic or ferromagnetic or super paramagnetic) with fabricated surface arrangement has just extended their extent of use in water treatment. Iron oxide-based ($Fe3O4$) nanomaterial is another sort of generally utilized nanoscaled adsorbent because of its ease of production, effortlessness applications, simple accessibility, and ecological acceptability in a simple manner of separation by an external magnetic force. [16].There have been various publications on their applications for toxic and heavy metals treatment on water. Giraldo et al. orchestrated magnetite nanoparticles by employing a co-precipitation system with the treatment Pb (II), Cu (II), Zn (II), and Mn (II) in a batch mode [17]. The outcomes exhibited that Nano-sized magnetite had the best adsorption impact towards Pb (II) (0.180 mmol.g−1) while the least for Mn (II) (0.140 mmol.g−1) [17]. This distinction could result from the different electrostatic connections between the ions of these metal particles and the surface of the nano-adsorbent. The pseudo-second-order model and Langmuir isotherm were seen to correspond with the adsorption figures accurately. It was found that the size of hydrated ionic radii may influence the associations with the anionic adsorption site. At the point when the hydrated ionic radii expanded, the direction to the adsorbing surface will be enlarged and the adsorption would be less active. Given that Pb (II) had the most minimal hydrated ionic radius and the greatest ability to interact with proton, it was then sensible that it had the most elevated adsorption limit [17]. Meanwhile, uncoated magnetite nanoparticles are effectively oxidized with oxygen because of the presence of Fe (II) in their structures, and they additionally will, in general, be eroded by acids or bases. With respect to the coatings and the stability of the systems with the shell structure, silica, sodium dodecyl sulfate, oleate, p-nitro aniline, polyethylene glycol, chitosan, and tannic acid, have been accounted for as a coating agents on the magnetite nanoparticles for the treatment of toxic heavy metals in wastewater treatment [17]. The four fundamental reasons for surface regulation of Nano-particles are to improve or control their scattering nature; to improve the surface action; to upgrade the physicochemical and mechanical properties; to improve biocompatibility and to forestall oxidation [18]. Tetraethyl orthosilicate [Si (OC2H5)4.], is a fluid that hydrolyzes in water. It is the ethyl ester of orthosilicic acid, Si (OH) 4 and the most predominant alkoxide of silicon [19]. It is mostly utilized as a crosslinking precursor in silicone polymers, an agent to silicon dioxide in the semiconductor industry, the production of certain zeolites, generation of aerogel, coatings for rugs and different items [20]. As their applications take advantage of the reactivity of the Si-OR bonds, It is the most well-known and generally utilized agent for the surface adjustment of Iron Oxide Nano-particles. Silica coatings on nanoparticles have the benefits of low agglomeration, upgrading the steadiness and controlling the cytotoxic impacts of MNPs. Accordingly, it has shown great biocompatibility, hydrophobicity, and stability [20]. Therefore, an approach to eliminate lead ions from water by active adsorption on a Nano silica stabilized magnetic iron oxide particles with a direct qualitative test was developed and established.

2. MATERIALS AND METHODS

2.1. Materials

Iron oxide Nano-particle precursors (FeCl3.6H2O (96% w/w); FeCl2.4H2O), coating agent (tetraethoxysilane (TEOS)
(Si (OC2H5)4), and 28% ammonia solution, absolute ethanol (96%), deionized DI-water, 0.1M HCl and 0.1M NaOH, pH meter,FTIR-4000 SERIES and TEM
(JEM-Z300FSC) were used for FTIR and TEM analysis respectively.

2.2. Synthesis of Magnetic Fe3O4 Nano-Particles

Magnetic Nano-particles were prepared based on the chemical co-precipitation method [21]. 4 g FeCl3.6H2O and 2 g FeCl2.4H2O were dissolved in 200 ml de-ionized water under a N2 (g) atmosphere with severely stirring at 80 °C. After that the solution was mixed for 30 min, then 20 ml of ammonia solution was poured drop wise into the solution until the pH raised to about 10 and the stirring continued for 45 min. When ammonium was being added to the solution, it was led to the changing of solution color from the brown to dark brown and then became black. After the temperature of the synthesized adsorbent
(Fe3O4 nanoparticles) lowered, they were repeatedly washed using ethanol until reaching pH to the neutral state and which followed by drying in an oven at 105 °C for 4 h.

$$Fe^{2+} + 2Fe^{3+} + 8NH_3{\cdot}H_2O \rightarrow Fe_3O_4\downarrow + 8NH^{4+} + 4H_2O$$

2.3. Synthesis of Silica coated Magnetic Iron oxide Nano-adsorbent (Si-Fe3O4).

With a modified co-precipitation technique; (Stöber method), Si-Fe3O4 Nano-Particles were synthesized [22]. A solution of Fe3O4 Nano-particles with 0.125 M (80 ml) was prepared via dispersion in absolute ethanol at 40 °C. When the suspension was formed, it was mixed with 4 ml of 21% ammonia, 7.50 ml de-ionized water and 0.56 ml of Tetra-ethyl orthosilicate (TEOS) for 2 h.

Afterward, the suspension was sonicated for 60 minutes. The composite was magnetically separated from the suspension using a bar of magnetic and then dispersed in 30 ml of ethanol. For improving the Si–O–Fe bonding, the solution was kept in a 60 °C water bath for 6 h. Then, it was washed several times by alcohol until its pH became neutral; and vacuum-dried at 70 °C for 12 h, and preserved in an airtight container.

2.4. Preparation of standard lead solution

20mg of lead nitrate was dissolved in 1000ml of distilled water (0.06M)

2.5. Adsorption of Pb+2 with Si-Fe3O4 magnetic nano-adsorbent.

5g of dried silica-coated magnetite nanoparticles were added to 10 ml of 0.06M of Pb+2aqueous solutions. Then, this mixture was ultrasonicated for 30 min at room temperature. Finally, the magnetic silica Nano composite-lead mixture was separated by an external magneti field.

Figure I. Dried Si-Fe_3O_4 Nano-particles

Figure II. The mixture of Si-Fe_3O_4/

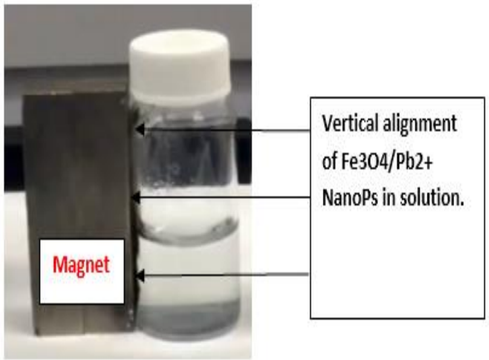


Figure III. Magnetized Si-Fe_3O_4/ Pb^{2+} ions in solution

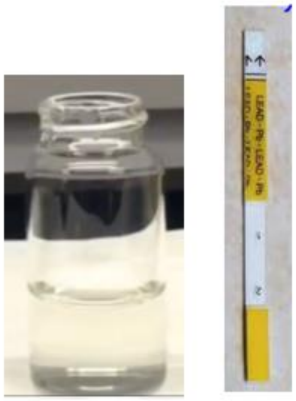


Figure IV. Treated water sample (Pb^{2+} free).

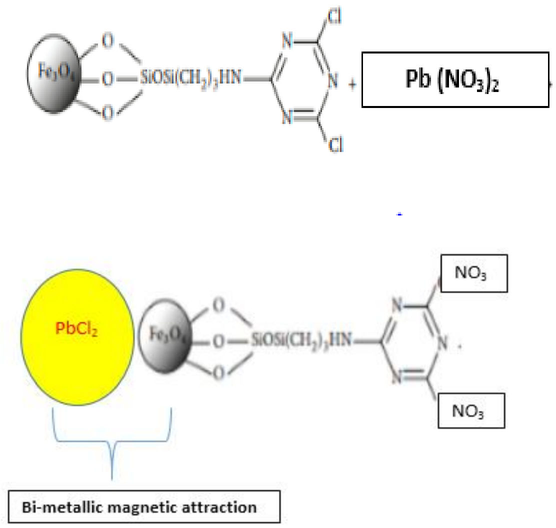


Figure V. Predicted Covalent combination of lead nitrate with silica-coated nano-adsorbent (Si-Fe3O4)

2.6. Qualitative detection of lead in water before and after treatment.

The lead test strip was adopted in detecting lead in solution before and after treatment. A little quantity of the water sample was taken with a dropper into a plastic vial. The test strip was dipped into the solution in a vial. The result is checked after 10minutes.


LEAD & PESTICIDE TEST INSTRUCTIONS

1) Open the foil pouch that contains the Lead & Pesticide test kits. The package should contain a test vial, dropper pippette, two test strips and a desiccant pack (to be discarded).
2) Using the dropper, place **exactly TWO dropper-fuls** of water sample into the test vial. To pick up a water sample squeeze the top bulb at the end of the dropper and place the open end into your water. Release the bulb to suck in the water sample into the lower dropper chamber. To expel the water in to your test vial simply squeeze the bulb again.
3) Swirl the test vial for a few seconds then place it on a flat surface.
4) With both arrows pointing **DOWN**, place both test strips into the vial.
5) Wait for 10 minutes. Do not disturb the test during this time.
6) After 10 minutes you will see blue lines appear on the strips. Take the strips out of the vial and lay them on a flat surface with the arrows pointing to the **LEFT**.

NEGATIVE RESULT

LEFT line next to the number 1 will be darker than the **RIGHT** line next to the number 2.

If you see only one line next to the number 1 then test is negative.

POSITIVE RESULT

RIGHT line next to the number 2 will be darker than the **LEFT** line next to the number 1.

If both LEFT and RIGHT lines are equally dark then test is positive.

(If a test strip shows a positive result then your water sample may contain pesticide or lead at a possibly toxic level. Further testing is highly recommended.)

PLEASE NOTE: If no lines appear or both of the lines are very faint, the test may not have run properly and the results are invalid.

Figure VI. Lead and pesticide test kit.

3.0 RESULTS AND DISCUSSION

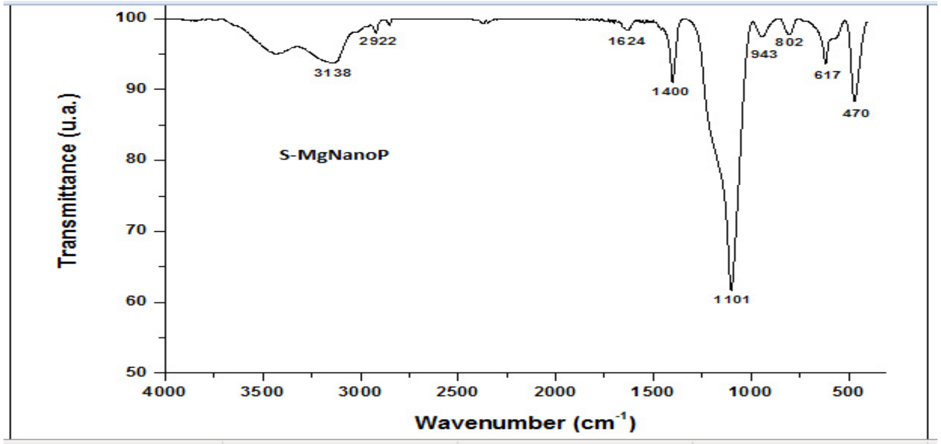
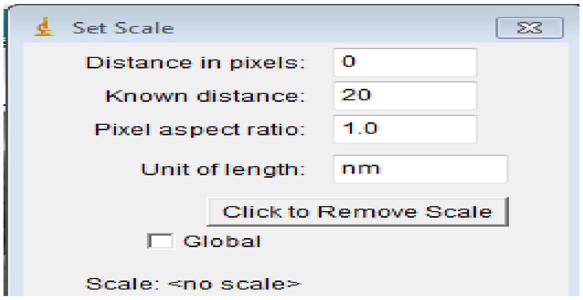


Figure VII. FT-IR of magnetic Si- Fe3O4 nano-adsorbent.



Distance in pixels: 0
Known distance: 20
Pixel aspect ratio: 1.0
Unit of length: nm
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Scale: <no scale>

Figure VIII. Set scale of the nano-adsorbent with image J particle analyzer.

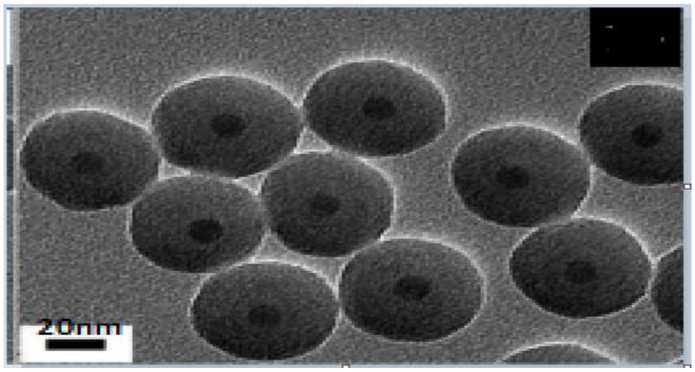


Figure 9. TEM of Si-Fe$_3$O$_4$ nano-adsorbent

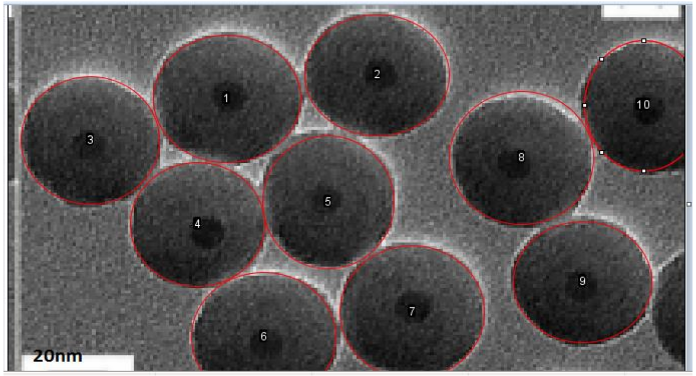
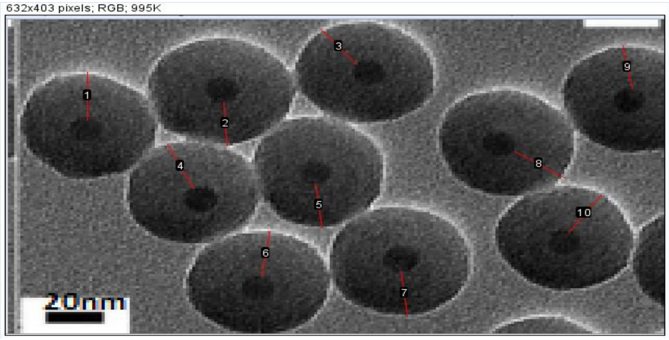


Figure 10.Silica coatings



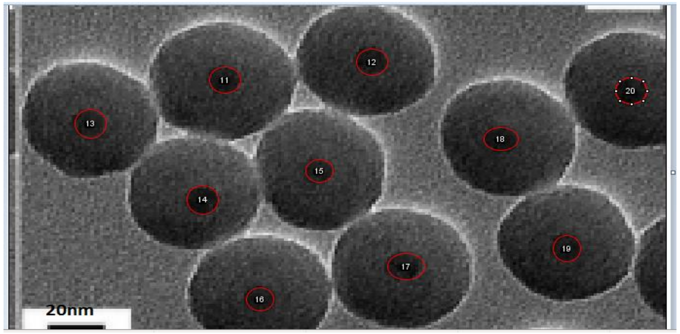


Figure 11.Radius between the Si-Fe_3O_4 and Fe_3O_4 nano-particles

Figure 12. Fe_3O_4 nano-particles

Table I. TEM area data for silica coatings and Fe_3O_4 Nano-particles

Label	Silica coatings measurement			Area of Fe_3O_4 NanoPs (nm^2)
	Width(R)nm	R^2 (nm^2)	Area=$\prod R^2$	
1	46	2116	6648.472	80
2	45	2025	6362.550	80
3	43	1849	5809.558	86
4	42	1764	5542.488	66
5	41	1681	5281.702	69
6	45	2025	6362.550	69
7	45	2025	6362.550	96
8	45	2025	6362.550	79
9	43	1849	5809.558	70
10	31	961	3019.462	80

Table II. Descriptive Area statistics of the Nano-particles

Descriptive statistics	Si-Fe_3O_4(nm^2)	Fe_3O_4(nm^2)
Mean	5756.144	77.5
Median	6086.054	79.5
Mode	6362.550	80.0
Standard error	333.884	2.922
Standard deviation	1055.833	9.241
Range	3629.010	30
Maximum	6648.472	96
Minimum	3019.462	66
Absolute Value	5756.144 ± 1055.833	77.5 ± 9.241

Table III. Polydispersities index (PDI) with Si- Fe_3O_4 and Fe_3O_4 Nano-particles.

Label	Standard deviation (Si-Fe_3O_4 Nano-Ps)	Standard deviation (Fe_3O_4 Nano-Ps)
1	41.19	71.51
2	25.05	67.99
3	35.28	80.54
4	20.47	81.83
5	14.83	88.90
6	20.38	55.54
7	11.76	12.69
8	34.90	72.21
9	27.16	56.41
10	19.46	90.49
Total	250.48	678.11
PDI	$\frac{250.48}{10} = 2504.800$	$\frac{678.11}{10} = 67.811$
Adsorption capacity	$\frac{(20-0) \times 10}{5} = 40$mg/g	
Pb^{2+} Removal efficiency	$\frac{20 - 0 \times 100\%}{20} = 100\%$	

Figure I, II, III, and IV are the pictures of the synthesized silica-coated iron oxide Nano-adsorbent, the mixture of the nano-adsorbent and the adsorbate (Pb^{2+}) in an aqueous solution for 30 minutes reaction time, the magnetized silica Nano adsorbent/lead ions matrix and the treated water sample after separation and negative confirmatory lead test respectively. In addition, the predicted covalent interaction of lead nitrate with the modified Si-Fe_3O_4 Nano-particles is presented in figure V, as the mechanism of lead adsorption at the molecular level. The lead test kit (Figure VI) with a sensitive strip (yellow) was adopted in qualitatively detecting lead ions in solution [0.06M $Pb(NO_3)_2$] before and after deliberate lead water contamination. The test was positive with the emergence of two lines and negative if otherwise.

Figure VII presented the FTIR spectrum of magnetic Si-Fe_3O_4 Nano-particles in dry form. This generates peaks at 943cm-1 and 1101cm-1 that were attributed to Silica-OH and Silica-O-Silica stretching vibrations. A broader peak at 3138cm-1 corresponds to O-H stretching, 1624cm-1 to O-H or N-H stretching vibrations. Also, at 2922cm-1 and 1624cm-1 were characteristics of $-CH_3$ and $-CH_2$ stretching vibrations respectively. Hence, these are clear indications that there was a successful modification of the nanoparticles at the Nano level. Transmission electron microscopy (TEM) two-dimensional settings with ten distinct nanoparticles were obtained with a defined known magnification of 20nm (Figure VIII) with image J particle analysis software. The first-hand TEM images were depicted in Figure IX as it reveals the circular shaped, clustered and irregular oriented Si-Fe_3O_4 magnetic nanoparticles.

In addition, figure X highlights the boundaries and perimeters of the silica coatings around the nano-particles. The areas and the circumference of these magnetic nanoparticles as a nuclear arrangement with the silica coatings are presented in table 1.

Descriptive area statistics for Si-Fe_3O_4 and Fe_3O_4 Nano-particles as presented on table 2 with respect to the absolute mean value and standard error which are (5756.144 ± 1055.833) nm2, 333.884nm2 and (77.5 ± 9.241) nm2, 2.922nm2 respectively. Table 3 is the polydispersity indices of both the Si-Fe_3O_4 (2504.800) and Fe_3O_4 (67.811) Nano-particles. This practice reflects the distribution of the nanocomposites in polydispersed non-uniform distributions with an adsorption capacity of 40mg/g and lead removal efficiency of 100% with Si-Fe_3O_4 magnetic nano-adsorbent.

4.CONCLUSION.

A modified polydispersed, reactive and magnetic 82.54nm/68.56nm nano-adsorbents under 20nm scale were developed with an adsorptive capability of 40mg/g on a lead ion in aqueous solution qualitatively at 30minute residence period at room temperature. This work, therefore, declares a simple and not complex approach in the application of silica-coated, stabilized and modified magnetic iron oxide nano-adsorbent (Si-Fe_3O_4) for the elimination of lead in the water sample.

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