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Nanomagnetites Green Synthesis Assisted by Sunflower Oil.

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ABSTRACT

Nanomagnetites were used as a most efficient agent for removal of heavy metals such as As and Cr for cleaning polluted water as heavy-metal contamination in groundwater is one of the severe global problems. In India, arsenic poisoning is very common but the major hurdle in synthesizing nanomagnetite in the lab is, high cost by decomposition method using FeOOH and oleic acid in 1-ODE. Here we are trying to synthesize cost effective nanomagnetites by using common materials present in our daily life such as sunflower oil, common vinegar and drain opener, which are freely available in the market. By this cost effective greener method, It is possible to synthesize high-quality nanocrystals. Our research confirms that by using this greener synthetic route we can reduce the cost of starting materials.

Keywords: Contamination, Arsenic remediation, Sunflower oil, Vinegar, Green synthetic, Magnetite nanocrystals.

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INTRODUCTION

Nanomaterials are substances having at least one dimension between 1-150 nm. Their properties differ from those of the same materials with micron- or mm-scale dimensions. Nanomaterials can be chemically or physically manipulated for specific application. Nanotechnology has been proved efficient in improving air, water, and soil quality. It can help in detection and sensing of pollutants and their control. Fine sized magnetite usually requires highly pure grade chemicals and lab tools such as stirrers, temperature-controlled heaters, and inert atmosphere. Non-aqueous mediums are also preferred for high monodispersity and uniformity [1].

In a typical synthesis, an iron salt or oxide is mixed with a surfactant and boiled in a high boiling point solvent under air-free reflux conditions[1]. The most notable examples of this type of synthesis are refluxing iron acetylacetonate, oleic acid, oleylamine and 1,2-hexadecanediol in diphenyl ether[2,3] , heating iron oxohydrate (FeOOH) with oleic acid in 1-octadecene (ODE)[4], precipitating FeCl3 with oleic acid and further heating to a boiling in 1 –octadecene (ODE)[5], and mixing FeCl3 and sodium oleate before refluxing the precipitate in a mixture of oleic acid and ODE[6].

All of these methods have limitations, as they require high-purity grade chemicals, restricting their use in very low cost operations. So our aim is to synthesize magnetite nanoparticles for environment-friendly uses through chemicals readily available in the open market. Earlier soya bean, corn and olive oil were used to synthesize nanomaterials by kitchen synthesis [12].

MATERIALS AND METHODS

Materials

Edible oil, Fortune sunflower oil, Pidilite klog remover, Top's vinegar was purchased from the market. Laboratory tap water. Rust collected from different sources of rusted iron, such as the iron sheet that was found inside university campus, iron angles and rods found on the play ground.

Soap making process

Pidilite klog remover (20 g) is dissolved in 50 ml of tap water and then poured warm into glass bowl containing 100 g of sunflower oil. A wooden spoon is used to stir the mixture. This is kept in an open area to dry and cure, until a solid hard soap is obtained.

Production of FAM (fatty acid mixture)

Finely grated 50 g of soap is mixed with 500 ml of tops vinegar. The solution is then boiled for 20–40 min, with constant stirring, till all the soap get dissolved. After cooling, there is formation of two distinct layers. The top layer is organic layer which is removed and transferred to a pan. This mixture is then heated until boiling so that all the remaining acetic acid and water evaporates.

Magnetite Nanocrystals synthesis

Rust powder (2 g) obtained for different sources is mixed with 40 g FAM (fatty acid mixture) and placed over a pan. This solution is boiled by closing with a lid for approx 2 hr, to produce a thick smoke. A black gelatinous magnetic material was obtained when this thick smoke diminishes (Fig.7). 5g slurry from the pan is boiled for 30 min. after mixing with the soapy water which is prepared by dissolving 5g soap in 75 ml of hot water and boiled until dissolved. The unreacted solid is removed by filtering. A magnet is used to collect water-soluble magnetite nanocrystals which are then washed with water and redispersed in water or ethanol.

RESULTS AND DISCUSSION

Limited greener and cost-effective synthetic methods are reported in the field of nanotechnology. Olive oil[9] and Therminol 66[10] are most widely used solvents.

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$$FeOOH + C_{18}H_{34}O_2 + C_{18}H_{36} \xrightarrow[320^0]{N_2/Air} Fe(oleate)_3 \xrightarrow[1\text{-}2hrs]{} Fe_3O_4 \text{ nanocrystals}$$

Iron oxohydrate Oleic acid 1-octadecene Intermediate

Figure 1: Mechanism of the decomposition of iron oleate for magnetite nanocrystals.

In this greener route, the main starting materials of the synthesis, iron precursor and the oleic acid, can be replaced with readily available chemicals. Edible oil such as sunflower oil can replace oleic acid with a mixture of fatty acids that are formed via saponification that is followed by acidification.

Table 1: Fatty acid composition of different types of edible oil [17]

Fatty acids %	Sunflower oil (n=5) Mean ± SD	Soybean oil (n=3) Mean ± SD	Mustard oil (n=5) Mean ± SD	Palm oil (n= 3) Mean ± SD	Coconut oil (n = 6) Mean ± SD
Caprylic (C8:0)	__	__	__	__	6.21 ± 0.34
Capric (C10:0)	__	__	__	__	6.15 ± 0.21
Lauric (C12:0)	__	__	__	__	51.02 ± 0.71
Myristic(C14:0)	__	__	__	1.23 ± 0.28	18.94 ± 0.63
Palmitic (C16:0)	6.52 ± 1.75	14.04 ± 0.62	4.51 ± 3.83	41.78 ± 1.27	8.62 ± 0.50
Stearic (C18:0)	1.98 ± 1.44	4.07 ± 0.29	2.78 ± 0.59	3.39± 0.65	1.94 ± 0.17
Oleic (C18:1)	45.39 ± 18.77	23.27 ± 2.43	38.21 ± 21.88	41.90 ± 1.20	5.84 ± 0.50
Linoleic (C18:2)	6.02 ± 16.75	4 52.18 ± 2.64	25.31 ± 5.74	11.03 ± .02	1.28 ± 0.18
Linolenic (C18:3)	0.12 ± 0.09	5.63 ± 3.48	11.30 ± 6.09	-- --	-- --
Arachidic (C20:0)	-- --	-- --	10.86 ± 3.29	-- --	-- --
Erucic (C22:1)	-- --	-- --	11.35 ± 13.83	-- --	-- --

FeOOH can be replaced by rust .The new chemical reaction [12] then becomes:

Rust (hydrated iron oxides) + Fatty Acid Mixture (FAM) ⟹ Magnetite (Fe_3O_4) Nanocrystals

Soap (mixture of fatty acid salts) is produced by saponification of sunflower oil , When soap is acidified with vinegar, FAM (mixture of long-chain organic acids) is formed. There are different fatty acids that constitute FAMs, but four of these are almost always dominant [13]: oleic acid [(9Z)-octadec-9-enoic acid], stearic acid (octadecanoic acid), palmitic acid (hexadecanoic acid) and linoleic acid [(9Z, 12Z)-octadeca-9, 12-dienoic acid] Fig.1.The formation, structure and size of nanomagnetites are confirmed by IR spectra, STEM and XRD analysis.

IR Spectrum

The peak at 570.95 cm^{-1} is due to the Fe- O bond vibration of Fe_3O_4 nanoparticles confirming the formation of nanomagnetites-Fig.2.

TEM Analysis

High resolution transmission electron microscopy (HRTEM) images were obtained at the main zone axes in order to determine the characteristics of magnetite nanoparticles,. Fig.3- HRTEM imagesInstrument name: FEI Tecnai G2 F20, Analyzed at 200KV. Courtesy: HRTEM Facility, NIPER, Mohali STEM analysis of nanomagnetites prepared from Mustard oil shows that general size is from 20-100 nm.

XRD Analysis

XRD pattern of the sample, which is quite identical to pure magnetite and matched well with that of it (RRUFFID=R080025)

Applications of Nanomagnetites

- Millions of people in south Asia are effected by arsenic (As) contamination in drinking water, including India and Bangladesh [11]. The toxicity of arsenic can cause from skin lesions to cancer of the brain, liver, kidney, and stomach Nanomagnetites were used as a most efficient agent for removal of heavy metals such as As and Cr for cleaning polluted water. Arsenic is naturally present in groundwater in the forms of arsenite (AsO_3^{3-}) and arsenate ($AsO_4^{\ 3-}$). These anions resemble phosphite ($HPO_3^{\ 2-}$) and phosphate ($PO_4^{\ 3-}$) ions, and it is this similarity that is the dominant source of their toxicity. Arsenite and arsenate block ATP-- ADP conversions by permanently replacing phosphate groups [14]. Although arsenic-contaminated groundwater belongs to local scale pollution, this problem prevails all over the world. Traditional treatment technologies are not effective and magnetite nanoparticle seems to be a good alternative due to its highly selective adsorption toward arsenic and feasibility on regeneration. This nanomaterial exhibited high As(V) adsorption capacity, up to 206.9 mg g-1, which is the highest reported [12].
- Nanomagnetites can be used as a green catalyst.
- Nanomagnetite can be used as Encapsulation within polycaprolactone microspheres for bone replacement.
- Nanomagnetite can be used in biomedical applications.
- The two-dimensional arrays of nanomagnetite particles can be used for fundamental rock magnetic studies.
- Nano-sized magnetite can be used in the wastewater treatment for ciprofloxin like biologically non-degradable antibiotics.
- Nanomagnetite can be used in target drug delivery to enhance the curative effect and minimize the adverse effects of an anticancer drug.
- Magnetite and maghemite nanoparticles and their suspensions are widely used in different industrial applications like magnetic sealing, oscillation damping, position sensing or magnetic storage media [15]. The ferrofluids contain iron oxide magnetite nanoparticles. Recently, ferrofluids have been used in conjunction with micro contact printing and capillary filling to fabricate patterned structures of magnetic materials on the micron scale. The ability to generate patterns of ultrafine magnetic particles has versatile technological applications, because of the information density on tapes, for instance, is inversely proportional with the size of the particles. Research has been done on finding the use of ferrofluids as magnetic inks for ink-jet printing. Magnetic inks are presently used in printing USA paper currency, as can be demonstrated by the attraction of a genuine dollar bill to a strong magnet [16].

Figure 1: Four major constituents of FAM oleic acid [(9Z)-octadec-9-enoic acid], linoleic acid [(9Z, 12Z)-octadeca-9, 12-dienoic acid], stearic acid (octadecanoic acid), and palmitic acid (hexadecanoic acid)

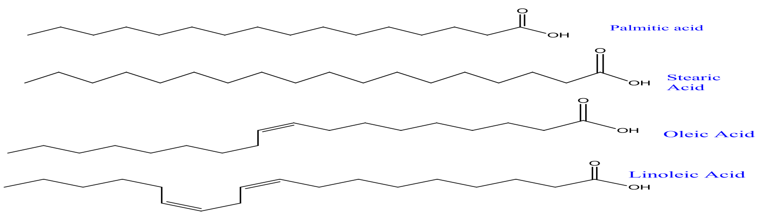
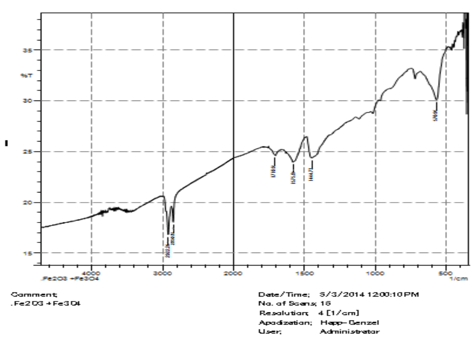


Figure 2: IR spectra



SHIMADZU

	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	570.95	30.104	2.964	619.17	516.94	50.935	1.872
2	1444.73	24.369	0.107	1448.59	1410.01	23.529	0.045
3	1575.89	24	0.03	1577.82	1570.11	4.777	0.002
4	1710.92	24.667	0.052	1726.35	1708.99	10.509	0.02
5	2850.88	18.025	1.777	2877.89	2430.39	299.625	-3.296
6	2922.25	16.815	2.498	2949.26	2877.89	52.637	1.765

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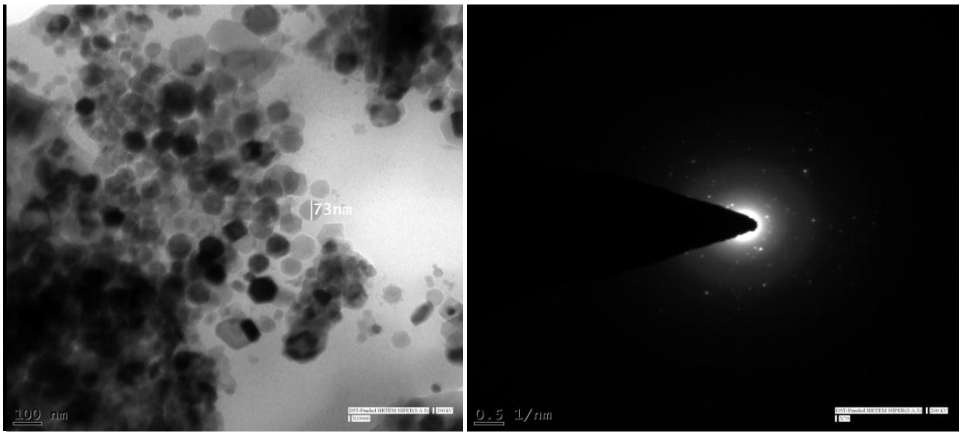
Figure 3: HRTEM images



Instrument name: FEI Tecnai G2 F20, Analysed at 200KV. Courtesy :HRTEM Facility,NIPER, Mohali STEM analysis of nanomagnetites prepared from Mustard oil show that general size is from 20-100 nm.

Figure 4a: X-ray diffraction of synthesized nanomagnetite Courtesy: PunjabUniversity, Chandigarh

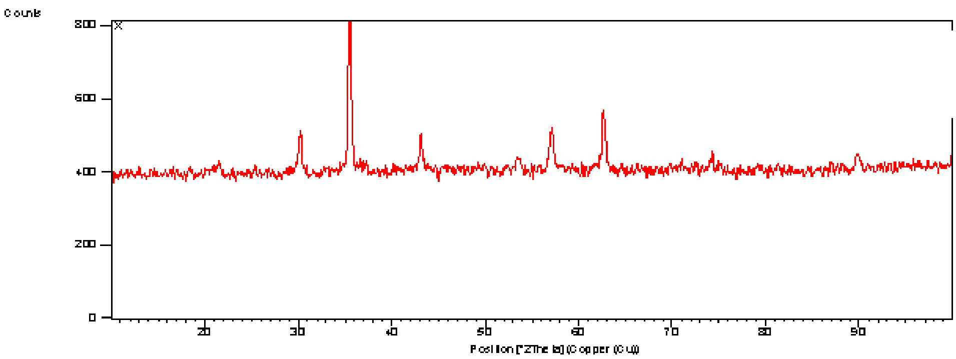


Figure 4b: X-ray diffraction of magnetite from database

Courtesy: http://rruff.info RRUFFID=R080025

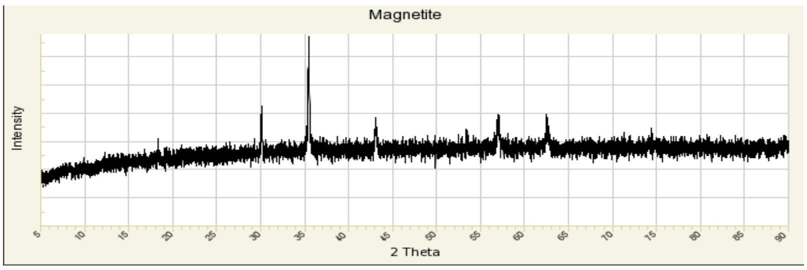


Figure 5: Scheme of the sunflower oil assisted synthesis of nanomagnetites

A, B, C & D: Ingredients for atypical nanocrystal synthesis include: Fortune brand sunflower oil, Tops vinegar, bowl, pan, D-klog drain cleaner, and rust.

Synthesis starts with soap making, the first step is to mix the sunflower oil with the D-klog drain cleaner and water.

F: The soap solidifies after curing for 1 day. The soap is grounded to a fine powder, then it is mixed with vinegar while heating. When all of the soap gets dissolved, there is formation of two layers: a yellow top layer of fatty acid mixture (FAM) and a cloudy white/yellow bottom layer. The top layer is then heated at 110^{0}C to remove excess water and vinegar by-products. Clear yellow FAM is collected. A fine powder Rust and FAM are mixed. This mixture is heated for 2 h at below and near boiling temperatures. The temperature is measured using a standard mercury thermometer.

G: Formation of Magnetite (black)

H: TEM micrograph is obtained after magnetic separation. Scale bar: 20 nm

CONCLUSION

By our research work it is confirmed that it is possible to synthesize high-quality nanocrystals by simple greener methods. Our research confirms that by using this greener synthetic route we can reduce the cost of starting materials for synthesis of nanomagnetite crystals, which have wide range of applications in current world.

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