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Magnetite Nanoparticles Synthesis by low intensity Ultrasonic Waves and Its Using as Adsorbent for Bromophenol Blue and Chlorophenol Red as model Pollutants

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Abstract

Magnetite nanoparticles (NPs) has been successfully synthesized in presence of low frequency ultrasonic waves and then characterized. It has been used as adsorbent for Bromophenol Blue (BPB) and Chlorophenol Red (CPR) as an Organic Pollutants. Langmuir and Fruendlich isotherms were choice and tested to fit by using different initial concentrations of BPB and CPR as a model compound. It was found that the Freundlich isotherm model could be best defined experimental data in comparison with Langmuir. Both of pollutants have big molecular structure that formed strong Van der walls forces that lead to multi-layered adsorption then Freundlich isotherm could be worked well. Also the adsorption rates were compared. It was be found BPB were more adsorbed than CPR. It can be demonstrated by more stable coupled bond that were formed between pollutants and NPs. BPB have more unpaired electrons then can be form more bonds to NPs.

Keywords: Ultrasound; Synthesis; Magnetite Nanoparticle; Adsorption; Pollutant; Isotherm

1. Introduction

Plastics, pharmaceuticals, pesticides and many other practical materials contain Phenolic compounds. Also one of the main by-products of many industries such as chemical processing is such these pollutants (Ahmaruzzaman, 2008). Nowadays, the world developed industries create a large number of pollutants that our unique planet has ever seen. Phenolic compounds because of their aromatic rings which have high stability remains for long time at natural water resources. In this regard, many researchers have a serious challenge to degrade or adsorb these compounds from industrial contaminated water, prior to its entrance to nature. One of the growing techniques for water contaminants elimination which is considered by many researchers is adsorption. It is worth to mention that some various methods in many papers have been introduced for organic polluted water purification such as; wet oxidation (Chaliha et al, 2008), activated clay adsorption (Hameed, 2007) and organo clays (Caqueret et al, 2008; Diban et al, 2008). Sonochemistry is a best of them because of its capabilities to be a facile route operating under ambient situations. Ultrasonic irradiation causes cavitations in a fluid medium where occur the formation, growth and implosive collapse of bubbles. These period of events lead to intense local heating around 5000 ^{0}C and high pressure over 1800 kPa that form any chemical reactions (Esmaeili-Zare et al, 2012; Sakka et al, 1984; Entezari et al, 2005; Bogush et al, 1987; Sakka et al, 1982; Masjedi-Arani et al, 2014). Nanotechnology introduces new practical aspects for many branches of science such as Chemistry (Tural et al, 2009), Materials (Kreylinga et al, 2010), Biology (Graham et al, 2005) and Medicine (Salvati et al, 2011) which have developed the best results in last couple of decades. Nanomaterials provide larger adsorption surface that make it an interesting domain for any researcher who work in water purification area. A crucial problem in this domain is focused on Phenolic removal study because of hydrophilic groups attached to its structure and their stability (Bujdosó et al, 2011). Magnetite NPs have large surfaces that increased these tendencies as an adsorbent (Ismail et al, 2013) and also can be separated easily by a magnet (Attia et al, 2013). The present scholar concentrates on two multi-ring contaminants adsorption by Fe_3O_4 NPs that are synthesized in assistance of low intensity ultrasonic waves and compares their adsorption with each other. On the other hand, it tries to tell us why adsorption forces may be weak or strong and where is molecular structure's role on these phenomena.

2. Materials and methods

2.1 *Fe_3O_4 NPs synthesis*

First dissolved $FeCl_3$ and $FeCl_2$ salts with 2:1 molar rates in 50 ml distilled water respectively. Nitrogen gas flow bubbled to solution for 3 minutes. The continuous 24 kHz ultrasonic waves at 50% intensity induced to solution while 1 M Ammonia added drop wise to solution every 5 seconds for 30 minutes. Afterwards, the black-brown participant is formed which is later centrifuged at 1000 rpm. The top water, then, is separated by decantation and the participant becomes rinsed 2 times by distilled water and once subsequent ethanol is added. The black magnetite NPs were obtained which are characterized by XRD and SEM techniques.

2.2 *Adsorption experiments*

Different concentrations of 10 ml pollutants at this natural pH are poured in some flask in which, 0.002 gr NPs are added to each of them. The flasks are shaken for 45 minutes (on a shaker at 240 rpm). The UV absorbance spectra were, then, recorded. Finally, the Isotherm study was performed at some varying concentrations that show the proper isotherm. Meanwhile, all experiments were performed at 25 ^{o}c room temperature.

3. Results and discussion

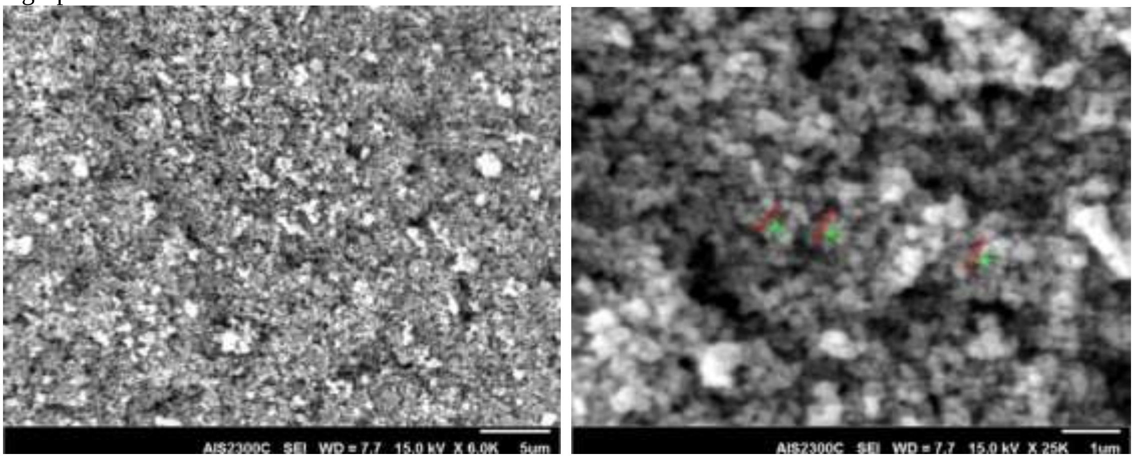
3.1 *Magnetite characterization*

The synthesized NPs were characterized by Philips Analytical X-Ray B.V. with Cu anode material, and NERON scanning electron microscope (SEM) to obtain some evidence from synthesized NPs.

3.1.1 SEM images

Figure 1 parts a and b show SEM images of synthesized NPs. The particle size range differs from (60-90) nm that may refer to grain agglomeration. The NPs, firstly, formed in small sizes, but some forces–such as quantum size effects–caused some particles to have strength surface interactions towards each other, which in turn, results agglomeration (Das et al, 2013).

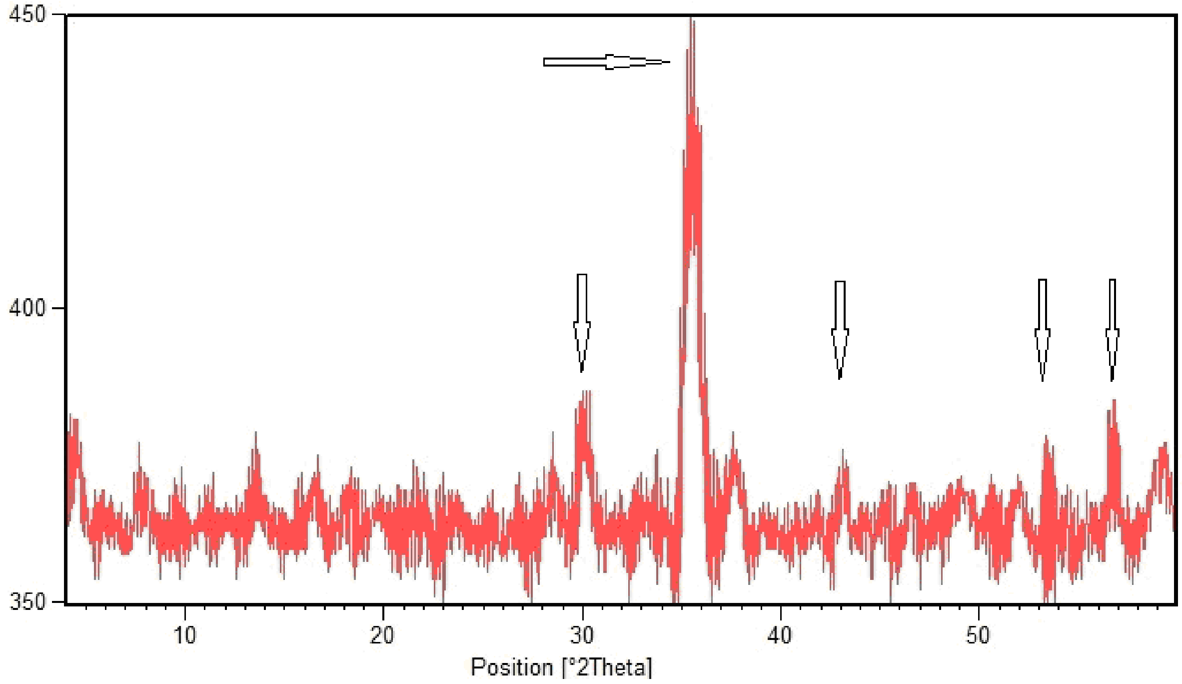
Fig1-parts a and b



3.1.2 XRD peaks

Figure 2 shows the XRD pattern of Fe_3O_4 NPs that synthesized in presence of ultrasonic waves. Some of the characteristic Fe_3O_4 crystalline peaks are shown at Figure 2 at 2θ=31.0, 36.0, 43.0, 53.0 and 57.0. By using the Debye-Scherrer formula $D = 0.9\lambda/\beta\cos\theta$ for the main peak which is observed in XRD diagram, the average size of the synthesized NPs is calculated 10.0 nm (λ =0.1541 nm). It differs with SEM results in size diameter that indicates agglomeration that caused NP diameter seem about (60-100) nm.

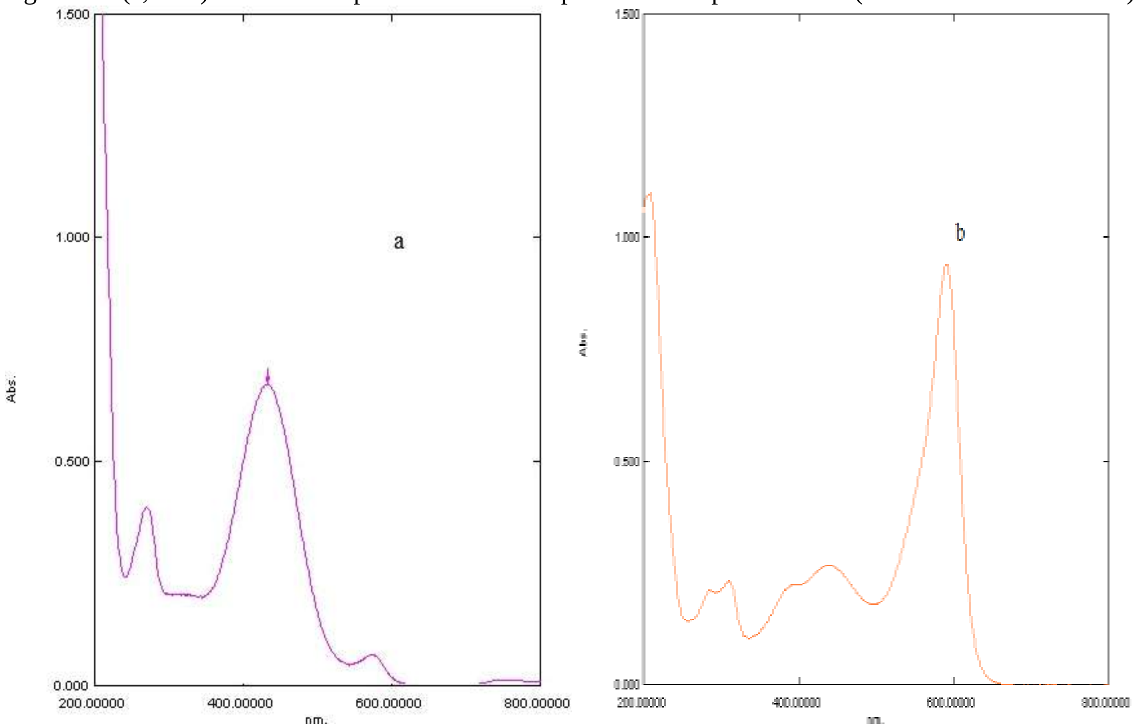
Figure 2: XRD diagram of Fe_3O_4 NPs



3.2 Bromophenol blue and ChloroPhenol red adsorption study by Fe_3O_4 NPs

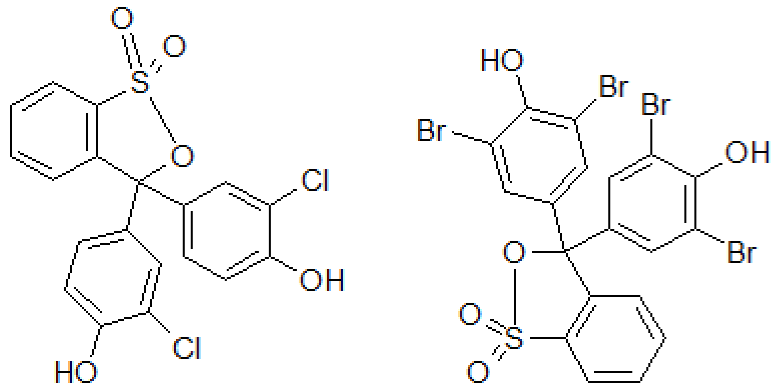
Experiments about BPB and CPR adsorption are carried out in many flasks contain 0.002 gr of Fe_3O_4 and 10 ml from different concentrations of pollutants that remains 45 minutes on a shaker at 240 rpm. The adsorption experiments reach to equilibrium after the time mentioned above. Contains filtered (also could be separated by a magnet) and UV/VIS spectra was recorded by Shimadzu spectrophotometer at the range of (200-800) nm. The pollutants show a strong UV/VIS peak at 591 nm and 428 nm for BPB and CPR respectively. Figure 3(a, b) shows the UV/VIS spectra for BPB and CPR.

Figure 3(a, b): A sample UV/VIS spectra of pollutants (a: CPR- b: BPB)



Some different factors may affect adsorption efficiency of pollutants by adsorbent. Three are assigned as more considerable of those. First of them, can be mentioned as interactions between pollutant's polar groups; mainly atoms with non-pair electrons and empty orbital of magnetite NPs. Another can be explained by van der walls forces that are based on dispersion interaction of particles dispersed throughout the solution and finally the last may be mentioned as hydrogen bonding interactions between the hydroxyl groups that chemically bonded to Fe_3O_4 NPs and some electrophil atoms bonded to pollutants such as Oxygen, Chlorine and some Bromine and Sulfur. At the same conditions, in presence of fixed magnetite after 45 minutes contact time the BPB was about 4% more adsorbed.

Figure 4: Molecular structure



This can be attributed to characteristic's structure of those (Figure 4). Both of them have three aromatic rings but BPB have a few more substitutions with unpaired electrons. Junctions between pollutant's molecules and magnetite NPs those bond them made by two contemporaneous bridges (Jayarathne et al, 2012). Thus it can be concluded that BPB may form more bridge junctions to NPs rather than CPR.

3.3 Isotherm studies

Those were be conducted by mixing 0.002 gr Fe_3O_4 at a flask contains 10 ml solution at different concentrations of pollutants. The initial concentrations were adjusted in the range of (1-20) ppm at its natural pH. The sample solutions first were shaken well for 45 minutes by a shaker at 240 rpm and then the filtered solutions were analyzed. The Langmuir and Freundlich isotherm models were worked to fit the experimental data. If q_e was adsorbing amount of BPB and CPR at equilibrium concentration (mgr/gr), C_e pollutant's equilibrium concentrations in solution (mgr/lit), q_{max} is the maximum adsorption capacity (mgr/gr) and finally k_l is the Langmuir constant (lit/gr); Langmuir model can be written same $\left({c_e}/{q_e} \right) = \left({1}/{k q_{\max}} \right) + \left({c_e}/{q_{\max}} \right)$. When k_f and n suppose as Freundlich constant, Freundlich can be write as $q_e = k_f c_e^{1/n}$ or $\ln q_e = \ln k_f + {1}/{n} \ln c_e$. Multilayered adsorption in gas phase was studied as BET model, which is then, generalized by a few researchers to liquid phase, but this supposition has not been established[21], therefore in present research we focused on Langmuir and Freundlich isotherm study. We recognized the Langmuir isotherm as monolayer adsorption theory, whereas the Freundlich model as an experimental isotherm does not have any opinion about adsorption behavior. Figure 5 part a and b show results for pollutant's adsorption which are fitted by Freundlich and Langmuir isotherm models respectively for both pollutants.

Figure 5-a: Freundlich model for BPB (◆) and CPR (▲)

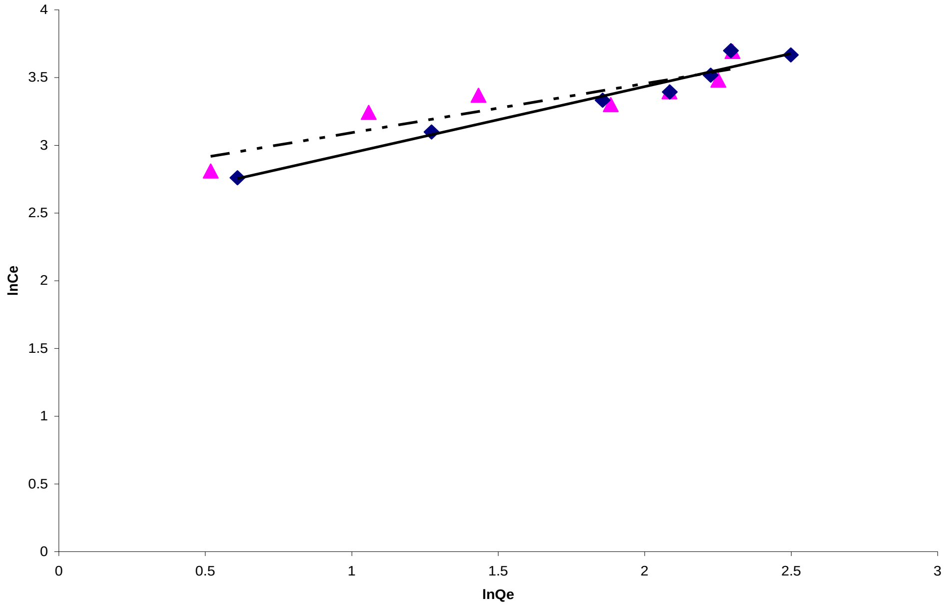
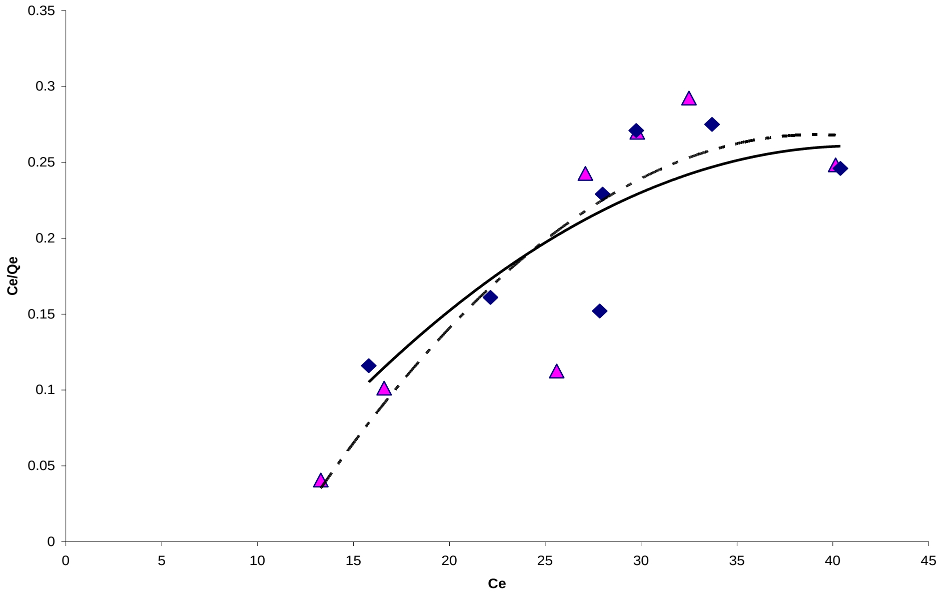


Figure 5-b: Langmuir model for BPB (◆) and CPR (▲)



The Freundlich isotherm may be better explaining adsorption phenomena for two pollutants rather than Langmuir isotherm. It must be related to complexity formed bonding forces those mentioned at last segment between pollutants and adsorbent that can't be explained by an initial isotherm model such as Langmuir and the experimental isotherm may be better explain.

4. Conclusion

In this work the nano-particles of magnetite by ultrasonic waves have successfully been synthesized. The result obtained analyzed by SEM images and XRD pattern to confirm. Then the synthesized magnetite NPs used as adsorbent for BPB and CPR as recognized pollutants. Results show BPB adsorbed better that can be related to more unpaired electron atoms at its structure in comparison with CPR. Both pollutants' adsorption may be better defined by Freundlich isotherm rather than Langmuir. It can be related to Van der walls forces that may be affect to form bonds more than one layer that insists by Langmuir model.

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