Journal of Soil Sciences and Agricultural Engineering

Journal homepage: <u>www.jssae.mans.edu.eg</u> Available online at: <u>www.jssae.journals.ekb.eg</u>

Application of Functionalized Iron Magnetic Nanoparticles (γfe₂o₃₎ by Humic Acid for Elimination of Anionic and Cationic Pollutants from Wastewater

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ABSTRACT



Due to expensive costs in wastewater treatment, humic acid (HA) functionalized onto Fe₂O₃ magnetic nanoparticles (FeMNPs-HA) was synthesized in this study to remove Cr-6 and Pb+2 from wastewater. FeMNPs-HA was synthesized by the co-precipitation method for cheap and eco-friendly materials. FTIR and TGA were used for the characterization of FeMNPs-HA. FTIR showed similar bands for both HA and MNPs-HA and this indicated that HA was successively functionalized at FeMNPs. Moreover, TGA analysis showed high stability of material synthesized, since loss of weight began over 600 °C. Batch adsorption experiment was conducted to state the optimum conditions for removal of positive and negative ions (Pb⁺² and Cr⁶) from the aqueous solution using FeMNPs-HA. Adsorption of the studied metals onto FeMNPs-HA reached equilibrium in less than5 minutes, whereas the adsorption process wasn't affected by pollutants concentrations. Langmuir adsorption model was suitable to explain the sorption process of Pb⁺² and Cr⁻⁶ onto MNPs-HA with maximum adsorption capacities reached 99.99 mg g⁻¹. The FeMNPs-HA proved to has the capability for elimination more than 99% of Cr^{-6} and Pb^{+2} from the wastewater at optimized pH. Synthesized material was applied for toxic metals elimination from industrial wastewater (IWW), FeMNPs -HA showed high removal efficiency for Cd, Cr and Ni. Based on the adsorption data; FeMNPs -HA could be considered as an efficient material for wastewater purification from heavy metals regardless their charge.

Keywords: Magnetic Nanoparticles; Humic Acid; Water Purification; Heavy Metals; Isotherm Study.

INTRODUCTION

Due to industrial activities such as tanneries, textiles, ceramics, photography, plating ...etc, different metals were discharged into wastewater and cause hazard impacts on the ecosystem, since many of these industries aren't connected with sewerage system (Li *et al.*, 2014). Consequently, they discharge their effluents directly to nearest water bodies, which resulted in risks to aquatic organisms, soils and plants irrigated with this kind of water and finally for humans consume on these plants (Sharma *et al.*, 2009). Many technologies was successfully used for elimination of toxic metals from wastewater such as precipitation, electrochemical reduction, ion exchange, electrodeposition, membrane technology, and adsorption.

Adsorption is considered as most common and effective technique for elimination of different toxic metals from wastewater for economic reasons. There are many adsorbent materials were used for metal removal from wastewater such as adsorption onto activated carbon (Khezami and Capart, 2005), hydrotalcite (Lazaridis and Asouhidou, 2003), coconut husk (Tan *et al.*, 1993), maple sawdust (Yu *et al.*, 2003), biogas residual slurry (Namasivayam and Yamuna, 1995), sugarcane pulp residue (Yang *et al.*, 2009), cellulosic graft copolymers (Eromosele and Bayero, 2000), cross-linked chitosan (Rojas *et al.*, 2004), lignin (Yun *et al.*, 2008), red mud (Pradhan *et al.*, 1999) andSuper-Amphiphilic Silica-Nanogel Composites (Atta *et al.*, 2016). Many scientists

had developed novel methods for production and employment of iron magnetic nanomaterials (FeMNPs) with marked characteristics and utilities, due to their diameter in nano size, large surface area to volume ratios and super-magnetism properties (McHenry and Laughlin, 2000; Afkhami*et al.*, 2010 and Pan *et al.*, 2010). Many scientists stated that FeMNPs can adsorb different kinds of pollutants from wastewater (Hu *et al.*, 2005; Mayo*et al.*, 2007; Yean *et al.*, 2005 and Yavuz *et al.*, 2006).

Humic acid has brilliant binding characteristics and electrostatic contacts with toxic metals, leading to metalorganic complexes (Sounthararajah *et al.*, 2015). These complexes can improve the sorption of toxic metals onto iron magnetic nanoparticles. We aim in this study to functionalize γFe_2O_3 nanoparticles with humic acid to improve its ability for removal of cationic and anionic pollutants (Cr⁻⁶ and Pb⁺²). Also to study some factors (pH, pollutant concentration and time) that can change removal efficiency of γFe_2O_3 nanoparticles. Moreover, the adsorption mechanism of Cr⁻⁶ and Pb⁺² onto adsorbent materials was evaluated during application of Langmuir and freundlich isotherms.

MATERIALS AND METHODS

Materials

Stock solution (1000 mg Cr(VI) L^{-1} and 1000 mg Pb⁺² L^{-1}) were produced by dissolving 2.83, 3.97 g of potassium di-chromate and lead acetate, respectively in 1

Liter of deionized water. Desired concentrations of the adsorption experimental solutions were obtained by dilution of stock solution with deionized water. Humic acid was purchased from Canada humic company, Egypt. All chemicals employed in this study were analytical grade.

Synthesis of MNPs (γFe₂O₃)

A magnetic nanoparticle was synthesized by coprecipitation method described by Jeon *et al.* (2009). Briefly, dissolving a molar ratio of Fe (Cl)₃ and Fe SO₄ using ultrasonic waves. NaOH (6.5 M) was drop-wise into the previous solution under stirring to precipitate magnetic nanoparticles (Fe₃O₄) with diameter around 10 nm. The black precipitate was collected by magnetic field and heated at muffle (300 °C) to produce γ Fe₂O₃ nanoparticles. FeMNPs were grinded and kept in desiccator for HA immobilization.

Functionalize FeMNPs with humic acid.

To functionalize yFe₂O₃ nanoparticles with humic acid, 1 g of humic acid was dissolved in 100 ml NaOH (0.1 N) using ultra-sonication for 1 h. Then the solution was added to 100 ml of n-heptane and stirred for 1 h using stirrer. Thereafter, 1 magnetic g of γFe₂O₃ nanoparticleswas added to the solution and stirred magnetically under heating for 48 h. The supernatant was poured and the precipitate was washed with methanol and several times with deionized water until the solution was neutralized. yFe2O3-HA (FeMNPs -HA) was oven dried at 70 °C and pulverized using a milling process.

Characterization of studied materials.

Functional groups initiated onto both materials synthesized were checked using Fourier transform infrared spectroscopy (FT-IR), data were got from the diffused reflectance style by employing Bruker Vertex 80 joined with Ram-FT module (RAM II) spectrometer. Thermogravimetric analysis (TGA) of FeMNPs -HA made by TA equipment SDTQ600 from ambient temperature to 1000 °C at a speed of 10 °C min⁻¹ at nitrogen atmosphere with gas flow at 20 ml/min.

Batch adsorption experiment.

Batch adsorption study was carried out to conduct the optimum conditions of Cr (VI) and Pb⁺² adsorption onto the studied materials at room temperature (30±1 °C). 0.1 g of studied materials was employed in a flask (250 mL) having 50 mL of pollutant solution (100 mg L⁻¹) at optimum pH. To state the efficacy of time on the optimum reaction time, the reaction solution was then subjected to agitation (200 rpm) by employing a horizontal shaker for different time intervals. Similar investigates were done to study the efficacy of pollutant concentrations (10-100mg L-1) under pH values of (2, 5, 7 and 9) for aqueous phase on the adsorption capacity. Wastewater was filtered and stored at 4 °C until analysis. Chemical analysis of elements under study was carried out using inductively coupled plasma (ICP-AES) with low detection limits of Cd (5.0 µg L^{-1}), Cr (5.0 µg L^{-1}), Pb (50.0 µg L^{-1}) and Ni (5.0 µg L^{-1}). The samples were diluted before ICP measurement where necessary.

Real industrial wastewater purification.

A real industrial wastewater (IWW) collected from industrial wastewater treatment plant (employed for El-Rubiky taw city) was employed for static adsorption experiment. Wastewater samples were collected using glass bottles (4 L) as reported by Ahrer *et al.* (2001). Samples were kept in an ice box until it brought back to the laboratory. Thereafter, samples were filtered and stored at 4 °C till adsorption study was done. Elemental analysis of collected wastewater (Table 1) showed that it contains higher amounts of Cr^{+3} and Ni^{+2} , while it showed trace concentrations of other elements. Batch adsorption study was carried out to conduct the capability of studied material for removal of Cd^{+2} , Cr^{+3} and Ni^{+2} at room temperature (30 ± 1 °C). 0.1 g of studied materials was placed in a 250 mL glass bottle containing 50 mL of IWW (0.09, 4.9 and 62.3 mg L⁻¹ for Cd^{+2} , Cr^{+3} and Ni^{+2} respectively) at actual pH (8.3).

 Table 1. Elemental analysis of effluents discharged from IWW (mg L⁻¹).

Elements	Fe	Mn	Zn	Cu	В	Cd	Cr	Ni	Pb
IWW Effluents	0.219	0.058	0.07	Nd	0.04	0.09	4.9	62.3	0.02
FeMNPs-HA treatment						N.d	N.d	N.d	
Limits for irrigation water (FAO 2007)	5.0	0.20	2.0	0.2	0.75	0.01	0.01	0.20	5.0

RESULTS AND DISCUSSION

Characterization of studied material.

Humic acid was chosen due to its brilliant binding characteristics and electrostatic interactions with different metals, resulted to make metal-organic complexes. These complexes have an efficacy on the adsorption of different metals onto sorbent material (Sounthararajah, et al., 2015). Being the products of stochastic synthesis, HA has an elemental composition that is non-stoichiometric, and structure which is irregular and heterogeneous (Haves et al., 1989). FTIR was made and showed bands at 3400 cm⁻¹ belonging to H, bounded OH groups and might including those of COOH (Stevenson and Goh, 1971). Absorption in 2920 and 2850 cm-1 region refers to aliphatic C-H stretching, while 2337 cm⁻¹ refers to extended C-H stretch groups (Reddy et al., 2018). MNPs-HA showed similar bands indicating successful coating of HA onto surface of MNPs. In the IR spectrum of FeMNPs -HA, the C=O extension were found at 1461 and 1630 cm⁻¹indicating the carboxylateanion interacting with the Fe-O surface (Yantasee et al., 2007). S-H extension were found at 2329 cm⁻¹, which are characteristically very weak and rolled up by pollution of the C=O extension bands from the background (Jun et al., 2005). Moreover, bands of carboxylate stretches at 1600 and 1400 cm⁻¹ is harmonious with the carboxylate anion reacting with the Fe-O surface since the free carboxylic acid would have a C=O stretch above 1700 cm⁻¹ (Silverstein et al., 1974).

The thermo-gravimetric analysis (TGA) was done to state the amount of weight loss of synthesized material (FeMNPs -HA), either as a mission of increasing temperature, or isothermally as a mission of time and is shown at Fig 1(b). Approximately 38% weight loss was observed in the synthesized material (FeMNPs -HA) above 650 °C. This was attributed to the combustible HA present in synthesized material. However, no significant weight loss was showed between 946 °C to 1000 °C (Fig. 1b). This reflected the stability of synthesized material. These results are in accordance with those reported by Lassoued *et al.*, (2017) who stated that After 660° C, the curve of

TGA became parallel to the temperature axis, which emphasized high stability of α -Fe₂O₃nanoparticles.



Fig. 1. Different characteristics of synthesized material (a) FTIR spectra of HA, MNPs and synthesized material (FeMNPs -HA), (b) TGA of FeMNPs -HA.

Batch adsorption experiment.

The removal of different chargeable pollutants to synthesized material is largely organized by the source and concentration of HA, metal ion concentration, pH, and other parameters (Hankins *et al.*, 2006; Liu *et al.*, 2004). Therefore, it is essential to state if the variance of these factors in the environmentally relevant range would effect on the removal of studied metals by FeMNPs-HA.

Influence of pH

pH considered an essential parameter in the adsorption capacity of studied material. Different pH ranges were affected the ionization grade and solubility of the solute as the surface charge of the adsorbent (Noh and Schwarz 1989; Nandi et al., 2009). To study the impact of initial pH on elimination of studied contaminants using FeMNPs -HA from aqueous solution, sorption study were achieved at different pH values (2, 5, 7 and 9) and observance all other study conditions constant (100 mgPb⁺² or Cr (VI) L⁻¹; temperature, $30 \pm {}^{\circ}$ C; agitation, 200 rpm; studied material, 1 g L⁻¹; contact time, 300 min). From the results got shown in Fig. (2), we state that the pH of the adsorption solution significantly influenced the adsorption capacity of studied material. Thus, as pH changes from acidic to basic states, Cr (VI) was less efficiently eliminated due to excess of hydroxyl ions resulted in the creation of aqua-complexes thereby delaying the sorption (Venkata et al., 2007a, b) and/or competing with Cr (VI) ions on the adsorbent material surface. Moreover, negative functionalized functional groups on adsorbent material considered a limited role in Cr (VI) adsorption, especially at basic conditions. Yoon et al. (2005) and Gao and Pedersen (2005) reported that pH of the solution influence on the amount adsorptive due to the spreading of surface charge of the adsorbent that could be changed (because of the formation of raw materials and the performance of activation), thus the amount of adsorption changeable consistent with the adsorbate functional groups. In general, FeMNPs -HA has the ability to remove more than 99% of Cr (VI) from aqueous solution at low pH. These results are in accordance with those obtained by Ferreira et al. (2017) who reported that the adsorption capacity of Cr(VI) using magnetic coated polymers was dependent on pH values, and it decreases the pH increases as a consequence of the charge repulsion between the surfaces of the solidnegatively-charged and the anionic species chromium(VI) CrO_4^{-2} . Adsorption exhibited a dependence on the electrostatic interactions. Also Hu *et al.*, (2007) studied the elimination of Cr(VI) on different magnetic particles and concluded that the maximum adsorption of Cr(VI) was obtained at pH 2.0.

While adsorption of Pb⁺²onto studied material wasn't affected by pH value. Since the removal of Pb⁺² recorded > 99% at different pH levels (Fig. 2). This might be attributed to excess of negative chargeable ions (at higher pH) on the adsorbent material which can hold positive chargeable ions (Pb⁺²). In addition to, brilliant binding characteristics and electrostatic interactions of HA with studied metals leading to metal-organic complexes at low pH. These complexes have an efficacy on the adsorption of studied metals on FeMNPs-HA. Also, hydroxyl groups functionalized onto synthesized material due to coated HA (fig. 1a) play an important role with adsorption of positive ions (Pb⁺²) at low pH.



Fig. 2. Influence of pH on the removal of Cr (VI) and Pb⁺² by nano FeMNPs -HA.

Influence of pollutant concentration

To state the effect of pollutant concentration on the adsorption capacity of studied material, batch adsorption experiment was employed using different pollutant concentrations varying from 0 to 100 mg Cr (VI) and Pb⁺² L⁻¹. Other operational conditions were stabilized at adsorbent dose 1 g L⁻¹, contact time 3h, optimum pH, temperature 30 \pm 1 °C and agitating at 200 rpm. Fig. 3 illustrates the influence of different pollutants

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concentrations on to removal efficiency of studied material. The results revealed that the removal of studied pollutant using FeMNPs -HA weren't affected by initial concentration. This was attributed to high adsorption capacity of synthesized material due to high surface area (Jeon et al., 2009). Moreover, humic acid functionalized has different kinds of functional groups as listed before in section 3.2.1 (see fig 1). This increase the chance of synthesized material to adsorb both kinds of chargeable pollutants (Cr⁻⁶ and Pb⁺²) especially at neutralization. This study revealed that compared to other adsorbent materials (Liu et al., 2008; Salem et al., 2014), the prepared MNPs-HA exhibited remarkable enhancement in different chargeable heavy metals. In addition to, the synthesized material (FeMNPs -HA) with adsorbed different chargeable pollutants could be easily desorbed from water with magnetic separations at very low magnetic field gradients (Liu et al., 2008), which can confidently decrease water treatment costs. It is estimated that the synthesized material FeMNPs-HA has wide applicability in the elimination of chargeable metals from wastewater.



Fig. 3. Influence of initial concentration on adsorption ratio of Pb⁺² and Cr (VI) onto FeMNPs -HA

Influence of contact time

Efficacy of contact time on the adsorption of studied pollutants was studied by changing contact time of the adsorption reaction from 10 to 600 minutes, and uniforms other operational conditions (optimum pH, pollutant concentration 100 mg L⁻¹, adsorbent dose 1 g L⁻¹, temperature 30 ± 1 °Cand agitating 200 rpm). The results revealed that contact time didn't affect significantly on the adsorption of studied pollutants, since optimum adsorption capacity was quickly achieved >99% removal during 5 minutes (Fig. 4). This implies that studies pollutants (Pb⁺² and Cr⁻⁶) can interact easily with the active sites of FeMNPs -HA and the adsorption process happened at monolayer, since the adsorption rate was independent on time. Davis and Bhatnagar (1995) stated that in the existence of HA, the oxidation of heavy metals to hydrous metal oxides is a comprehensive result of numerous interactions. If the oxide using the same sites for binding HA and metals, the binding of HA directly on the oxide surface may reduce the metal adsorption due to the sites blockage and competition. On the other hand, the binding of HA to oxide may prefer the uptake of metals because of the complexation between HA and metals, whereas the HA in solution could stop the fraction of metal from adsorbing to the oxide (Liu et al., 2008). The adsorption reached to equilibrium during first 5 minutes, this gives the

synthesized materials a preferable choice for wastewater treatment especially resulted from industrial activities.



Fig. 4. Influence of time on the removal of Pb⁺² and Cr (VI) using FeMNPs -HA

Isotherm study

Isotherm study was employed to explain the nature of adsorption onto studied material. Langmuir and Freundlich isotherms equation were studied for describing adsorption capacity data.

Langmuir isotherm is a theoretical isotherm developed in 1916; the Langmuir isotherm is expressed as the following equation (Balasubramaniam *et al.*, 2009).

Ce/qe= 1/(qmaxb) + (1/qmax) Ce

Where q_e is the amount (mg g⁻¹) of pollutant adsorbed at equilibrium, C_e is the equilibrium pollutant concentration (mg L⁻¹) in-water samples, KL and q_{max} (maximum adsorption capability) are the Langmuir constants of adsorption. A plot of *Ce/qe* versus *Ce* for the adsorption of Pb⁺² and Cr⁻⁶ ions onto FeMNPs -HA gives a straight line of the slop *1/qmax* and intercept *1/(qmax b)* as shown in Fig. (5).

Freundlich isotherm is commonly used to describe adsorption characteristics for heterogeneous surface. Freundlich isotherm can be expressed as the following equation:

$$q_e = K_f C_e^{1/n}$$

The linearized form of the Freundlich isotherm equation is:

lnqe= lnKF+ 1/n lnCe

Where K_f is the constant related to overall adsorption capacity (mg g^{-1}); 1/n is the constant related to surface heterogeneity (dimensionless).

The applicability of these two isotherm models was quantified by the square of the correlation coefficient r (r^2). The adsorption of Pb⁺²an Cr⁻⁶ onto FeMNPs were fitted well with Langmuir isotherm model, since the R² were close to unit using Langmuir equation than Freundlich equation. This implies that the adsorbent material has smooth surface and that all sites are identical and energically equivalent, thermodynamically this implies that each site can hold one adsorbate molecule, adsorption can't proceed beyond monolayer; the ability of a molecule to be adsorbed at a given site is independent of the occupation of neighboring sites, which mean there will be no interactions between adjacent molecules on the surface and immobile adsorption (Coulson *et al.*, 1991).



Fig. 5. Langmuir adsorption isotherm for Pb⁺² and Cr⁻⁶ adsorption onto FeMNPs -HA.

IWW experiment.

Effluents of IWW located at El-Rubiky industrial city (Cairo, Egypt) was employed for this experiment. Efficacy of FeMNPs -HA for removal of different metals from real IWW was tested during batch adsorption experiment (Table 1). The results showed that FeMNPs -HA has the ability to adsorb much amounts of chargeable elements from real environment without adjusting optimum pH. This was attributed to high adsorption capacity of MNPs-HA beside low concentration values of metals at tested real IWW. Moreover, checked elements were positively charged ions which are preferably adsorbed at higher pH. Synthesized material proved to has the ability to purify IWW to meet the legislation of irrigation water (FAO, 2007).

CONCLUSION

FeMNPs was synthesized and successfully embedded with HA by agitating with n-heptane and HA for 48 hours to increase its removal efficiency for anionic (Cr-6) and cationic (Pb+2) pollutants. Material synthesized was characterized by FTIR and TGA equipment. TGA results showed high stability for synthesized material. Batch adsorption experiment was employed to study the efficiency of studied material for removal of Cr (VI) and Pb⁺². The pH of the adsorptive medium markedly influence on the removal efficiency of Cr (VI), while adsorption of Pb⁺²onto studied material wasn't affected by pH value. Since the removal of Pb^{+2} recorded > 99% at different pH levels. Adsorption of cationic (Pb+2) and anionic (Cr-6) pollutants onto adsorbent material (FeMNPs -HA) weren't affected by pollutant concentrations or reaction time. Adsorption data was fitted well with Langmuir adsorption isotherm.

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تطبيق حبيبات أكسيد الحديد المغناطيسيه المتناهية الصغر والمشبعه بحمض الهيوميك في ازالة الملوثات الانيونيه والكاتيونيه من المياه العادمه

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نتيجة التكاليف الباهظة لمعالجة المياه العادمه. في هذه الدراسه تم تحميل حمض الهيوميك على حبيبات أكسيد الحديد المغناطيسيه المنتاهية الصغر لاز الة الكروميوم والرصاص من المياه العادمه. تم تحضير حبيبات اكسيد الحديد المغناطيسيه المحملة بحمض الهيوميك بطريقة الترسيب باستخدام أملاح الحديد الرخيصه والامنه وحمض الهيوميك. لتوصيف الماده المصنعه تم عمل اختبارات FTIR و TGA للتأكد من تحميل حمض الهيوميك على حبيبات اكسيد الحديد المغناطيسيه المعناطيسيه المحملة بحمض الهيوميك بطريقة الترسيب باستخدام أملاح الحديد الرخيصه والامنه وحمض الهيوميك. الاطوال الموجيه في حمض الهيوميك والماده المصنعه مما يؤكد تحمل حبيبات أكسيد الحديد بحمض الهيوميك بنجاح. أظهر اختبار TGA (مدي التحمل الحراري) ثبات عالى للماده المصنعه حيث بدأ فقدان في الوزن بعد 600 درجة مئويه. تم عمل تجربة ادمصاص ستاتيكيه بالمعمل لدر اسة الظروف المثلي لاز الة الايونات الموجبة والسالبه (الكروميوم السداسي والرصاص الثنائي) من المحلول الملوث باستخدام الماده المصنعه. أظهرت النتائج الاتي, ادمصاص العناصر العناصر المعناب على الماده والرصاص الثنائي) من المحلول الملوث باستخدام الماده المصنعه. أظهرت النتائج الاتي, ادمصاص العاصر المعناص العناص العنادي إلى خلي المعاد معنا من التفاعل, بينما لم تناثر تنائج عملية الادمساص بتركيز الملوث. تم تطبيق معادلات الادوميوم المداسي ولول حمس معاد لا التعاص يصل الي وي 9.90 محراجم. ود أن الماده المصنعه في تزيل أكثر من 99 % من الكروميوم والرصاص من الموث الموث المعادلة لانجبير بأقصي معدل ادمصاص وحبر الي وي 9.90 محراجم. ود أن الماده المصنعه يمكنها أن تزيل أكثر من 99 % من الكروميوم والرصاص المعاد معل ادمصاص يصل الي وي 9.90 محراجم. ود أن الماده المصنعه يمكنها أن تزيل أكثر من 99 % من الكروميوم والرصاص من المحلول الملوث عند رقم حموضه مناسب. تم معدل المصاص الانعام من المول المادي المواد المعادي وي وي من 90 % من الكروميوم والرصاص مان الموري الملول الملوث المعاد لم معل المصاص يصل الي و9.99 محراجم. ود أن الماده المصنعي أظهرت الماده المصنعه قدرة فائقه علي زالة الكرميوم النيكل. اعتمادا علي نتائج تجربة تطبيق الماده المصنعه في از اله العاص الشؤلة من مواه الملوث الماده المصنعي قدرة فائقه علي زالة الكرميوم النيكل. اعمادا علي نتائج تجربة الطبي معرب الماده المصدعه ماده قوية