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Preliminary Evidence for Enhanced Adsorption of Cadmium(II) Ions using Nano-Magnetite Aligned in Silica Gel Matrix

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The effect of aligning nano-magnetite particles in silica gel matrix to the adsorption was studied. Nano-magnetite particles were first synthesised and then aligned in a silica gel matrix to form nanocomposite. As such, it prevents the agglomeration of nanoparticles while providing porous path for the adsorbate to adhere on the adsorption sites. By aligning the nanoparticles in gel matrix, mutual cancellations of local magnetic fields among nanoparticles can be minimised. It is hypothesised that aligning the nano-magnetite particles in gel matrix can enhance its adsorption performance. Adsorption of Cd^{2+} ions were carried out using both non-aligned and aligned nanocomposite. Two adsorbent dosage was used, i.e., 0.1 g and 1 g in 50 mL of 100 ppm Cd^{2+} solution. Enhanced adsorption capacity was observed in aligned nanocomposite under both of these dosages. For the low dosage adsorption, the equilibrium adsorption capacity (Q_e) obtained from pseudo-second order model is 978.8 mg/g, which is 68 % higher than the non-aligned nanocomposite. Whereas for high dosage adsorption, Q_e does not show significant difference in both the aligned and non-aligned nanocomposites. It is evident that aligning nano-magnetite particles in gel matrix enhanced adsorption performance of nanocomposite. However, the advantage of such nanocomposite diminished with high adsorbent dosage due to near-field interactions of adsorbent. Proper adsorption scheme should be carefully designed to utilise the full potential of such nanocomposite.

1. Background

Ions adsorption was found enhanced by using nano-ferrimagnetic particles such as magnetite (Chiavola et al., 2016) and maghemite (Mohammed et al., 2014). Such observation is attributed to; (i) large surface area of nanoparticles that provides more adsorption sites for adsorption (Gomez-Pastora et al., 2016) and, (ii) alteration of electron density in adsorbate in the presence of magnetic field (Uheida et al., 2006). Nonetheless, there are two major problems that limit the effectiveness of such mechanism. The first problem arises due to strong cohesive force between nanoparticles. This causes severe agglomeration of nanoparticles, which led to reduction of surface area. Second, the magnetic effect of nanoparticles may not be fully utilised when they distributed randomly in adsorbate. Mutual cancellation of local magnetic field may occur among neighboring nanoparticles. As a result, the magnetic effect of nanoparticles in overall is masked during the adsorption. In this work, it is aimed to align the nano-magnetite in silica gel matrix to overcome these problems as illustrated in Figure 1. By aligning nano-magnetite in silica gel, the nanoparticles are locked in the matrix to reduce agglomeration. Silica gel matrix is used because it is relatively inert and contains porous structure for adsorbate to anchor on nanoparticles. Nanoparticles aligned in gel matrix can reduce mutual cancellation of local magnetic fields among nanoparticles. The adsorption performance may be further enhanced as the overall magnetic field strength increased. Silica gel in this work was synthesised from silicon-rich biomass instead of toxic alkoxides precursors. This makes the nanocomposite more economical to be produced, while turning the agriculture waste into more value-added product.

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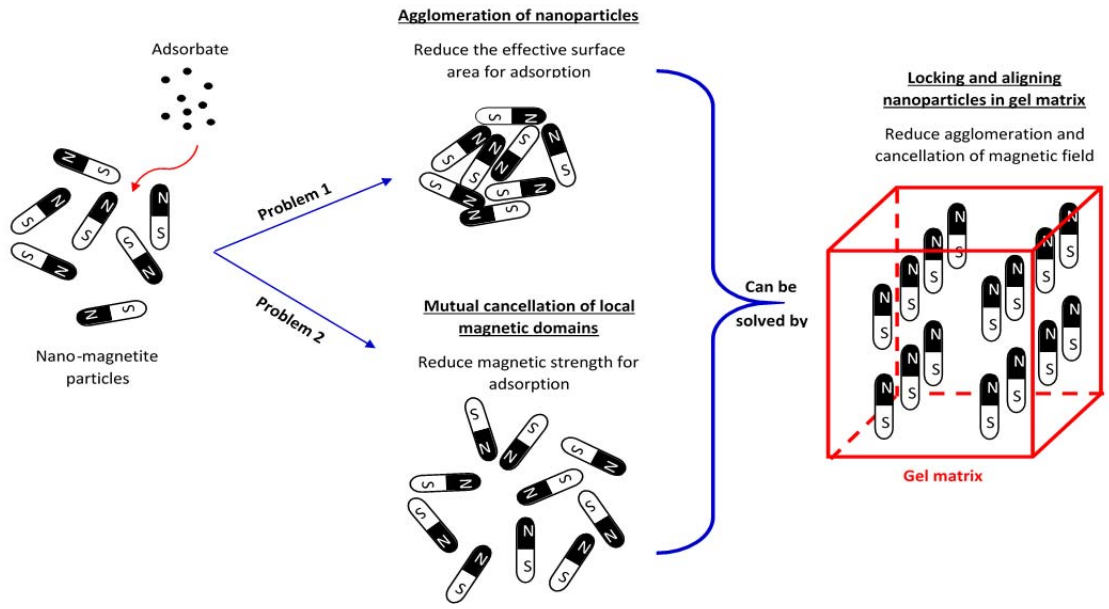

Figure 1: Problems that may reduce effectiveness of nano-magnetite in adsorption methodology

Figure 2 summarises the process flow of experiments carried out in this work. The waterglass, i.e., precursor of silica gel was prepared from rice husks as described in previous work, including dissolution of silica (Kien-Woh et al., 2014) and conversion of waterglass into gel (Kien-Woh et al., 2014). Co-precipitation method was used to synthesise nano-magnetite as described elsewhere (Charles, 2002). Iron salts $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ with the mass ratio of 2 : 1 was dissolved and stirred vigorously in 100 ml of distilled water and heated to 90 °C for 30 min. Then, 10 ml of 25 % ammonia solution, NH_4OH solution was added into the mixture according to Massart's method and stirred for 10 min. The nano-magnetite precipitated is washed with and stored in distilled water.

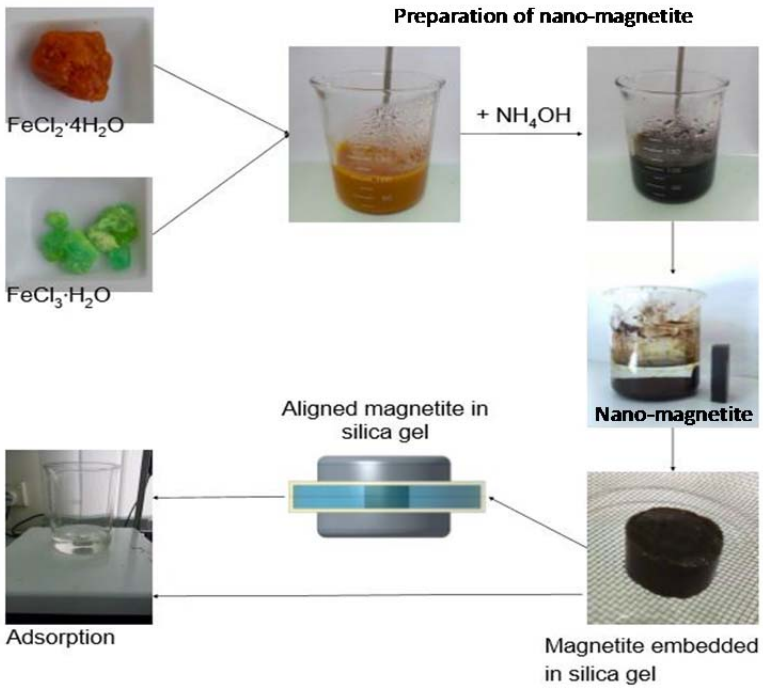

Figure 2: Process flow of experiments

Nano-magnetite was embedded in silica gel by ultrasonication. Nano-magnetite was first dispersed in waterglass and the mixture was then gelled by adjusting the pH of mixture. A constant particle loading of 0.1 g nano-magnetite in 13 g of gel was used throughout the experiments. To align the nano-magnetite particles in gel, the nanocomposite prepared in disk shape was placed inside a petri dish which sandwiched between two ring magnets with axial field (B_z) of 85 Gauss for 24 h as shown in Figure 3. The nanocomposite prepared was sieved to 600 micron size granules (see Figure 4) to ease the adsorption. The microstructure of nanocomposite was viewed SEM (Phenom, ProX) at accelerating voltage of 10 kV. An X-ray diffractometer (XRD, X'Pert³ Powder) with a 2θ range of 10° – 90° (step size 0.05°) was used detect any difference in crystal structure between the aligned and non-aligned nanocomposite.

Cd^{2+} solution was used in the adsorption study. Two adsorbent dosages were used in the adsorption of 50 mL (100 ppm) Cd^{2+} solution, i.e., 0.1 g and 1 g of nanocomposite. The concentration of Cd^{2+} solution was measured at different contact time using UV-Vis spectrophotometry. The percentage of ion removal was calculated using Eq(1):

$$\% \text{ Ion removal, } R = \frac{C_0 - C_t}{C_0} \times 100\ \% \tag{1}$$

where C_0 and C_t are the initial and is the final concentration of Cd^{2+} in ppm. The corresponding adsorption capacity, q in mg/g was calculated based Eq(2):

$$q = \frac{(C_0 - C_t)V}{1000\ m} \tag{2}$$

where V is the volume of Cd^{2+} solution (50 mL) and m is the mass of adsorbent used in g. The adsorption capacity at contact time (t) was fitted into pseudo-second order model in Eq(3):

$$\frac{t}{q} = \left(\frac{1}{q_e}\right)t + \frac{1}{kq_e^2} \tag{3}$$

where q_e is the adsorption capacity (mg/g) at equilibrium and k is the rate of sorption (g/mg.min). Both q_e and k were determined by fitted the data into MATLAB. For comparison purpose, experiments were repeated with non-aligned nanocomposite.

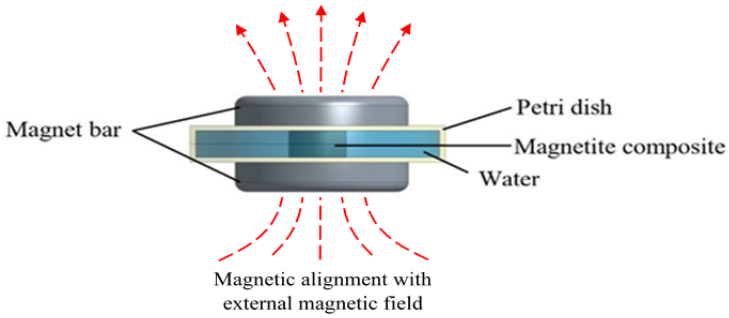

Figure 3: Setup to align nano-magnetite in gel matrix using axial ring magnet

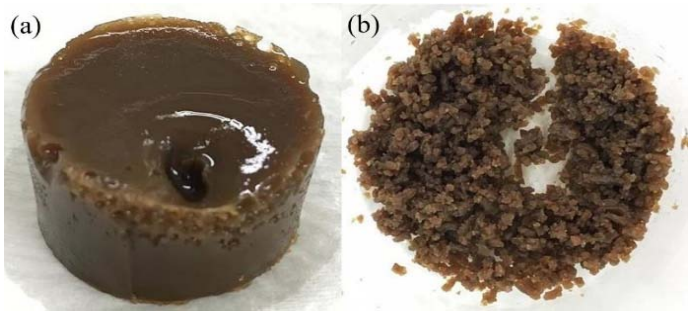

Figure 4: Nanocomposite after (a) gelled, (b) sieved

2. Results and discussion

The microstructure of nanocomposite is shown in Figure 5. The porous structure of blank silica gel is clearly observed in Figure 5(a). This proves that silica gel matrix can provide porous path for adsorbent to diffuse through and later anchor on the active sites of nano-magnetite. In Figure 5(b), it is observed that another smaller particle phase (darker phase) is distributed in the silica gel matrix. These smaller particles are nano-magnetite and it can be verified that nano-magnetite are not agglomerated in the silica gel matrix.

All the sharp peaks in Figure 6 are the characteristics peaks of magnetite (Luo et al., 2015). It is confirmed that both the aligned and non-aligned nanocomposites are having the same crystal structure and magnetism remains in these samples. The diffuse peaks between 2θ of 20° to 28° show characteristics of amorphous silica phase. These peaks, which are less obvious is non-aligned nanocomposite because it was suppressed by the very high intensity of magnetite at 2θ of approximately 31°.

The results of adsorption study are shown in Figure 7. In both low (0.1 g/ 50 mL) and high (1 g/ 50 mL) dosage, the adsorption capacity of aligned nanocomposite is higher than the non-aligned samples. The data were fitted into second-pseudo order model in Eq(3) and results are tabulated in Table 1. For dosage of 0.1 g/ 50mL, the adsorption capacity of aligned sample (978.8 mg/g) is 68 % higher than the non-aligned sample (582.5 mg/g). Both of these values are much higher than the values reported elsewhere previously, i.e., 14.15 mg/g (Yu et al., 2016), 223.7 mg/g (Ahmed et al., 2013) and 88.39 mg/g (Karami, 2013). This is a strong proof that embedding nano-magnetite in silica gel has successfully reduced agglomeration and thus increased the effectiveness of adsorption. This also indicates less nano-magnetite is required in adsorption if these particles are embedded in a porous matrix such as silica gel and/or magnetically aligned within the matrix. Such advantage gradually diminished when high absorbent dosage (1 g/ 50 mL) was used. The adsorption capacity is approximately 4.1 - 7.6 times lower than those observed in 0.1 g/ 50 mL.

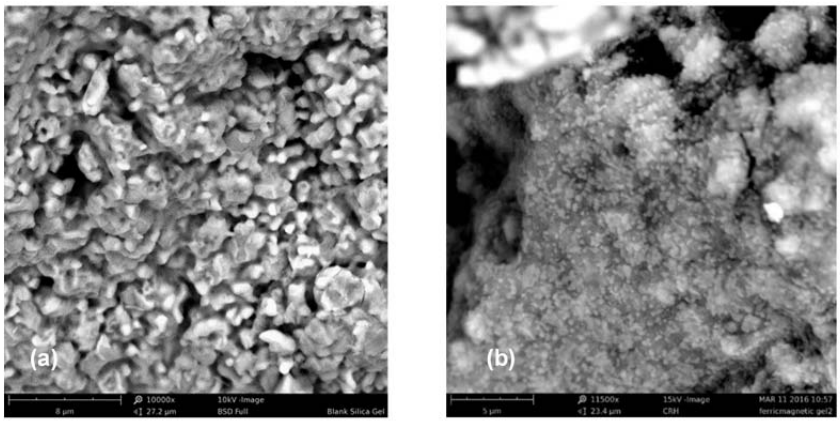

Figure 5: FESEM images of (a) blank silica gel, (b) silica gel embedded with nano-magnetite

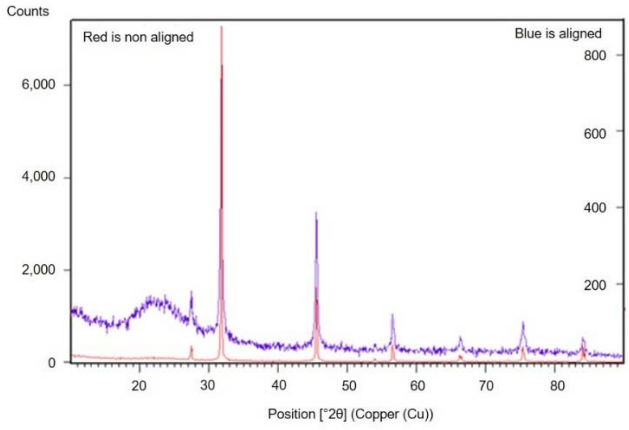

Figure 6: XRD diffractograms of the nanocomposite with nano-magnetite aligned and non-aligned in the silica gel matrix

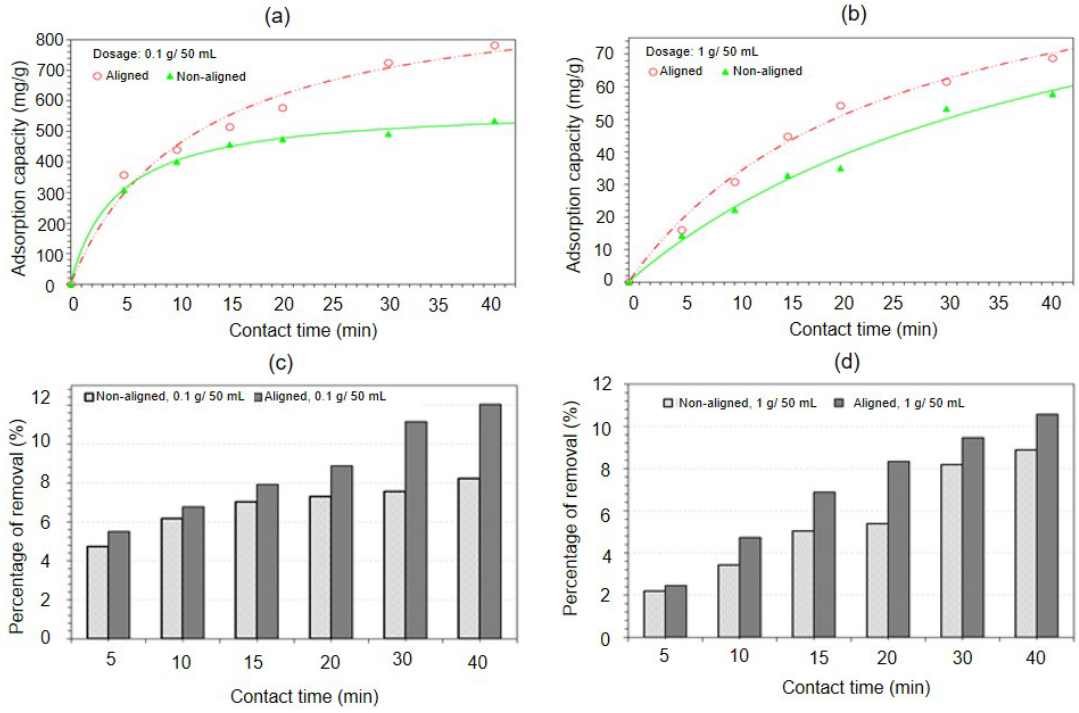

Figure 7: (a) Adsorption capacity with dosage 0.1 g/ 50 mL, (b) adsorption capacity with dosage 1 g/ 50 mL, (c) percentage removal with dosage 0.1 g/ 50 mL, and (d) percentage removal with dosage 1 g/50 mL

Since the nano-magnetite are embedded in gel in both of these cases (i.e., 0.1 g nanoparticles in 13 g of gel), it rules out the possibility of such difference is caused by degree of agglomeration. Under stirring, the nanocomposite granules were in random motion. Such motion can cause granules with antiparallel field to cancel each other. Under low dosage, these granules were separated from a larger distance in solution as compared than in high dosage. It is well-known that magnetic field strength decays quickly with the cube of distance. Assuming that nanocomposite granules are in spherical shape with radius R, the magnetic field B varies following Eq(4):

$$B = B_r \frac{2}{3} \frac{R^3}{(R+z)^3} \tag{1}$$

where B_r is the remanence field which independent of the geometry, and z is the distance from the edge of sphere. The magnetic fields of granules that separated far away from each other do not interact and cancel each other even they had antiparallel field. The advantage of local aligned magnetic field can then be fully utilised (as illustrated in Figure 8). As the distance between granules decreased at higher dosage, these local aligned magnetic field began to sense each other and results in field cancellation. This weakened the advantage of magnetic-induced adsorption when high dosage was used. In term of removal percentage, it seems was not affected by the dosage but rather depends on whether the nanocomposite is aligned or not. Aligned nanocomposite exhibits higher removal percentage and this again proves that aligned samples had enhanced the magnetic-induced adsorption. This also indicates that high dosage nanocomposite is not necessary required to remove Cd^{2+} ions. Table 1 summarised the important parameters obtained from adsorption studies.

Table 1: Summary of adsorption data fitted into pseudo-second order model

Dosage	Sample	Removal (%)	Q_e (mg/g)	Sorption rate (g/mg.min)	Adj-R^2
0.1 g/ 50 mL	Non-aligned	8.23	582.5	0.385	0.997
	Aligned	12.04	978.8	0.087	0.976
1.0 g/ 50 mL	Non-aligned	8.88	122.8	0.187	0.986
	Aligned	10.58	113.5	0.356	0.990

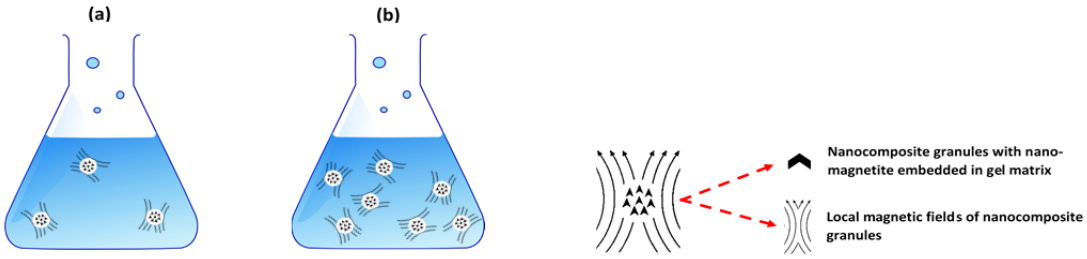

Figure 8: Magnetic interactions between nanocomposite in adsorption under (a) low, (b) high adsorbent dosage

3. Conclusions

It can be concluded that: (i) adsorption of Cd^{2+} ions with nano-magnetite can be greatly enhanced by aligning the nanoparticles in a silica gel matrix and (ii) low dosage of nanocomposite shows better adsorption performance. Though the percentage of removal was only about 10 %, multiple serial adsorption with low dosage may be used to achieve higher ions removal without much expense in nanocomposite. The spent nanocomposite can be regenerated and thus improving its potential in economical and sustainability aspect. These preliminary results can be further explored in the adsorption of other substances and may be further enhanced by using different configuration of external magnetic field in the alignment process.

Acknowledgments

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