Modifying humic acids on magnetite nanoparticles to sorption of p-chlorophenol

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Abstract. Modifying humic acids on magnetite nanoparticles (M/HA) to sorption of p-chlorophenol have been studied. The M/HA was synthesized by coprecipitation method in alkaline condition using ammonium hydroxide and humic acids (HA) was isolated from peat soil in Samarinda, East Kalimantan. Modification of M/HA was prepared using mass ratios of M and HA = 20:1, 20:2, 20:4, 20:6. The four adsorbents of M/HA were characterized by determination of pH point zero charge (pHζC), magnetic properties by vibrating sample magnetometer and morphology were observed by scanning electron microscopy. The result showed that sorption of p-chlorophenol on four of M/HA materials was optimum at pH 3.0 and fitted well to pseudo second-order kinetic models and Langmuir isotherm. The adsorption capacity of M/HA between 0.27-0.57 mmol/g. Generally, the performance of four M/HA materials to sorption of p-chlorophenol was M/HA=20:6 > M/HA=20:4 > M/HA=20:2 > M/HA=20:1.

1. Introduction

Chlorophenols are harmful and toxic organic pollutants and then is one of dangerous pollutants recommended by Environmental Protection Agency (EPA) [1]. They are generally used for agriculture and industry such as pesticides, wood preservatives, disinfectants and intermediates in industries [2] and can be produced from natural chlorination of organic matter, biodegradation of phytodefensive chemicals or the use of large quantities of disinfectants in drinking water [3]. Chlorophenols may cause severe environmental contamination problems because of their toxicity to organisms, potential carcinogenic and mutagenic activity and low threshold levels causing odor and taste in water up to 0.1 ppb [4]. Degradation of chlorophenols from aquatic environment can be done with various methods for example photodegradation [5], solvent extraction [6], irradiation [7], chemical oxidation [8] or adsorption [9] and then adsorption is one methods of efficient, easily separated and which can be regerated and reused [10].

Humic substances are a kind of natural organic macromolecular produced by the decomposition of plant material in soil [11]. The presence of humic substances are influenced by climatic condition as and determines of functional groups contenst such as carboxyl (–COOH), hydroxyl (–OH), amine (–NH₂) and phenolic (Ar-OH) [12]. The functional groups on HA have different abilities in binding metal ions through the formation of complex stability [13]. HA is able to stabilize metal oxide
particles due to characteristic of affinity for metal ions and content of multi-functional group content [14, 15]. The modifying of HA on the surface metal oxides particles can prevent particle aggregation, increases colloidal and stability of chemical [16].

Nanoparticles metal oxides have been studied as powerful adsorbents for greater specific surface area, higher surface reactivity and small internal diffusions resistance [17]. Nowadays, magnetic materials derived from certain iron oxides (Fe₃O₄,γ-Fe₂O₃,α-Fe₂O₃) became increasingly popular as nano-sorbs not only in water-treatment technologies [18] but also in biomedical applications [19] or in analytical chemistry [20] because of their excellent sorption ability, good mechanical properties and facile separability with a simple magnetic process [21]. Binding HA on magnetic materials influences the sorption properties because the coating of HA result polyanionic organic on magnetic surface [22].

Recent research, modification of HA coated magnetite (M/HA) and its application to sorption of pollutant. The sorption of RhB on M/HA was reached equilibrium in less than 15 min, able to remove 98.5% of RhB in water at pH 2.53 and has adsorption capacities of 161.8 mg/g [23]. Jonas et al (2013) was prepared various of contents HA (6.6%-15.5%) coated magnetite for sorption of Cu. The metal-binding capacity of M/HA was related to the content of HA. The presence of HA in M/HA plays a crucial role in sorption adsorbate was attributed to the presence of functional groups [24]. Sorption of phenol on M/HA was followed well the Langmuir isotherm model while the sorption capacity increased with the increasing HA content [25]. In this research, the sorbents of M/HA has been prepared by coating HA on magnetite using mass ratios of M and HA = 20:1, 20:2, 20:4, 20:6 and then applied to sorption of p-chlorophenol in aqueous solutions. The physical and chemical characterization of four M/HA sorbents were conducted and the applicability of M/HA for p-chlorophenol sorption was evaluated based on sorption kinetics and isotherm.

2. Experimental section

2.1. Materials

All chemicals and reagents used were of analytical grade i.e., FeCl₃.6.H₂O (Merck), FeSO₄.7.H₂O (Merck), NH₄OH 25% (Merck), C₆H₅OHCl (Merck), HCl (Merck), HF (Merck), NaOH (Merck), N₂. Humic acid (HA) was isolated from peat soil, Samarinda, East Kalimantan by alkaline solutions and was purified by HCL/HF method.

2.2. Procedures

2.2.1. Modifying of HA on magnetite (M/HA). Modifying of M/HA by co-precipitation methods, 1.525 g FeCl₃.6.H₂O and 1.050 g FeSO₄.7H₂O were dissolved into 25 mL of distilled water and heated at 90°C. In solutions was added of NH₄OH 25% until pH 11 and then 0.25 g HA in 12.5 mL NaOH (M/HA=20:1). The solution was mixed by magnetic stirring at constant temperature (90 °C) for 30 minutes and then cooled to room temperature. The precipitate was separated from solutions and washed to neutral with distilled water. The sorbent of M/HA=20:2, 20:4 and 20:5 was prepared with the same procedure by addition of 0.5, 1.0 and 1.5 g HA in 12.5 mL NaOH. Characterization of M/HA was determined pH point of zero charge of M/HA, magnetic properties by vibrating sample magnetometer and morphology by scanning electron microscopy (SEM) JEOL SSM-6510 LA.

2.2.2. Sorption kinetic and capacity of p-chlorophenol. Sorption studies of p-chlorophenol on M/HA were carried out using batch technique. Ten mg of M/HA was added to a series of 10 mL p-chlorophenol 100 mg/L were adjusted pH from 3, 4, 5, 6, 7, 8 and 9 using HCl or NaOH solution and then the mixture were interacted for 90 minutes. Adsorption kinetics experiments were prepared at pH optimum and initial p-chlorophenol of 100 mg/L with contact time of adsorbate and adsorbent was varied from 0, 15, 30, 60, 90, 180 and 240 minutes. The sorption capacity was also conducted using batch experiments of a series of solution concentrations of 10, 30, 50, 100, 200 and 300 mg/L of p-chlorophenol with pH and contact time optimum. After separating the supernatants, p-chlorophenol
in supernatants was determined by UV-Spectrophotometer. The same experiments with the sample solution, the blank was also analyzed. The data obtained was determined using Freundlich and Langmuir isotherm adsorption model.

3. Results and discussion

3.1. Characterization of M/HA

The four material of M/HA were modified by co-precipitation at condition of pH 11 and heated 90°C with various of mass ratio M and HA = 20:1; 20:2; 20:4 and 20:6. Interaction of HA and magnetite was successfully under alkaline conditions at pH > pH pZc. In this condition, the magnetite is negative and the binding of HA to magnetite is dominated by reaction of ligand exchange [25, 26]. The pH_{PZC} of M/HA value of this research was between 6.85 to 6.24. The presence of interaction HA and magnetite was confirmed by FT-IR spectroscopy. FT-IR spectra showed the C=O stretches as free carboxylate acids at 1404 cm^{-1}, corresponds interacting HA with magnetite surface and this indicating that binding HA on magnetite using functional group of carboxylate [25, 27, 28]. The XRD patterns of M/HA at mass ratio of 20:1, 20:2, 20:4 and 20:6 shows similar diffraction peaks at 2θ = 30.1°, 35.4°, 43.1°, 57.0°, 62.68° and 74.5° which is the reflection (220), (311), (400), (511), (440) and (533) planes [27, 28]. These diffractogram was not significantly different with diffractogram peaks of standard (JCPDS 65-3107) [29, 30]. This result indicates that modifying of HA on magnetite did not change structure of crystal in magnetite and only decreasing of peak intensity and crystallite size [25, 26]. The magnetic properties of M/HA was analyzed using VSM. The value of specific saturation magnetization (Ms) of M/HA was decreased with the increasing content of HA in M/HA due to the reduction in crystallinity of the magnetic domain. These research shows that the magnetic properties of MnP-HA are getting smaller with increasing of HA. Decreasing Ms of MnP-HA was still effective for the separation using magnetic field [24, 27, 29]. The characteristics of sorbent of M/HA at mass ratio of 20:1; 20:2; 20:4 and 20:6 shown in table 1.

| pH_{PZC} (point of zero charge) | M/HA=20:1 | M/HA=20:2 | M/HA=20:4 | M/HA=20:6 |
|---------------------------------|-----------|-----------|-----------|-----------|
| Average crystallite size (nm)   | 6.52      | 6.50      | 6.25      | 6.24      |
| Saturation magnetization (emu/g)| 10.79     | 10.27     | 9.48      | 9.36      |
|                                 | 63.31     | 57.80     | 46.20     | 38.89     |

The table morphology and particle size were determined by scanning electron microscopy (SEM). The SEM analysis of M/HA at mass ratio of 20:1; 20:2; 20:4 and 20:6 as shown in figure 1. Sorbents of M/HA consist of relatively coarse irregular particles covered in HA at 50× magnification (figure 1a), at 5000× magnification, surface of very small sub-micron particles composed presumably of iron-humate compounds (figure 1b) and then shaped of spherical nanosize of M/HA at 20,000× magnification. The modifying HA on magnetite were indicated HA efficiently reduced the aggregation of magnetite [31].
3.2. Sorption p-chlorophenol on M/HA

The effects of pH on sorption of p-chlorophenol depends on the stability of sorbents M/HA in aqueous solutions. Stability of M/HA in mass ratio of 20:1, 20:2, 20:4 and 20:6 at pH range 3.0-9.0 [27]. The influence of pH on p-chlorophenol sorption onto M/HA as shown figure 2. Adsorption of p-chlorophenol on M/HA was optimum at pH 3.0, may be caused by protonation of functional groups -COOH in adsorbent M/HA and then adsorbate of p-chlorophenol become positively charged at lower pH solution. Therefore, the binding between M/HA on p-chlorophenol was a hydrogen bonding. If pH solutions was higher, the sorption of p-chlorophenol on M/HA was decreased by increasing the pH solution. Dissociation of p-chlorophenol into negatively charged and deprotonation of M/HA becomes negatively charged. Therefore, the interaction between p-chlorophenol and M/HA to be weak and then the sorption getting down.
Figure 2. The influence of pH on p-chlorophenol sorption on M/HA at mass ratio of 20:1, 20:2, 20:4 and 20:6.

Adsorption kinetics of p-chlorophenol on M/HA occurred rapid sorption within 90 minutes and slow sorption until the p-chlorophenol adsorbed reached the equilibrium value, as shown in figure 3.

Figure 3. The influence of contact time on p-chlorophenol sorption on M/HA at mass ratio of 20:1, 20:2, 20:4 and 20:6.
The sorption kinetics were analyzed using Lagergren’s pseudo-first-order, Ho’s pseudo second-order and second-order and Santosa’s. The Lagergren’s equation for pseudo first-order kinetics can be formulated as equation (1) [32]

\[
\ln(q_e - q_t) = \ln q_e - k_1 \cdot t
\]  

(1)

where \( q_e \) (amount of p-chlorophenol adsorbed, mmol/g at equilibrium) and \( q_t \) (amount of p-chlorophenol adsorbed, mmol/g at time \( t \)) and \( k_1 \) (the pseudo first-order rate constant, min\(^{-1}\)). The relationship of \( \ln (q_e - q_t) \) versus \( t \) was determined slope (rate constant of Lagergren’s first-order = \( k_1 \)) and intercept (equilibrium adsorption capacity = \( q_e \)).

The kinetics of sorption p-chlorophenol for Ho’s pseudo-second-order equation was explained as equation (2), where \( q_e \) and \( q_t \) have the same meaning as mentioned previously, \( k_2 \) is pseudo second-order rate constant. (g/mmol.min) is pseudo second-order rate constant. The plots of \( t/qt \) versus \( t \) [33]

\[
\frac{t}{qt} = \frac{1}{h} + \frac{1}{q_e} \cdot t
\]  

(2)

The Santosa’s first order model was represented as equation (3), where \( C_{ao} \) is the initial concentrations of p-chlorophenol (mmol/g), \( C_a \) and \( C_{ae} \) were the remaining concentrations of p-chlorophenol in solution after adsorption at \( t \) and equilibrium (mmol/g), respectively, \( k_s \) is the Santosa’s first order rate constant, and \( t \) is the interaction time. The plots of \( \frac{1}{C_e} \ln \left( \frac{C_a}{C_{ao} - C_{ae}} \right) \) versus \( t \) [34].

\[
\frac{1}{C_e} \ln \left( \frac{C_a}{C_{ao} - C_{ae}} \right) = k_s \cdot t
\]  

(3)

The calculated kinetics parameters for sorption p-chlorophenol on M/HA shown in table 2. The pseudo-second-order equation was successfully provided the best kinetics studies for the experimental, with \( R^2 > 0.962 \). The obtained \( k_2 \) for the p-chlorophenol sorption on M/HA at mass ratio of 20:1, 20:2, 20:4 and 20:6 were 6.3×10\(^4\), 6.5×10\(^4\), 6.8×10\(^4\)and 7.1×10\(^4\) min.g/mol, respectively.

**Table 2.** Kinetic parameters of the pseudo first-order, pseudo second-order and first-order model for p-chlorophenol sorption on M/HA.

| Model                     | Parameters | M/HA= 20:1 | M/HA= 20:2 | M/HA= 20:4 | M/HA= 20:6 |
|---------------------------|------------|------------|------------|------------|------------|
| Lagergren’s pseudo first-order | \( R^2 \)  | 0.857      | 0.926      | 0.903      | 0.902      |
| \( q_e \) (mmol.g\(^{-1}\)) | 52.08      | 61.31      | 68.40      | 69.26      |
| \( k_1 \) (min\(^{-1}\))   | 0.007      | 0.006      | 0.006      | 0.006      |
| Ho’s pseudo second-order   | \( R^2 \)  | 0.962      | 0.973      | 0.981      | 0.982      |
| \( q_e \) (mmol.g\(^{-1}\)) | 0.499      | 0.535      | 0.575      | 0.583      |
| \( k_2 \) (g.mmol\(^{-1}\).min\(^{-1}\)) | 0.063      | 0.065      | 0.068      | 0.071      |
| Santosa’s first-order      | \( R^2 \)  | 0.875      | 0.987      | 0.977      | 0.953      |
| \( q_e \) (mmol.g\(^{-1}\)) | 0.036      | 0.037      | 0.052      | 0.060      |
Adsorption’s capacity of M/HA at mass ratio of 20:1, 20:2, 20:4 and 20:6 towards p-chlorophenol, the respective sorption isotherms are shown in figure 4. Initial concentrations of p-chlorophenol was 10, 30, 50, 100, 200 and 300 mg/L. The increasing of initial concentration of p-chlorophenol, so the higher of adsorption's capacity. At this initial concentration of p-chlorophenol 200 mg/L getting constant sorption.

![Figure 4. The influence of initial concentration on p-chlorophenol sorption on M/HA at mass ratio of 20:1, 20:2, 20:4 and 20:6.](image)

To quantitatively describe the p-chlorophenol sorption on M/HA, adsorption isotherm of Langmuir and Freundlich explain into equations (4) and (5) [35].

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L C_m} \quad (4)
\]

\[
\ln q_m = \ln K_f + \frac{1}{n} \ln C_e \quad (5)
\]

Where \( q_m \) is the sorption capacity, \( K_L \) and \( K_f \) are Langmuir and Freundlich equilibrium constant respectively (L.mmol\(^{-1}\) and mmol.g\(^{-1}\).(mmol.L\(^{-1}\))\(^n\)), \( n \) (dimensionless) is the Freundlich exponential coefficient. The resulted of parameters of Langmuir and Freundlich model of sorption p-chlorophenol on M/HA at mass ratio of 20:1, 20:2, 20:4 and 20:6 were summarized in table 3.

**Table 3.** Adsorption isotherm parameters of Langmuir and Freundlich for sorption p-chlorophenol on M/HA

| Model and parameters | M/HA=20:1 | M/HA=20:2 | M/HA=20:4 | M/HA=20:6 |
|----------------------|-----------|-----------|-----------|-----------|
| Langmuir             |           |           |           |           |
| \( R^2 \)            | 0.989     | 0.983     | 0.986     | 0.977     |
| \( q_m \) (mmol g\(^{-1}\)) | 0.268     | 0.375     | 0.372     | 0.570     |
| \( K \) (L mmol\(^{-1}\)) | 1508      | 1055      | 1414      | 1008      |
| \( E \) (kJ mol\(^{-1}\)) | 18.255    | 17.364    | 18.094    | 17.249    |

| Freundlich           |           |           |           |           |
| \( R^2 \)            |           |           |           |           |
| \( q_m \) (mmol g\(^{-1}\)) |           |           |           |           |
| \( K \) (L mmol\(^{-1}\)) |           |           |           |           |
| \( E \) (kJ mol\(^{-1}\)) |           |           |           |           |
The Langmuir model explains that adsorption surface has the same energy site and then each adsorbed molecule occupies a single site so that was occured formation of mono-layer between adsorbate and adsorbent. The isotherm model of Freundlich explains equilibrium on heterogeneous surfaces and did not describe adsorption’s capacity in the monolayer [36]. Adsorption’s isotherm of sorption p-chlorophenol on M/HA follow isotherm model of Langmuir. The adsorption surface of p-chlorophenol on M/HA has same energy sites and each adsorbed molecule occupies a single functional group carboxylate in HA. Adsorption’s capacity of p-chlorophenol increases with increasing content of functional group carboxylate HA in M/HA. Generally, the performance of four M/HA materials to p-chlorophenol sorption on M/HA=20:6 > M/HA=20:4 > M/HA=20:2 > M/HA=20:1.

4. Conclusion

The HA coated magnetite magnetite (M/HA) was successfully prepared through co-precipitation method and HA isolated from peat soil in Samarinda, East Kalimantan. Adsorption of p-chlorophenol on four of M/HA=20:1, 20:2, 20:4 and 20:6 were optimum at pH 3.0 and fitted well to pseudo second-order kinetic models with R^2>0.986. The Adsorption capacity of M/HA followed well the isotherm model of Langmuir with q° was 0.27 until 0.57 mmol/g. Generally, the performance of four M/HA materials to sorption of p-chlorophenol was M/HA=20:6 > M/HA=20:4 > M/HA=20:2 > M/HA=20:1.

Acknowledgment

We gratefully acknowledge thank the Directorate General of Technology Research and Higher Education, Ministry of Technology Research and Higher Education Republic Indonesia for providing the financial support through doctoral dissertation research grant 2017.

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