Reinforcement of Quaternary Ammonium Modified Silica (QAMS) with Magnetite and its Application by Solid Phase Adsorption (SPA) to Adsorb Chromate Ions

Ngatijo Ngatijo a,*, Restina Bemis a,2, Abdul Aziz b,3,4, Rahmat Basuki c,4

* Department of Chemistry, Universitas Jambi, Jambi, Indonesia
b Master of Chemistry Program, Department of Chemistry, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia
c Department of Chemistry, Universitas Pertahanan, Bogor, Indonesia

* Corresponding author: (1,* tijog2@yahoo.co.id; (2) bemisrestina@gmail.com; (3) azizgb@gmail.com; (4) rhmtbsq@gmail.com

https://doi.org/10.14710/jlsa.2310.333-337

1. Introduction

Gold mining activities harm the environment [1]. The gold mining process potentially causes environmental pollution because it causes turbidity and heavy metal pollution in river water used as a source of drinking water by society. One of the dangerous heavy metals is Cr metal [2, 3], chromium metal can be generated from chromium taken from the earth and the mining machines. Chromium ion in the form of Cr (III) ion and Cr (VI) ion is a chromium form widely found in the environment. The hexavalent (Cr(VI)) form receives more attention due to its toxic nature [4, 5]. Chromium (IV) is known to have 100 times more toxic than chromium (III) for both acute and chronic exposures because of its high water solubility and mobility, as well as easy reduction [6].

One effective way to overcome Cr metal pollution is by the adsorption method [7, 8]. Potential material used as an adsorbent is silica gel (SG) from rice husk ash (RHA). Silica gel from RHA is obtained from the burning process of rice husk. SG from RHA is more superior to quartz because it has high crystallinity and stability [9]. However, the use of SG from RHA as an adsorbent has a weakness: the low capacity caused by the low acidity of Si-OH groups [10]. Modification of silica by functionalization with a quaternary ammonium group to Quaternary Ammonium Modified Silica (QAMS) with a quaternary group (–N+(CH3)3) has the advantage that protonation will not occur; thus remains positively
charged and persists in absorbing chromate anions [11, 12]. However, this material was challenging to re-collect after the adsorption process [13].

Magnetite (Fe₃O₄) is one of the materials with various potential applications, including in magnetic recording technology, pigments, catalysis, photocatalysis, medical use, and environmental improvement [14]. Previous studies reported that magnetite modification of silica could increase the surface area of silica [13, 15]. Also, magnetic materials such as magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) have been reported to be incorporated into silica, i.e., silica-encapsulated particles, to rapidly separate the silica from aqueous environments after adsorption [16]. Coating Fe₃O₄ by silica also prevented the magnetite from aggregation and oxidation [17, 18, 19] and exhibited excellent stability in an acidic environment compared with the uncoated ones [14, 20]. However, few authors have reported the preparation of QAMS coated magnetic materials and their application to remove pollutants [16, 20]. Nuryono et al. [21] reported that magnetite coating with mercapto-modified silica as an adsorbent has more effective interaction with metals with high chemical stability and easy to separate after the adsorption/desorption process.

The adsorption process was usually carried out using a batch method [22]. However, in recent years, a new adsorption method has been developed, which can be an option in the adsorption process; it was called the Solid Phase Adsorption (SPA) method. SPA is an adsorption method that uses columns as adsorption media [23]. This method was claimed more efficiently because it can minimize the analyte, regenerate the adsorbent, and be used repeatedly for the same analysis, easy preparation, and high selectivity [24]. Liu et al. [25] reported that adsorbent from polymer resin to adsorb Cr(III) using SPA had a high selectivity, good stability, and high adsorption capacity.

From the literature above, magnetite (Fe₃O₄) seems a suitable candidate to modify QAMS to increase QAMS handling. This work objective was to reinforce the QAMS handling after the adsorption/desorption process by maintaining the magnetic moment of magnetite, Fe₃O₄, as modifier QAMS. The magnetic moment preservation of QAMS–Fe₃O₄ was conducted by synthesis Fe₃O₄ first and then coated with QAMS. The obtained material (QAMS–Fe₃O₄) was then applied to adsorb chromate (Cr(VI)) anion by using the Solid Phase Adsorption (SPA) method. Characterization of synthesized material (QAMS–Fe₃O₄) and adsorption studies of Cr(IV) onto QAMS–Fe₃O₄ with SPA will further discussed in this paper.

2. Methodology
2.1. Materials

Rice husk to produce rice husk ash (RHA) and analytical grade reagent, i.e., HCl 37% (E–Merck), HNO₃ 68% (E–Merck), NaOH (E–Merck), 3-Aminopropyltrimethoxysilane (3–APTMS, Sigma–Aldrich), FeSO₄·7H₂O (E–Merck), FeCl₃·6H₂O (E–Merck), CH₃Cl (E–Merck), NH₄OH 24% (E–Merck), CH₄ (Sigma–Aldrich), K₂Cr₂O₇ (E–Merck), ethanol 60% (E–Merck), and Dimethylformamide (DMF, Sigma–Aldrich).

2.2. Instrumentations

Supporting instrumentation was a set of standard glass tools (Erlenmeyer flask, volume pipette, beaker glass, and so forth), oven, furnace, analytical balance, desiccator, plastic tube, centrifuge, shaker, magnetism, pH meter, and reflux. Elemental analysis performed by Flame Atomic Absorption Spectroscopy (FAAS, Shimadzu AA6650) with Air–Acetylene flame gas, wavelength 357.9 nm. Crystallinity analysis conducted by X-Ray Diffraction using Shimadzu X-ray diffraction (XRD) and using CuKα radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA with the step size of 0.02°. Fourier Transform Infrared (FTIR, Shimadzu IR Prestige 21) analyzed the functional group of materials in the KBr pallet that scans the region between 4000 and 400 cm⁻¹ with 4 cm⁻¹ resolution. The morphology and the elemental composition of material performed by Scanning Electron Microscope–Energy Dispersive X-Ray (SEM–EDX, JEOL SSM–6510 LA) operating at an accelerating voltage of 15.00 kV through an aliquot of a dilute particle suspension was allowed to air dry on glass slides and then were coated with evaporated carbon. Magnetization was recorded as a function of field (–1.0 to +1.0 T) at 297.2 K by Vibrating Sample Magnetometer (VSM, OXFORD VSM 2.6H).

2.3. Destruction of silicic acid from RHA

Rice husk was furnace at 700 °C to produce RHA. The mixture of 100 g RHA, 80 g of NaOH crystals, and 500 mL of distilled water was stirred and boiled for 2 hours and then filtered after it was cooled. The 200 mL of its filtrate was mixed with 15 mL of 3–APTMS, and drop by drop gently of 2 M HCl to reach pH nine until formed sol. The sol was then aged for 3×24 h to form a gel (Ammine Modified Silica, AMS) was formed. AMS was washed until the pH was neutral, filtered, and dried at 70 °C to generate dry AMS, ≈Si(CH₂)₃NH₂.

2.4. Methylation reaction to form QAMS from AMS

Methylation reaction was performed by the procedure proposed by de Campos et al. [26]. The mixture of 12 g AMS, 20 mL DMF and 10 mL methyl iodide in 250 mL volume 3 neck flask was refluxed for six hours and heated to 70 °C while a periodically dropwise of methyl iodide added in a darkroom. The solid products were filtered and washed with water, then with a 2% sodium bicarbonate solution and again with water. The materials were dried under a vacuum at 50 °C for six hours. The methylation reactions were repeated twice by replacing AMS with the previous methylated product to generated QAMS, ≈Si(CH₂)₃N(CH₃)₃F.

2.5. Synthesis of Magnetite (Fe₃O₄)

Magnetite synthesis was carried out based on Yang et al. [27] through the co-precipitation method by dissolving 1.05 g FeSO₄·7H₂O and 1.525 g FeCl₃·6H₂O into 25 mL of distilled water and heated to 90 °C. NH₄OH 25% was added to that homogenous mixture until pH 11, and
the mixture was stirred at 90 °C for 30 min as magnetic fluids. After aged 24 h, the resulted black sediment was separated from the solution, washed until neutral pH, and dried to generate magnetite, Fe₃O₄.

2.6. Coating Fe₃O₄ with QAMS

Following Yang et al. [27] method with some modifications, the Fe₃O₄ with QAMS was carried out through the sol–gel approach in a basic ethanol/water mixture at 30 °C by using magnetic fluids as seeds. The method begins with the synthesis of Fe₃O₄ with the same recipe. After the magnetic fluid is formed and cooled to room temperature, under continuous mechanical stirring, a homogenous neutral suspension of 0.2 g of QAMS in 40 mL ethanol 60% was dropwise added to this dispersion. After stirring for 12 h, the obtained product was collected by an external magnetic field and washed with ethanol three times. The dry solid (QAMS–Fe₃O₄) was then analyzed by the FT–IR, XRD, SEM–EDX, and VSM instrument.

2.7. Stability Test of QAMS

Ten mg of QMAS–Fe₃O₄ was inserted into a 25 ml pH solution with a variation of pH 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10. The solution was stirred for 15 min. The remaining solids were filtered, dried, and weighed.

2.8. Chromate Anions Adsorption by SPA

A hundred mg of QAMS–Fe₃O₄ was inserted into the column, and then 10 mL of 10 mg/L chromate solution (pH 4) flowed into it. The tap column was opened to accommodate the solution that came out from the column. The exact procedure was repeated with different pH 5, 6, 7, and 8. Cr(VI) infiltrate was analyzed by AAS.

The flow rate variation also conducted in this study by varied flow rate at 0.05, 0.30, 0.70, 1.10, and 1.50 mL/min of 10 mL chromate ion 10 mg/L at optimum pH. The remain Cr(VI) infiltrate was analyzed by AAS.

3. Results and Discussion

3.1. Characterization of QAMS–Fe₃O₄

Fourier Transform–Infra Red (FT–IR) study of synthesized Fe₃O₄ AMS, QAMS and QAMS–Fe₃O₄ was presented in Figure 1. For the sample of synthesized Fe₃O₄, the vibrational bands at around 890 and 520 cm⁻¹ are characteristic of the ν(Fe–O) lattice vibrations [28]. The QAMS–Fe₃O₄ sample shows a band at 788 and 1034 cm⁻¹ corresponding to the stretching vibrations of ν(Si–OH) and ν(SiO–Si), respectively [29]. The absorption band at 1636 cm⁻¹ in the AMS, QAMS, and QAMS–Fe₃O₄ might be assigned to the ν(C–N) stretching mode [30]. The broad absorption band at 3375 cm⁻¹ was due to ν(O–H) stretching vibration, which corresponds to hydroxyl groups on the surface of iron oxide, and this band can be assigned to the adsorbed water molecules [31]. Additional bands were observed at 2939 cm⁻¹ corresponding to the –CH₃ and –CH₂– vibrations. The ν(C–O) stretches were found at 2361 cm⁻¹, which are typically very weak and convoluted by contamination of the background’s CO₂ stretching bands.

![Figure 1. FTIR spectra of QAMS–Fe₃O₄, QAMS, AMS, and Synthesized Fe₃O₄](image)

The absorption band at 1388 cm⁻¹ (bend vibration of N–H from –NH₂ group) in AMS indicated the AMS still has –NH₂ group. However, QAMS and QAMS–Fe₃O₄ have not this absorbance that indicates there is no –NH₂ group in QAMS and QAMS–Fe₃O₄. C–H stretching vibration from the methyl group emerged at 2939 cm⁻¹ [32] was emerged only in QAMS, and QAMS–Fe₃O₄ indicates formed –CH₃ at QAMS and QAMS–Fe₃O₄. The differences of AMS and QAMS was disappearing absorbance at 1388 cm⁻¹, and emerging absorbance at 2939 cm⁻¹ in QAMS and QAMS–Fe₃O₄ indicated a transformation of N–H from –NH₂ group to [–N'-(CH₃)] [31]. However, due to the similarity of the other functional groups of the QAMS and QAMS–Fe₃O₄, the infrared spectra were not conclusive about coating Fe₃O₄ on QAMS results were further supported by crystal, magnetic properties, morphology, and elemental chemical analysis.

| Table 1 Experimental d (Å) spacing of synthesized Fe₃O₄ and QAMS–Fe₃O₄ from XRD pattern d (exp) and d (ASTM) spacing from ASTM data cards for iron oxide Fe₃O₄ |
|---|---|---|---|
| QAMS–Fe₃O₄ | Synthesized Fe₃O₄ | ASTM Fe₃O₄ |
| 2θ (°) | d (exp) | 2θ (°) | d (exp) | d (ASTM) |
| 30.26 | 2.954 | 30.15 | 2.972 | 2.967 |
| 35.61 | 2.521 | 35.53 | 2.529 | 2.532 |
| 43.12 | 2.082 | 43.12 | 2.082 | 2.099 |
| 57.23 | 1.611 | 57.23 | 1.611 | 1.616 |
| 62.90 | 1.478 | 62.90 | 1.478 | 1.485 |
Figure 2. XRD pattern of QAMS–Fe$_2$O$_3$, QAMS, and synthesized magnetite, Fe$_3$O$_4$.

X-ray diffractogram (XRD) analysis of AMS and QAMS shows that these all material are non-crystalline (amorphous), and SiO character emerges at $2\theta = 20–25^\circ$ (JCPDS No. 29–0085) [22, 25, 26, 27]. This condition was also reported by Della et al. [31] that there is no significant change in the diffractogram peak of the incinerating time of rice hull ash to form silica gel. The diffractogram of QAMS–Fe$_2$O$_3$, QAMS, and AMS was presented in Figure 2. From the synthesized Fe$_2$O$_3$ diffractogram can be seen that there are peaks which indicate the iron oxide as Fe$_2$O$_3$ crystal which identified at $2\theta = 30.15^\circ$ (220); 35.53$^\circ$ (311); 43.12$^\circ$ (400); 57.22$^\circ$ (511), and 62.90$^\circ$ (440) (JCPDS No. 00–033–0666) [29, 30]. Based on the matching of $d$ (exp) with $d$ (ASTM) spacing from ASTM data cards for iron oxide Fe$_2$O$_3$ [34] (Table 1), it can be concluded that the iron oxide particles are mainly composed of the inverse cubic spinel structure [30, 32]. Emerging peak at $2\theta = 30.15^\circ$; 35.53$^\circ$; 43.12$^\circ$; 57.22$^\circ$; and 62.90$^\circ$ on QAMS–Fe$_2$O$_3$ demonstrated the success of the Fe$_2$O$_3$ coating with QAMS (Figure 2).

Figure 3. Hysteresis loops of synthesized Fe$_2$O$_3$ and QAMS–Fe$_2$O$_3$ at room temperature.

The core/shell QAMS–Fe$_2$O$_3$ material must possess sufficient magnetic and paramagnetic properties for practical application. The hysteresis loops of synthesized Fe$_2$O$_3$ and QAMS–Fe$_2$O$_3$ are shown in Figure 3. Both of them showed the paramagnetic character. The saturation magnetization of Fe$_2$O$_3$ by reduction co-precipitation method was 37.6 emu/g, which agreed with the reported value [32, 35, 36]. The reduction of a saturation magnetization value was expected due to the QAMS coat [37]. The coating of the Fe$_2$O$_3$ with QAMS only caused a decrease of a further 9.3%, giving a final value of 34.1 emu/g, making it still very strongly responsive to an external magnetic field. The magnetically separated QAMS–Fe$_2$O$_3$ was not permanently magnetized and can be re-dispersed without any signs of re-aggregation when the external magnetic field is removed.

Figure 4. Morphological image (2500× magnitude) and elemental composition by EDX of (a) Fe$_2$O$_3$, (b) QAMS, and (c) QAMS–Fe$_2$O$_3$.

The surface morphology by SEM–EDX analysis before and after the coating of QAMS and QAMS–Fe$_2$O$_3$ shows that the surface morphology of QAMS–Fe$_2$O$_3$ more homogenous topological spherical form with an average particle size 0.006 µm (from image J) than QAMS (Figure 4). From EDX data, QAMS only consists of elements Si, O, C, and N. However, in QAMS–Fe$_2$O$_3$, there was Fe (1.77%). Compared to Fe$_2$O$_3$ (Table 2), the Fe percentage in QAMS–Fe$_2$O$_3$ (76.10) was relatively low.
Table 2. The elemental analysis by EDX of QAMS, synthesized FeO₄, and QAMS–FeO₄.

<table>
<thead>
<tr>
<th>Elements</th>
<th>QAMS</th>
<th>Synthesized FeO₄</th>
<th>QAMS–FeO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (%)</td>
<td>Atom (%)</td>
<td>Mass (%)</td>
</tr>
<tr>
<td>C</td>
<td>12.16</td>
<td>20.64</td>
<td>4.17</td>
</tr>
<tr>
<td>O</td>
<td>32.00</td>
<td>41.67</td>
<td>19.73</td>
</tr>
<tr>
<td>Si</td>
<td>49.28</td>
<td>35.78</td>
<td>–</td>
</tr>
<tr>
<td>Fe</td>
<td>–</td>
<td>–</td>
<td>76.10</td>
</tr>
<tr>
<td>N</td>
<td>5.27</td>
<td>1.16</td>
<td>–</td>
</tr>
<tr>
<td>I</td>
<td>1.29</td>
<td>0.23</td>
<td>–</td>
</tr>
</tbody>
</table>

RHA was generated from incinerating rice husk at 700 °C, as represented in equation reaction (1). The destruction process of RHA by NaOH would dissolve silica to generate red filtrate Na–Silica (eq. reaction (2)). Na–Silica has a very high solubility in pH > 10. To separate it, HCl added into pH neutral to isolated Na–Silica (condensation, eq. reaction (3)) [38]. The mechanism reaction for AMS formation was silane from 3-APTMS as a coupling agent release the amine functional group and then replaced by the silanol functional group. The amine group binds to the silica surface through a mechanism of electrophilic proton substitution reaction [39]. The AMS Methylation process is believed to be a nucleophile substitution (SN2) reaction by three carbon atoms with a methyl group being attacked by the nucleophile, an amine group replacing two H atoms with three methyl group generate QAMS with a naturally positive charge [26]. The proposed mechanism of QAMS formation from AMS is based on the reaction equation by de Campos et al. [26] presented in Figure 1. The primary evidence of QAMS formation was the FTIR spectra, i.e., disappearing absorbance at 1388 cm⁻¹, and emerging absorbance at 2939 cm⁻¹ in QAMS indicated a transformation of N–H from –NH₂ group to –N+(CH₃)₃ (Figure 1) and the existence of I (iodide) as the counter anions of QAMS (EDX data, Table 2).

Substance C, H, and Si (s) + O₂ (g) → CO₂ (g) + H₂O (l) + SiO₂ (s)  
SiO₂ (s) + 2NaOH (aq) → Na₂SiO₃ (aq) + H₂O (l)  
Na₂SiO₃ (aq) + H₂O (l) + 2HCl (aq) → Si(OH)₄ (s) + NaCl (aq)

Figure 5 The proposed mechanism of QAMS formation from AMS and the proposed structural model of QAMS–FeO₄.

Coating magnetite by QAMS occurs in pH neutral to prevent magnetite damage in acid and QAMS in alkaline [21]. The physical appearance of QAMS–FeO₄ (dark grey) was the coherence of its constituent magnetite (black) and QAMS (pale white). Based on the characterization of XRD (QAMS–FeO₄ have very similar position 2θ and d spacing with the standard d spacing), VSM (QAMS–FeO₄ have a magnetic moment: 34.1 emu/g), SEM (QAMS–FeO₄ have a spherical shape), and the literature with similar methods [13, 29, 40], it can be deduced that the FeO₄ was core shell by QAMS (Figure 5).

3.2. Stability Test of QAMS–FeO₄

The stability of the adsorbent was a vital parameter to know how much FeO₄ reinforces the SMQA. The higher the acidity, the more stable the QAMS–FeO₄. By increasing pH, the more adsorbent dissolved (Figure 6). This result indicates that the character of adsorbent is still dominated by SMQA stable in the acid medium [11]. The role of FeO₄ that should stabilize QAMS in an alkaline medium was not significantly seen yet. This result will be used as a reference for improving the coating method FeO₄ on QAMS in future research.

3.3. Chromate Anions Adsorption Study by SPA

In pH variation medium (flow rate 0.7 mL/min), the highest sorbed of Cr(VI) was at pH 6 (99%), and the smallest remaining concentration is at pH 8 (76%). Conversion sorption percentage to sorbed chromate anions in this condition was 9.99 mg/g adsorbent. It was estimated that the capacity of QAMS–FeO₄ higher than that value. The capacity of the adsorbent has an optimum value at a flow rate of 1.00 mL min⁻¹. The sorbed chromate anions estimated continues to decrease, along with increasing pH (Figure 7). Previously, treated rice husk for Cr(VI) removal was 71.0% and 76.5% respectively for dilute solutions at 20 g L⁻¹ adsorbent dose [41].

Recently, a similar adsorbent was reported by Huang et al. [42], graphene oxide-mesoporous silica (GO–MS) nanosheets with 3-(2-amino ethyl amino) propyl trimethoxysilane as the functional monomer showed that capacity of its adsorbent was 438.1 mg/g adsorbent to adsorb Cr(VI). From the result in Figure 7, the optimum pH occurs at pH 6, where the chromate anions maximum sorbed. Adsorption at pH 6 was also in accordance with the diagram of the relationship between
ion strength to pH (Pourbaix diagram) where Cr(VI) was in chromate anion form [43]. Optimum adsorption of chromate anions occurs at a flow rate of 0.7 mL/min (90.5%). This result proves that the more contact chromate solution, the more it sorbed to the adsorbent. The sorbed Cr(VI) on QAMS-Fe₃O₄, as a function of pH and flow rate can be seen in Figure 7.

Figure 7. Cr(VI) sorbed on QAMS–Fe₃O₄ as function of (a) pH at flow rate 0.7 mL/min and (b) flow rate.

4. Conclusions

It was remarkable research of pre-study in coating Fe₃O₄ on QAMS. Instrumental characterization of QAMS–Fe₃O₄ by FT-IR (disappearing absorbance at 1388 cm⁻¹, and emerging absorbance at 2939 cm⁻¹ in QAMS and QAMS–Fe₃O₄ indicated a transformation of N–H from –NH₂ group to [-N(CH₃)]₃). XRD (2θ = 30.15°, 35.53°, 43.12°, 57.22°, and 62.90°) (ICPD No. 00-033-0664) fathomed as a characteristic peak of magnetite). SEM–EDX (the homogenous topological spherical form with average particle size 0.006 μm that dominated by Si element (52.81%), and VSM (magnetic moment value = 34.1 emu/g) indicate the Fe₃O₄, convincingly coated by QAMS. Although it is necessary to improve the method to increase the binding of Fe₃O₄ to QAMS because QAMS–Fe₃O₄ is still not stable in an alkaline medium, the optimal pH is obtained in the range of 4 – 7, with more than 90% of the chromate ions adsorbed. This indicates that the synthesized adsorbent for chromate ion adsorption by the SPA method was successful. Even the SPA method is more suitable for adsorbent that is difficult to separate after the adsorption process. The SPA could also be applied in the very vast adsorbent and easy handling of desorption due to the adsorbent reusability.

Acknowledgment

The authors acknowledge LPPM Universitas Jambi for funded this research through PNBP LPPM Universitas Jambi by contract number 453/UN21.18/PG/SPK/2020.

References


[4] Jisuan Tan, Yiheng Song, Xiaohua Huang, Li Zhou, Facile Functionalization of Natural Peach Gum Polysaccharide with Multiple Amine Groups for Highly Efficient Removal of Toxic Hexavalent Chromium (Cr(VI)) Ions from Water, ACS Omega, 3, 12, (2018), 17309–17318 https://doi.org/10.1021/acsomega.8b02599


[20] Efehreema Nawaz, Sonia Zulfiquar, Muhammad Ilyas Sarwar, Mudassir Iqbal, Synthesis of diglycolic acid functionalized core-shell silica coated FeOx nanomaterials for magnetic extraction of Pb(II) and Cr(VI) ions, *Scientific Reports*, 10, 1, (2020), 10076 https://doi.org/10.1038/s41598-020-67168-2


[24] JYI-Wei Wu, Jing Zhang, Jun-Feng Liu, Lin Chen, Zhen-Li Deng, Mu-Xian Han, Xiao-Shui Wei, Ai-Min Yu, Hai-Li Zhang, Fe3O4@ZrO2 nanoparticles magnetic solid phase extraction coupled with flame atomic absorption spectroscopy for chromium(III) speciation in environmental and biological samples, *Applied Surface Science*, 258, 18, (2012), 6772-6776 https://doi.org/10.1016/j.apsusc.2012.03.057


and recovery of Hg from water, Water Research, 46, 12, (2012), 3913–3922
https://doi.org/10.1016/j.watres.2012.04.032

https://doi.org/10.1016/j.jnoncrysol.2011.02.022

https://doi.org/10.1016/S0167-577X(02)00879-0

https://doi.org/10.1016/j.colsurfa.2005.04.009

https://doi.org/10.1021/ie0203227

https://doi.org/10.14710/jkasa.22.2.52–57

http://dx.doi.org/10.1039/C1JM10111K

https://doi.org/10.1016/j.apsusc.2015.11.238

https://doi.org/10.3390/ma9060660

https://doi.org/10.1007/BF03353693

https://doi.org/10.1016/j.jhazmat.2008.05.037

[42] Renfeng Huang, Xiaoguo Ma, Xin Li, Lihui Guo, Xiaowen Xie, Menyuan Zhang, Jing Li, A novel ion-imprinted polymer based on graphene oxide–mesoporous silica nanosheet for fast and efficient removal of chromium (VI) from aqueous solution,