

Water Remediation by Adsorption of Phenol onto Hydrophobic Modified Clay

Sandro Froehner · Raquel Fernandes Martins ·
Willian Furukawa · Marcelo Risso Errera

Received: 25 June 2008 / Accepted: 6 September 2008 / Published online: 19 September 2008
© Springer Science + Business Media B.V. 2008

Abstract In this work we studied the phenol sorption from contaminated water onto modified clay mineral vermiculite and bentonite by insertion of hexadecyltrimethylammonium in the interlayer of clays. The non modified clays showed negligible interaction with phenol. The experimental data were treated using the Freundlich equation which had a good fit. The removal percentages were higher than 35% for modified vermiculite and for modified bentonite, 30%. Vermiculite and bentonite were compared for the removal of phenol from an aqueous solution based on the maximum adsorption capacity of each adsorbent, and no significant difference was found. The adsorption mechanism for both is the same, according to the results. Although, there is a lack of studies using vermiculite for this purpose, it can be concluded that hydrophobic modified vermiculite is very effective for removing phenol from water. Hydrophobic modified bentonite also remove phenol, but in lower proportions.

Keywords Remediation · Pollutants removal · Organoclays · Water pollution · Xenobiotics

1 Introduction

Water pollution is indeed of great concern since it is a major carrier of both organic and inorganic contaminants. In this work our attention is drawn to the removal of organic pollutants from water. Biological and physicochemical methods have been successfully applied to remove organic contaminants from water. The physicochemical methods include some based on adsorption by clay minerals and synthetic adsorbents. Clay minerals are known to have excellent adsorption properties and therefore they are widely used to remove organics from water (Yapar et al. 2005; Rytwo et al. 2007). Nevertheless, the performance of clay minerals may vary depending on the behavior of the contaminant with respect to water.

Hydrophobic organic contaminants often reach groundwater as result of industrial spills. Those chemicals are a long term source of soil and aquifer contamination, and they are quite difficult to remove because of their low solubility and high surface tension (Lee et al. 2002). A good example of the inefficiency of this process is using clay minerals to remove phenol from water (Banat et al. 2000).

Phenols are contaminants widely used in industry. They are considered to be a major pollutant since they can be harmful to living organisms even at low concentrations. In addition, phenols also present potential harm to human health.

Clays are widely used to remove liquid impurities from water due to their highly specific area and their

S. Froehner (✉) · R. F. Martins · W. Furukawa ·
M. R. Errera
Departamento de Engenharia Ambiental,
Centro Politécnico, Universidade Federal do Paraná,
Curitiba, Paraná 81531-990, Brazil
e-mail: froehner@ufpr.br

chemical and mechanical stability (Juang et al. 2002). However, their performance in removal is compromised in groundwater decontamination, since hydration of exchangeable alkali and alkaline earth metal cations creates a hydrophilic environment on the surface and in the interlayer region of natural clays. (Abate and Masini 2000).

The adsorbent properties can be improved by replacing the natural inorganic cations with organic cations such as quaternary ammonium cations of the $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$ form. The main purpose of such a modification is to increase the hydrophobic nature of the mineral surface and consequently enhance the affinity to organic compounds.

Organoclays show different hydrophobic properties depending on the organic cations structure and its uptake into the gallery. This is an important feature because the treatment of the mineral can be adjusted according to need. Therefore organoclays may be employed to remove several pollutants in water, namely: heavy metal ions, inorganic anions such as chromate, organic compounds and pesticides (Krishna et al. 2001).

The modification proposed in this work enhances the removal of non-ionic organic solute from aqueous solution.

The organophilic properties of the modified clay result in part from the reduced degree of hydration of the organic cations as compared to natural inorganic exchangeable cations (Abate and Masini 2000). Modified clays have proved effective in removing various organic contaminants (Banat et al. 2000) and may be useful to treat contaminated water (Bowman et al. 2005). Much attention has been drawn to the modification of clay mineral properties, because it is low cost and readily available in several technological applications (Nir et al. 2007).

Recently there has been increasing interest in utilizing natural clay minerals such as montmorillonite, kaolinite, illite, bentonite and zeolite for the removal of toxic metals and organic contaminants from aqueous solutions (Bowman 2003; Aguiar et al. 2002; Béguin and Ania 2007).

Surfactant modified zeolite has shown the ability to remove chromate from water (Bowman et al. 2000) and

monoaromatic compounds (benzene, toluene, ethylbenzene and xylene) from contaminated water (Bowman et al. 2005). In the same work it was concluded that hexadecyltrimethyl ammonium is too large to enter the internal position of the zeolite and that amine adsorption only occurs on the external exchange sites of the zeolite.

The use of modified clays to remove phenols and chlorinated phenols from water can also be seen in early works such as Banat and Al-Ashed (2000) and Rytwo et al. (2007), among others.

Another very important attribute when clay modification is proposed for organoclay is the cation exchange capacity (CEC). Vermiculite and bentonite are clay minerals with high CEC. The CEC for vermiculite, for instance, is approximately 100–150 meq per 100 g (Abate and Masini 2000). Furthermore, vermiculite and bentonite are widely available in Brazil and in some other countries.

Despite the potential use of vermiculite as an adsorbent in environmental applications, few studies have been published on this subject. For that reason, the purpose of this work is to shed some light on the use of modified vermiculite and bentonite as adsorbents to remove phenol from water and its possible application for others contaminants in water.

2 Materials and Methods

2.1 Reagents

The phenol used in the tests was from Merck (Darmstadt, Germany) with 99.5% purity. The physicochemical properties of phenol are listed in Table 1. Hexadecyltrimethylammonium chloride, at 99% purity, was purchased from Aldrich Chemical Company Inc. (Milwaukee, USA). All others reagents were also acquired from Aldrich. Water used in all experiments was distilled and deionized.

2.2 Organoclay Syntheses

In this work two organoclays were used. Vermiculite (VT) samples were supplied by Brasil Minerios Ltda.

Table 1 Physicochemical properties of phenol

| MW (g/mol) | pKa (25°C) | Water solubility (g/L) | Octanol–water partition coefficient (25°C) |
|------------|------------|------------------------|--|
| 94.11 | 9.92 | 87 (20°C) | 30.2 |

from a mine located in Central Brazil, and bentonite (BT) was supplied by Colorminas SA (Southern Brazil). Both samples were ground to less than 1 mm.

Later the cation exchange capacity (CEC) for both, vermiculite and bentonite was determined in triplicate by sodium saturation method as seen in Hesse (1971). Vermiculite CEC turned out to be 115 meq/100 g of mineral and the CEC of the bentonite was 82 meq/100 g of mineral. The chemical composition of both clays was given by suppliers (see Table 2).

The organoclays were synthesized by cation exchange with 10 mmol/L hexadecyltrimethylammonium chloride (HDTMA) solution with thorough stirring. An amount of mineral (either vermiculite or bentonite) suspension was added to HDTMA solution in order to provide a unitary HDTMA-Mineral ratio (the surfactant in an amount equivalent to 100% of CEC). According to Klapysa et al. (2001) higher proportions would not enhance the cation exchange.

The suspensions were stirred for 8 h at room temperature. The solid phase was then separated by centrifugation and washed with deionized water; this step was repeated until no more surfactant was found in the wash water, determined spectrophotometrically by the reaction between surfactant and Orange II, the salt was extracted with chloroform and spectrophotometrically determined (Scott 1968). The samples were then ready for testing.

2.3 Phenol Adsorption Isotherms

The purpose of testing was to determine the adsorption isotherms.

Phenol adsorption isotherms from aqueous solutions were obtained using the batch equilibration technique. For each isotherm, 100 mg of organoclay, HDTMA-VT (modified vermiculite) and HDTMA-

BT (modified bentonite), were weighed into 250 mL Erlenmeyer flasks, followed by addition of aqueous phenol solution in concentrations of 0.02–0.15 mmol/100 mL. The flasks were closed and stirring continued for 12 h at 25°C, according the procedure described by Boyd et al. (1998). After the contact time, the pH of the suspensions was measured and the solids phases were centrifuged and the supernatant was subsequently analyzed for residual concentration of phenol. The same procedure was followed when the clay was natural, with no modification.

All experiments were run in triplicate to ensure reproducibility.

2.4 Analysis of Phenol

The phenol concentration in water was determined according to the method of Gales and Booth (1976). This method is based on the spectrophotometric analysis of the developed color resulting from the reaction of phenol with 4-aminoantipyrine. The final equilibrium concentrations were determined spectrophotometrically using a Shimadzu UV-Visible 1601 PC model at 269 nm absorption.

2.5 Data Analysis

The results of the sorption tests were treated by the linear form of the Freundlich isotherm model only, which is summarized by the following equation:

$$\log(q) = \log K_f + 1/n \log C \quad (1)$$

where q is the concentration of the studied compound in the solid phase ($\mu\text{mol kg}^{-1}$), C is the solution concentration ($\mu\text{mol L}^{-1}$) after a given contact time. The Freundlich constants are named K_f ($\mu\text{mol kg}^{-1} \text{L}^{1/n} \cdot \mu\text{mol}^{-1/n}$) and n are related to the adsorption capacity and adsorption intensity, respectively. The values of K_f and n can be obtained from the intercept and slope, respectively, of the linear form of the equation.

The values of K_f and n can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\log q$ versus $\log C$.

The sorption distribution coefficients K_d were calculated using the equation:

$$K_d = q/C \quad (2)$$

Table 2 Chemical analysis of vermiculite and bentonite

| Compound (wt, %) | Vermiculite | Bentonite |
|--------------------------------|-------------|-----------|
| SiO ₂ | 34–43 | 66 |
| Al ₂ O ₃ | 7–15 | 23 |
| Fe ₂ O ₃ | 5–13 | 0.99 |
| CaO | 0.2–1.0 | 0.20 |
| MgO | 20–28 | 0.62 |
| Na ₂ O | 0.1–0.3 | 0.13 |
| K ₂ O | 0.01–0.1 | 1.60 |

The sorption coefficients were normalized to the organic carbon (OC) content of the material using Eq. 3, providing the K_{OC} values.

$$K_{OC} = (K_d/\%OC) \times 100 \quad (3)$$

The results were then ready to be analyzed.

3 Results and Discussion

Various mechanisms control the kinetics in the adsorption phenomena (Shukla et al. 2005) such as mass transfer of solute from solution to the boundary film, mass transfer of phenol from boundary film to surface, sorption of phenol onto sites, internal diffusion of solute. Some of them are fast, such as sorption onto sites, and others are slow depending on some parameters, like agitation and surface homogeneity. Figure 1 shows the sorption isotherms of phenol on clay (modified and natural).

The chart shows that the removal rate of both natural clays utilized is limited—as expected there is saturation and no more phenol can be adsorbed.

In cases when the adsorbent is organoclay, i.e., modified clay with hexadecyltrimethylammonium, C-type isotherms were observed. This agrees with previous studies (e.g., Banat et al. 2000; Abate and Masini 2000). Furthermore, it can also be observed that when the clay is natural, with no artificial hydrophobic environment on the mineral surface, the

phenol removal from aqueous solution is poor. The sorption parameters of the Freundlich model are reported in Table 3.

Table 3 shows that the values of the regression, r^2 are almost unitary. This agreement indicates that the partition model represents the experimental data appropriately.

Another interesting result shown in Table 3 is the near unitary values of the exponent n of the model. Abate and Masini (2000) provided a meaning for the unitary value of n . They claimed that in those cases non-specific interactions occur between solute and sorbent.

In above mentioned work, however, this conclusion was drawn after experiments with compounds of the family of atrazine series. The chemical structure of atrazine compound series is an amino group, and it is also as soluble in water as phenol. Phenol has a good solubility in water (8.2 g/100 mL) that results from hydrogen bonds between water and phenol molecules. Therefore an intense sorption of phenol cannot be expected. In addition, the hydrophobic interactions are weak due to low hydrophobicity of phenol.

As to K_f , which represents the adsorption capacity, both values are very similar for modified vermiculite and bentonite alike. These findings are in good agreement with the value reported by Banat et al. (2000) who used bentonite modified with hexadecyltrimethylammonium to remove phenol from water. From the K_f values, the following sorption order can be depicted for vermiculite and bentonite, in natural form and modified, HDTMA-VT>HDTMA-BT»VT and BT.

Summing up, the amounts of phenol adsorbed using bentonite and vermiculite agree with the findings of earlier studies (Banat et al. 2000; Boyd et al. 1998; Abate and Masini 2000).

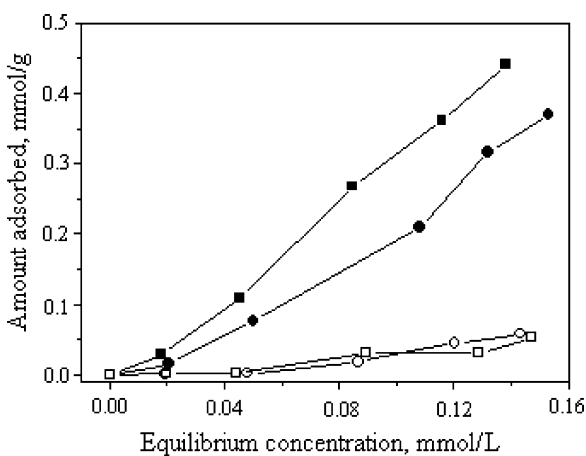


Fig. 1 Sorption of phenol from water by HDTMA-VT (filled square), HDTMA-BT (filled circle), VT (empty square) and BT (empty circle)

Table 3 Freundlich parameters: K_f ($\mu\text{mol kg}^{-1}$) ($\mu\text{mol l}^{-1}$) $^{1/n}$ and n for sorption of phenol onto HDTMA-VT, HDTMA-BT

| | K_f | n | r^2 |
|----------|-------|-------|-------|
| HDTMA-BT | 38 | 0.905 | 0.992 |
| HDTMA-VT | 45 | 0.962 | 0.994 |
| VT | 11 | 1.78 | 0.995 |
| BT | 10 | 1.85 | 0.991 |

Values show are the average of three replicate analyses, standard deviation <3.5%

According to Boyd et al. (1998) and also Hamaker and Thompson (1972) the phenol is adsorbed on negatively charged surfaces through hydrogen bonding and/or charge transfer complexes.

In cases when the clay was modified the n values are close to one, indicating that the partition model properly represents the experimental data (de $r^2 > 0.99$). Abate and Masini (2000) suggested that when n values are close to 1 the partition model represents the experimental aspect, and non-specific interactions occur between solute and sorbent, although compounds of the atrazine family were used. The chemical structure of the atrazine compound series includes an amino group, even though it is as soluble in the water as the phenol. The values of K_f , which represent the adsorption capacity are very similar for modified vermiculite and bentonite, but when the adsorbent is vermiculite and bentonite in natural form the amount adsorbed was insignificant. This poor interaction could be accounted for the inexistence of a hydrophobic site for the accommodation of phenol or electrostatic interaction between clay and phenol (Polubesova et al. 2008). These values obtained are in good agreement with the value reported by Banat et al. (2000) using modified bentonite with hexadecyltrimethylammonium for removing phenol from water.

According to Boyd et al. (1998) and Hamaker and Thompson (1972) the phenol is adsorbed on negatively charged surfaces through hydrogen bonding and/or charge transfer complexes. The amount of phenol adsorbed using bentonite and vermiculite is in agreement with the findings of others authors (Banat et al. 2000; Boyd et al. 1998; Abate and Masini 2000).

The apparent inability of HDTMA-clay to sorb this group of phenols may stem from the fact that the interlayer pore sizes are not large enough to accommodate phenol or its chlorinated isomers (Banat et al. 2000). Thus, the different sorption behaviors by the organoclays in water are due to a difference in interlayer pore structure induced by the presence of water. This can be attributed to the greater hydration of interlayer HDTMA, and a larger hydration sphere surrounding HDTMA in the interlayer region. The quaternary alkylammonium leaves some polar room between the groups that can be occupied by water molecules, probably associated with basal oxygen of the clay network or to residual inorganic cations (Koskinen et al. 2004). According to Mortland et al.

(1989) the organoclay effectively removed phenol from hexane but not from water. In the former case the HDTMA cations were apparently not strongly hydrated and hence, the sorptive regions between HDTMA cations were large enough to accommodate phenol.

We also compared vermiculite and bentonite concerning their performance to remove phenol from aqueous solution. The comparison was based on the maximum adsorption capacity of each adsorbent. No significant difference was found (Table 3).

The results of the present work also show that the adsorption mechanism was the same for both vermiculite and bentonite. The adsorption mechanism for both, according to the results, is the same.

Abate and Masini (2000) concluded that modified vermiculite can remove more than 60% of propazine and Boyd et al. (1998) observed that bentonite removed more than 40% of phenol from the aqueous solution. In both cases, propazine and phenol are very soluble in water. Here, we found that the hydrophobically vermiculite can remove more than 45% of phenol dissolved in water, the modified bentonite showed a similar behavior, approximately 39%. The system composed by natural vermiculite and natural bentonite showed percentages much lower, 5%, for both systems. It is important to know that the pH of the final solutions containing phenol and adsorbent were in the range of 6.8 thru 7.5, thus below the pK_a of phenol (known to be 9.92). This means that, in the equilibrium, the protonated species are predominant and no phenoxi ion is present. The phenoxi ion might interact with natural clay, therefore the amount would be more. Such behavior was already observed for the adsorption of antibiotics by natural montmorillonite (Polubelova et al. 2008).

The results presented in this work in addition to the lack of studies on vermiculite as phenol adsorbent lead us to infer that there is no significant difference in the amount of phenol adsorbed. Our early experi-

Table 4 Coefficients of distribution and organic carbon

| | K_d | K_{OC} |
|----------|-------|----------|
| HDTMA-BT | 26 | 260 |
| HDTMA-VT | 32 | 266 |
| BT | 3 | 11 |
| VT | 4 | 12 |

ations, however, were that there would be many more hydrophobic sites for organovermiculite and consequently more phenol should have been removed.

The results of the sorption of phenol onto organically clays are summarized in Table 4 through the values sorption distribution coefficients, K_d , and their counterpart after normalization to the organic carbon (OC).

It is shown that the values of K_d for both organo clays are in the same order of magnitude as those values of K_f estimated for the Freulich model. This statement can only be true because the parameter n of the Freulich model was found to be close to one, i.e., they show the same order of affinity. Furthermore, the organic carbon contents in both organoclays, expressed as K_{OC} , reveal that affinity is not significantly different for both forms of organically modified minerals.

4 Conclusions

In this work we investigated the possibility of removing phenol from aqueous solution by modifying clays with hexadecyltrimethylammonium (HDTMA) in the interlayer of clays. Experiments were carried out with modified vermiculite and bentonite under different equilibrium concentrations of phenol.

Firstly we observed that HDTMA is completely adsorbed by vermiculite as well as bentonite. The lab results also showed that the proposed modification significantly enhanced the sorption capacity of these minerals for phenols in aqueous solution.

We also found that the partition model was suitable to represent the sorption isotherms of phenol for modified vermiculite and bentonite.

Based on theoretical assumptions we believe that the performance of modified clays can be further extended to some other hydrophobic compounds.

In conclusion, vermiculite has great potential for removing others hydrophobic contaminants from water and, moreover, the expected efficiency can be a little higher than HDTMA-BT suggesting that non-specific interaction occurs between organoclays and phenol, indicating that the chain interactions are strong enough to keep HDTMA in the adsorbed layer. The vermiculite could be very useful for removing others hydrophobic contaminants from water and the efficiency is a little higher than HDTMA-BT.

Acknowledgments We are grateful to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) for the financial support of this work (Processo 409955/2006-0 and Processo 471211/2006-0). Also we thanks to the anonymous reviewer for helpful suggestions.

References

- Abate, G., & Masini, J. C. (2000). Sorption of atrazine, propazine, deethylatrazine, deisopropylatrazine and hydroxyatrazine onto organovermiculite. *Journal of the Brazilian Chemical Society*, 16, 936–943.
- Aguiar, M. M. R. P., Novaes, A. C., & Guarino, A. W. S. (2002). Removal of heavy metals from wastewaters by aluminosilicate. *Quimica Nova*, 25, 1145–1154. doi:10.1590/S0100-40422002000700015.
- Banat, F., & Al-Ashed, S. (2000). Biosorption of phenol by chicken feathers. *Environmental Engineering and Policy*, 2, 85–90. doi:10.1007/s100220000022.
- Banat, F. A., Al-Bashir, B., Al-Ashed, S., & Hayajneeth, O. (2000). Adsorption of phenol by bentonite. *Environmental Pollution*, 107, 391–398. doi:10.1016/S0269-7491(99)00173-6.
- Béguin, F., & Ania, C. O. (2007). Mechanism of adsorption and elutrosorption of bentazone on activated carbon cloth in aqueous solution. *Water Research*, 41, 3372–3380. doi:10.1016/j.watres.2007.03.031.
- Bowman, R. (2003). Applications of surfactant-modified zeolites to environmental remediation. *Microporous and Mesoporous Materials*, 61, 43–56. doi:10.1016/S1387-1811(03)00354-8.
- Bowman, R., Sullivan, E. J., & Li, Z. (2000). *Natural zeolites for the third millennium*. Napoly, Italy: C. Colella and F. A. Mumpton.
- Bowman, R. S., Ranck, J. M., Weeber, J. L., Katz, L., & Sullivan, E. J. (2005). BTEX removal from produced water using surfactant-modified zeolite. *Journal of Environmental Engineering*, 131, 434–442. doi:10.1061/(ASCE)0733-9372(2005)131:3(434).
- Boyd, S. A., Lawrence, M. A. M., & Kukkadapu, R. K. (1998). Adsorption of phenol and chlorinated phenols from aqueous solution by tetramethylammonium- and tetraethylphosphonium-exchanged montmorillonite. *Applied Clay Science*, 13, 13–20. doi:10.1016/S0169-1317(98)00009-X.
- Gales, M., & Booth, R. (1976). Automated 4AAP phenolic method. *Journal of the American Water Works Association*, 68, 540.
- Hamaker, J. W., & Thompson, J. M. (1972). Adsorption. In C. A. Goring, & J. W. Hamaker (Eds.), *Organic chemicals in the soil environment, vol. 1* (pp. 19–143). New York: Marcel Dekker.
- Hesse, P. R. (1971). *A textbook of soil chemical analysis*. London: Murray.
- Juang, R. S., Lin, S., & Tsao, K. H. (2002). Mechanism of sorption of phenols from aqueous solutions onto surfactant-modified montmorillonite. *Journal of Colloid and Interface Science*, 254, 234–241. doi:10.1006/jcis.2002.8629.

- Klapyta, Z., Fujita, T., & Iyu, N. (2001). Adsorption of dodecyl- and octadecyltrimethylammonium ions on a smectite and synthetic micas. *Applied Clay Science*, *19*, 5–10. doi:10.1016/S0169-1317(01)00059-X.
- Koskinen, W. C., Carrizosa, M. J., & Hermosin, M. C. (2004). Interaction of acidic herbicides bentazone and dicamba with organoclays. *Soil Science Society of America Journal*, *68*, 1863–1866.
- Krishna, B. S., Murty, D. S. R., & Prakash, J. B. (2001). Surfactant-modified clay as adsorbent for chromate. *Applied Clay Science*, *20*, 65–71. doi:10.1016/S0169-1317(01)00039-4.
- Lee, D. H., Cody, R. D., Kim, D. J., & Choi, S. (2002). Effect of soil texture on surfactant-based remediation of hydrophobic organic-contaminated soil. *Environment International*, *27*, 681–688. doi:10.1016/S0160-4120(01)00130-1.
- Mortland, M. M., Boyd, S. A., Chiou, C., & Lee, J. F. T. (1989). Shape-selective adsorption of aromatic molecules from water by tetramethylammonium-smectite. *Journal of the Chemical Society, Faraday Transactions 1*, *85*, 2953–2962. doi:10.1039/f19898502953.
- Nir, S., Zadaka, D., Mishael, Y. G., & Polubesova, T. (2007). Modified silicates and porous glass as adsorbent for removal of organic pollutants from water and comparison with activated carbons. *Applied Clay Science*, *36*, 174–181. doi:10.1016/j.clay.2006.04.012.
- Polubesova, T., Zadaka, D., Groisman, L., & Nir, S. (2008). Water remediation by micelle-clay system: Case study for tetracycline and sulfonamide antibiotics. *Water Research*, *40*, 2369–2374.
- Rytwo, G., Kohavi, Y., Botnick, I., & Gonen, Y. (2007). Use of CV- and TPP-montmorillonite for the removal of priority pollutants from water. *Applied Clay Science*, *36*, 182–190. doi:10.1016/j.clay.2006.04.016.
- Scott, G. V. (1968). Spectrophotometric determination of cationic surfactants with Orange II. *Analytical Chemistry*, *40*, 768–773. doi:10.1021/ac60260a038.
- Shukla, S. S., Yu, L. J., Dorris, K. L., & Shukla, A. (2005). Removal of nickel from aqueous solutions by sawdust. *Journal of Hazardous Materials*, *B121*, 243–246. doi:10.1016/j.jhazmat.2004.11.025.
- Yapar, S., Özbudak, V., Dias, A., & Lopes, A. (2005). Effect of adsorbent concentration to the adsorption of phenol on hexadecyl trimethyl ammonium. *Journal of Hazardous Materials*, *B121*, 135–139. doi:10.1016/j.jhazmat.2005.01.021.