Effects of the combinations of 6 materials on the improvements in contaminant removals from surface water: purification mechanisms and adsorption kinetics

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Abstract. The study aims to improve the pollution control and eutrophication reduction in surface water by adding various materials and explore corresponding purification mechanisms. Methods: Six materials (H₂O₂, NaClO, persulfate, polyacrylamide, zeolite, and montmorillonite) were added into surface water. Different dosage combinations and treatment periods were arranged in the experiments. After the treatment, the contaminant removal performance was determined the water quality and toxic effects were analyzed. Results: The optimal dosages of the 6 materials were experimentally confirmed as follows: 0.3 mg/L H₂O₂, 0.03 mg/L NaClO, 5 g/L persulfate, 0.4 mg/L polyacrylamide, 20 mg/L zeolite, and 10 mg/L montmorillonite. The purification mechanisms involve chemical reactions and material adsorption. Conclusion: The combination of the 6 materials can be applied in surface water treatment as a green option.

1. Introduction
Environmental pollution directly affects organisms [1]. Excessive urban development generally results in environmental problems, such as surface water pollution [2]. Organics, nitrogen and phosphorus in surface water lead to algal blooming, fish death/floating, and deterioration of biodiversity and eventually negatively affect human health [3]. In some metropolises, discharged domestic wastewater has reached an alarming level and water has become black and odorous [4-5]. Therefore, it is necessary to develop an efficient, fast and eco-friendly way to improve the surface water quality in urban areas.

The main ways to improve the performance of contaminant removals in surface water are biological and physico-chemical ways [6]. In physico-chemical ways, the oxidation-reduction process triggered by ions (electrolyzed or hydrolyzed from chemicals) in surface water improves water quality. Flocculation and precipitation reactions also happen in surface water and low-solubility products of contaminants fall in the sediment layer, thus improving water quality. Chemical materials added in surface water lead to fast contaminant removal, but over-dosing may result in ecological threat and waste.

Due to the high purification performances of these materials, such as hydrogen peroxide (H₂O₂), NaClO, polyacrylamide (PAM), persulfate, natural zeolite, and montmorillonite power, they are applied in wastewater treatment. These materials are easily controlled as an effective and fast option to improve surface water quality. Hydrogen peroxide is the major oxidant generated from superoxide. In water, oxygen can be generated slowly from H₂O₂, which can reduce chemical oxygen demand (COD)
as well [7]. Peroxydisulfate (PDS) was used in organic pollution treatment and the contaminant removal performance was improved with 0.5 M PDS [8]. Polyacrylamide (PAM) is a high-molecular-weight and water-soluble polymer with different charges (anionic, cationic, or neutral) [9] and can interact with other particles via bridging flocculation [10]. Zeolite is an abundant, non-toxic, and eco-friendly material and has been used in wastewater treatment as a sorbent material (usually dosage of 4-30 mg/L) [11]. Montmorillonite (Mt) has the high cation exchange capacity (CEC), layer expansion capacity [12], and high surface area [13] and shows the high adsorption and storage ability for various cationic contaminants [14]. Nowadays, adsorbent materials were used wastewater treatments, but the combination of different material with optimal dosage was not reported yet. The mechanism of removal and the possible interaction of different material was not studied. As a result, this study aims to explore different combinations of easily manipulated materials with the optimal dosages based on the removal performance of different contaminants, and treatment cost. The materials with optimal dosages were verified in surface water as well. Moreover, the removal mechanism was explored by adsorption isotherms, thermodynamics and adsorption kinetics analysis.

2. Material and methods

2.1 Descriptions of surface water to be treated
Surface water to be treated is located in Shanghai (31°2’ N, 121°4’ E) and the water quality parameters are 28±1°C of temperature, 6.8±0.3 of pH, 3.8±0.1 mg/L of DO, 59±3 mV of ORP, 5±2 NTU of Turbidity, 33.5±0.5 μg/mL of Chlorophyll a, 5.8±0.15 mg/L of TN (NH₄⁺: 5.1±0.1 mg/L, NO₃⁻: 0.6±0.11 mg/L), 1.1±0.01 mg/ of DTP (DIP: 0.6±0.01 mg/L), and 65±3 mg/L of COD. The local climate is moderate and humid in the whole year. Surface water is drainage water from the urban area and contains 80% of domestic sewage.

2.2 System operation
This experiment was performed from November, 2016 to July, 2017. Air temperature was measured by an Air Quality Measure Meter (Pranus, China). 30% mass fraction of H₂O₂ (0.2 mg/L), 10% active chlorine of NaClO (0.03 mg/L), PDS (5 g/L), PAM (0.4 mg/L), Zeo (20 mg/L), and Mt (10 mg/L) were respectively added into surface water to confirm the optimal combination in Stage 1. Water sample analysis was completed in 3 h after adding the 6 materials. All the materials were purchased from Sinopharm Chemical Reagent Co., Ltd. In Stage 2, the combinations of 6 materials were added. Different temperatures (10 °C (T1), 15 °C (T2), 20 °C (T3), 25 °C (T4), 30 °C (T5)) and different reaction intervals (10 min (t1), 20 min (t2), 30 min (t3), 45 min (t4), 60 min (t5), 90 min (t6), and 120 min (t7)) were arranged in the experiments to confirm optimal environmental conditions and reaction time based on adsorption isotherms, thermodynamics, and adsorption kinetics analysis. When ambient temperature reached each temperature, the experiments of different reaction intervals were launched in our laboratory after sampling treated surface water.

2.3 Water sampling and analysis
In the experiment, 3 replicate samples were obtained for each treatment. The samples were collected into a plastic boxes (50 L) from the targeted surface waters, carried to the laboratory within 30 min, and filtered through glass-fiber filters (0.22 μm) for analysis. The pH, DO, water temperature, ORP, and chlorophyll a (Chl-a) of water samples were analyzed by digital analysis instrument (HQ40d, HACH, USA), and a water quality meter (Manta 2, EURERA, USA) immediately after sampling. According to the standard methods described by the American Public Health Association (2002), TN, NH₄⁺-N, NO₃⁻N, DTP, DIP, and COD in water samples were analyzed with a spectrophotometer (DR900, HACH, USA).

2.4 Data and Statistical Analysis
The measured water flows were used to calculate contaminant removal efficiencies and physico-chemical indexes. The contaminant concentration measurements of 3 samples from influent and effluent were respectively averaged, and the experiment results were plotted as standard error bars. The curves were plotted in Origin Pro 9.0. The data were analyzed by variance (ANOVA) at $P < 0.05$. All statistical analyses were performed in the software SPSS 20.0.

3 Results and discussion

3.1 Adsorption analysis of the combination of materials

3.1.1. Contaminant removal performance of different combinations

The Combination I of PDS, H$_2$O$_2$, and NaClO showed the better removal performances of organic matters and Chl-a. Algae reduction still depended on NaClO and the effect of Combination I on COD removal was better than that of single material (Table 1), indicating that microbial activities were enhanced and oxygen required for removing organic matters was increased [15-16]. The Combination II with PAM, Mt, and Zeo showed the better removal performance of organic matters. The main mechanism of Combination II involved adsorption and ion exchange.

| Combination | Materials | Parameters (%) | Cost (USD/L) |
|-------------|-----------|----------------|--------------|
| I           | PDS+H$_2$O$_2$+NaClO | 57±1$^a$ | 53±1$^a$ | 45±3$^a$ | 73±1$^a$ | 87±2$^a$ | 0.015 |
| II          | PAM + Mt +Zeo | 49±3$^b$ | 33±2$^b$ | 69±1$^b$ | 70±1$^b$ | 39±3$^b$ | 0.004 |
| III         | PDS+H$_2$O$_2$+NaClO + PAM + Mt +Zeo | 84±2$^c$ | 54±2$^a$ | 72±1$^c$ | 81±2$^b$ | 91±4$^c$ | 0.019 |
| CK          | Not added | 3±1$^d$ | 2±2$^c$ | 4±1$^d$ | 3±1$^c$ | 5±1$^d$ | - |

Note: Values are expressed as mean ± standard deviation. Values in a column with different letters indicate the significant results with $P < 0.05$.

Combinations I & II & III improved TN removal, indicating that ammonia was removed in treated surface water. Ammonia remains as a long-term pollutant in the methanogenic phase of decomposition [17] and domestic wastewater contains almost much more ammonium compared to phosphate (N/P=5 in China) [18]. Ammonium is the main contaminant in surface water receiving domestic wastewater. Kinetics analysis was performed based on the ammonium concentration in this study.

3.1.2. Adsorption isotherms

Ammonia removal data were used in the analysis with mathematical models such as Langmuir, Freundlich, and Temkin models to establish the most appropriate correlation for the equilibrium curves. The adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent ($q_e$, $q_e = R_A$) to the adsorbate concentration under equilibrium conditions ($C_e$) at constant temperature [19]. In the Langmuir model, it is assumed that adsorption happens on a homogeneous surface, where each molecule owns constant enthalpy and sorption activation energy [20]. The Langmuir isotherm model is given as:

$$q_e = \frac{k_L C_e q_{max}}{1+k_L C_e}, \quad (1)$$

where $k_L$ refers to the equilibrium constant of Langmuir model and $q_{max}$ refers to maximum adsorption capacity. As shown in Tables 2 & 3, when $0 < R_L < 1$, the adsorption isotherms fit well the adsorption amounts of ammonia onto Combination III and Combination II with $q_{max}$ = 20.9128 mg/L and 18.883 mg/L, respectively. This value of Combination III was much lower than the tested results, indicating that the improved performance of ammonia removal driven by Combination III depended on the monolayer adsorption process and the interaction between adsorbate and specific adsorbents in this study.

In the Freundlich model (Eqs. (2)), it is assumed that adsorption happens on a heterogeneous surface with the interaction among adsorbed molecules [21]. In Temkin isotherm model (Eqs. (3)), it is
assumed that the heat of adsorption of all the molecules in the surface layer is linearly decreased and that the adsorption process is characterized by a uniform distribution of binding energy [21].

\[ q_e = K_f C_e^{\frac{1}{n}}. \]  
\[ q_e = B_T \ln A_T C_e. \]

In Table 6, the value of \( B_T \) is higher than 8 kJ/mol, indicating that the heat of adsorption of ammonia ion onto Combination III is a chemical adsorption process [22]. This result was in accordance with Freundlich model.

According to the isotherm analysis with different models, the adsorption process of Combination II was a physical process. According to Freundlich and Temkin models, the adsorption process of Combination III was a chemical adsorption process, but the results of Langmuir model with the higher \( R^2 \) suggested that the process was a physical adsorption process. As mentioned above, the improved ammonia removal performance depended on the layer adsorption and the interaction between adsorbates and specific adsorbents (Eqs. (2) and (3)).

3.1.3 Thermodynamics

The energy of an isolated system is constant and cannot be gained or lost in thermodynamics, and the entropy change is the only driving force [20]. In order to find out the spontaneous process in a system, both energy and enthalpy factors should be considered [23].

The thermodynamic parameters, standard free energy (\( \Delta G^\circ \)), standard enthalpy (\( \Delta H^\circ \)) and standard entropy (\( \Delta S^\circ \)) can be determined by Eq. (4):

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \]

Eq. (4) is a well-known equation of free energy change at a constant temperature and Eq. (5) expresses the relationship between free energy change and temperature:

\[ \Delta G^\circ = -RT \ln k_c. \]

where the equilibrium constant, \( k_c = \frac{q_e}{C_e} \), can be approximated by the Langmuir model; \( T \) is the absolute temperature; \( R \) is the gas constant (8.314 J/(mol·k)). The negative values of \( \Delta H^\circ \) and \( \Delta S^\circ \) (Table 4) confirmed an exothermic adsorption process [24] and the lower randomness [20,23].

The negative value of \( \Delta G^\circ \) indicated that the adsorption process of ammonia ion onto Combination III and Combination II was spontaneous. \( \Delta G^\circ \) value was changed from the negative value to the larger negative value with the increase in temperature, indicating that the adsorption process was feasible and favorable at T1 (10 °C). The features of Combination III and Combination II are conducive to the bioremediation of surface water treatment at low temperature. In thermodynamics, the negative value of enthalpy in the study indicated that the adsorption process was a physical adsorption process. This result was opposite to isotherm analysis results by Freundlich and Temkin models because of the difference between Combination II and Combination III. The improved ammonia removal performance of Combination II (PAM + Mt +Zeo) depended on adsorption in surface water treatment. Therefore, the adsorption process can be explained by the theory of electric double layer.

3.1.4 Adsorption kinetics

Adsorption kinetics describe the variations of the rate of adsorption with the adsorbate concentration or solution concentration. In order to investigate the adsorption kinetics of ammonia ion on the materials at different temperatures (Figure 1), the pseudo-first-order model and pseudo-second-order model were used to fit the experiment data for adsorption identification.
Table 2 Reduction of ammonia (mg/L) after the treatment with the Combination II & III at different temperatures.

| Temperatures | $C_i$ (mg/L) | Combination II | Combination III |
|--------------|--------------|----------------|-----------------|
|               | $C_e$ (mg/L) | $R_A$ (mg/L)  | $q_e$ (mg/L)    | $C_e$ (mg/L) | $R_A$ (mg/L) | $q_e$ (mg/L) |
| T1           | 1±0.2        | 0.57±0.01     | 0.43±0.01       | 5.51         | 0.71±0.01   | 0.29±0.01    | 9.67          |
| T2           | 1.6±0.2      | 0.816±0.01    | 0.784±0.0       | 7.07         | 1.18±0.02   | 0.416±0.0    | 13.87         |
| T3           | 2.1±0.1      | 0.987±0.01    | 1.113±0.0       | 7.57         | 1.62±0.01   | 0.483±0.0    | 16.1          |
| T4           | 2.9±0.1      | 1.247±0.02    | 1.653±0.0       | 8.48         | 2.38±0.03   | 0.522±0.0    | 17.4          |
| T5           | 5.1±0.1      | 3.141±0.01    | 1.959±0.0       | 10.24        | 4.20±0.01   | 0.8±0.01     | 26.67         |

Note: $R_A = C_i - C_e$

Table 3 Models of adsorption isotherms.

| Model          | Parameters | Combination II | Combination III |
|----------------|------------|----------------|-----------------|
|                |            | Values         | Values          |
| Langmuir       | $q_{max}$ (mg/L) | 18.883         | 20.9128         |
|                | $k_L$ (L/mg)  | 0.1032         | 0.0048          |
|                | $R_L$       | 0.6553         | 0.9761          |
|                | $R^2$       | 0.9879         | 0.9738          |
| Freundlich     | $n$        | 6.7295         | 0.7586          |
|                | $1/n$      | 0.1486         | 1.3182          |
| Temkin         | $K_f$ (mg/L) | 2.5501         | 4.0220          |
|                | $R^2$      | 0.9617         | 0.9588          |
|                | $B_T$ (kJ/mol) | 2.7065         | 15.467          |
|                | $A_T$ (L/mg) | 2.2952         | 2.7183          |
|                | $R^2$      | 0.9699         | 0.9536          |

Table 4 Thermodynamic parameters.

| Combinations | $\Delta H^\circ$ kJ/mol | $\Delta S^\circ$ kJ/mol | $\Delta G^\circ$ kJ/mol |
|--------------|--------------------------|--------------------------|-------------------------|
|              | T1                       | T2                       | T3                       |
| II           | -25.620                  | -0.077                   | -3.547                   |
| III          | -20.210                  | -0.049                   | -6.222                   |

Table 5 Fitting kinetic parameters of the adsorption amount of ammonia on the Combination II obtained with the pseudo-first-order model and pseudo-second-order model.

| $C$ (mg/L) | $R_A$ (mg/L) | $q_e$ (mg/L) | Pseudo-first-order model | Pseudo-second-order model |
|------------|--------------|--------------|--------------------------|--------------------------|
|            |              |              | $q_e$ (mg/L) | $k_1$ | $R^2$ | $q_e$ (mg/L) | $k_2$ | $R^2$ |
| 1          | 0.43         | 5.51         | 3.381              | 0.233 | 0.8325 | 4.91         | 0.744 | 0.9931 |
| 1.6        | 0.78         | 7.07         | 5.071              | 0.199 | 0.8011 | 6.89         | 0.811 | 0.9922 |
| 2.1        | 1.11         | 7.57         | 5.127              | 0.201 | 0.8572 | 7.31         | 0.662 | 0.9935 |
| 2.9        | 1.65         | 8.48         | 6.811              | 0.217 | 0.8123 | 8.12         | 0.799 | 0.9917 |
| 5.1        | 1.96         | 10.2         | 8.431              | 0.221 | 0.8812 | 10.01        | 0.801 | 0.9971 |
Table 6 Fitting kinetic parameters of the adsorption amount of ammonia on the Combination III obtained with the pseudo-first-order model and pseudo-second-order model.

| C (mg/L) | R_A (mg/L) | q_e (mg/L) | Pseudo-first-order model | Pseudo-second-order model |
|----------|------------|------------|--------------------------|--------------------------|
|          |            |            | k_1 | R² | q_e (mg/L) | k_2 | R² |
| 1        | 0.71       | 9.67       | 6.299 | 0.019 | 0.7445 | 8.405 | 0.065 | 0.914 |
| 1.6      | 1.21       | 13.87      | 10.872 | 0.013 | 0.7754 | 11.807 | 0.065 | 0.916 |
| 2.1      | 1.62       | 16.1       | 11.032 | 0.007 | 0.6993 | 13.807 | 0.062 | 0.911 |
| 2.9      | 2.35       | 17.4       | 14.051 | 0.005 | 0.7143 | 14.897 | 0.062 | 0.918 |
| 5.1      | 4.25       | 26.67      | 22.438 | 0.003 | 0.7373 | 24.057 | 0.063 | 0.915 |

Figure 1 Reduction of ammonia as a function of time (t) after the treatment with Combination III at different temperatures (T).

The removal rate of ammonia ion was increased until t3/t4 and then became stable. Therefore, the optimal reaction interval was 45 min to 60 min. Table 5 shows the values of adsorption kinetics parameters for ammonia ions onto Combination III in the pseudo-first-order model and pseudo-second-order model. The results of correlation coefficients (R²) and q_e values indicated that the pseudo-second-order model could better describe the adsorption kinetics of ammonia ions onto Combination III than the pseudo-first-order model (Table 6).

In Combination III (PDS+H_2O_2+NaClO + PAM + Mt +Zeo), the interaction among the materials and the oxidation-reduction process might be responsible for the ammonia removal in the treatment. The improved ammonia removal performance of Combination III was partly driven by physical adsorption and partly depended on chemical reactions. Due to the physical process, an electrical double layer existed around each particle in Combinations II & III. The first layer was occupied by strongly bound ions and the second layer was occupied by less decisively bound ions. This binding process of ammonia ions existed when the total potential was positive. Otherwise the binding processes vanished and the adsorption process disappeared. The adsorption process for ammonia removal in Combination III stopped under the same conditions in Combination II. The better ammonia removal performance of Combination III could be explained by chemical reactions in surface water treatment.
4. Conclusion
In this study, a green combination of 6 materials is proposed for surface water treatment. The combination of 6 materials were confirmed as 0.3 mg/L H₂O₂, 0.03 mg/L NaClO, 5 g/L persulfate, 0.4 mg/L polyacrylamide, 20 mg/L zeolite, and 10 mg/L montmorillonite by surface water treatment experiments. The performance was proved by adsorption isotherms, thermodynamics and adsorption kinetics analysis. The adsorption of this material combination is a physical process, as verified by adsorption isotherms and thermodynamics. The adsorption kinetics of this material combination is well described by the pseudo-second-order model. The contaminant removal performance of the combination depends on the adsorption process and chemical reactions in surface water treatment.

5. References
[1] Manzano B C, Roberto M, Hoshina M, Menegario A and Marin-morales M A. Evaluation of the genotoxicity of water impacted by domestic and industrial effluents of a highly industrialized region of São Paulo State, Brazil, by the comet assay in HTC cells 2015 J. Environ. Sci. Pollut. R. 22 1399-1407.
[2] Sousa JMDE, et.al. Physico-chemical and genotoxicity analysis of Guaribas river water in the Northeast Brazil 2017 J. Chemosphere. 177 334-38.
[3] Wang Z, Zou R, Zhu X, He B, Yuan G, Zhao L and Liu Y. Predicting lake water quality responses to load reduction: a three-dimensional modeling approach for total maximum daily load 2014 J. Int. J. Environ. Sci. Technol. 11 423-36.
[4] Palmer M A. Reforming watershed restoration: science in need of application and applications in need of science 2009 J. Estuar. Coast. 32 1-17.
[5] Caraballo M A, Macias F, Rötting T S, Nieto J M and Ayora C. Long term remediation of highly polluted acid mine drainage: a sustainable approach to restore the environmental quality of the Odiel surface water basin 2011 J. Environ. Pollut. 159 3613-19.
[6] Liu X N, Tao Y, Zhou K Y, Zhang Q Q, Chen G Y and Zhang X H. Effect of water quality improvement on the remediation of surface water sediment due to the addition of calcium nitrate 2017 J. Sci. Total. Environ. 575 887-94.
[7] Hammandi L, Ponton A, Belihadi. Effects of Heat Treatment and Hydrogen Peroxide (H₂O₂) on the Physicochemical and Rheological Behavior of an Activated Sludge from a Water Purification Plant 2012 J. Pro. Eng. 33 293-302.
[8] Li Z J, Yang Q, Zhong Y L, Zhou X M, Xin L L, Zeng X and Guang M. Granular activated carbon supported iron as a heterogeneous persulfate catalyst for the pretreatment of mature landfill leachate 2016 J. RSC Adv. 6 987-94.
[9] Ho YC, Norli I, Alkarkhi AFM and Morad N. Characterization of biopolymeric flocculant (pectin) and organic synthetic flocculant (PAM): a comparative study on treatment and optimization in kaolin suspension 2010 J. Bio. Tech. 101 1166-74.
[10] Li T, Zhu Z, Wang DS, Yao CH and Tang HX. Characterization of floc size, strength and structure under various coagulation mechanisms 2006 J. Pow. Tec. 168 104-10.
[11] Wibowo E, Rokhmat M, Sutisna M, Sutisna K and Abdullah M. Reduction of seawater salinity by natural zeolite (Clinoptilolite): Adsorption isotherms, thermodynamics and kinetics 2017 J. Desal. 409 146-156.
[12] Brigatti MF, Galan E, et al. 2013 Structure and mineralogy of clay minerals A. (Italy: Handbook of Clay Science, Part A) pp 21-82.
[13] Jia FF, Song SX. Exfoliation and Characterization of Layered Silicate Minerals: A Review 2014 J. Surf. Rev. Lett. 21 1430001.
[14] Lagaly G, Ogawa M, Dekany I. 2013 Clay mineral-organic interactions A. (Italy: Handbook of Clay Science, Part A) pp 435-506.
[15] Kim NH, Park TH, Rhee MS. Enhanced bactericidal action of acidified sodium chlorite caused by the saturation of reactants 2014 J. J. Appl. Microbial. 116 1447-57.
[16] Deshwal BR, Jo HD, Lee HK. Reaction kinetics of decomposition of acidic sodium chlorite 2003 J. Can. J. Chem. Eng. 82 619-23.
[17] Otal E, Vilches LF, Moreno N, Querol X, Vale J and Fernandez PC. Application of zeolitised coal fly ashes to the depuration of liquid wastes 2005 J. Fuel. 84 1440-46.

[18] Zhang BH, Wu DY, Wang C, He SB, Zhang ZJ and Kong HN. Simultaneous removal of ammonium and phosphate by zeolite synthesized from coal fly ash as influenced by acid treatment 2007 J. J. Environ. Sci. 19 540-45.

[19] Inglezakis VJ, Stylianou MA, Loizidou M and Zorpas AA. Experimental studies and modeling of clinoptilolite and vermiculite fixed beds for Mn2+, Zn2+, and Cr3+ removal 2016 J. Desalin. Water Treat. 57 11610-22.

[20] Kumar PS, Ramalingam S, Senthamarai C, Niranjanaa M, Vijayalakshmi P and Sivanesan S. Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions 2010 J. Desal. 261 52-60.

[21] Gunay A, Arslanka E, Tosun I. Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics 2007 J. J. Haz. Mat.146 362-71.

[22] Joanna KK, Czeslawa RD, Franus M, Patrycja AS, Czupiol J and Krzyzewski I. Sorption capacities of natural and synthetic zeolites for Cu (II) ions 2015 J. Pol. J. Environ. Stu. 24 1111-23.

[23] Yousef RI, El-Eswed B, Al-Muhtaseb AH. Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism, and thermodynamics studies 2011 J. Chem. Eng. J. 171 1143-49.

[24] Liu Y. Is the free energy change of adsorption correctly calculated? 2009 J. J. Chem. Eng. Data. 54 1981-85.

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