A QM/MM investigation on the mechanism of adsorptive removal of heavy metal ions by lignin: single and competitive ion adsorption

Abstract

In this paper, adsorption removal mechanism of heavy metal ions (Pb, Cu, Cd, Zn, and Ni) by lignin is investigated by molecular and quantum chemical modeling. First, the lowest energy sites of lignin for heavy metal ions were investigated using Metropolis Monte Carlo search and simulated annealing. Then, the equilibrium adsorption capacities of lignin for heavy metal ions were calculated by using the conductor-like screening models with segmented activity coefficients model together with density functional theory of generalized gradient approximate and Volsko-Wilk-Nusair functional following the local pseudo-thermodynamic equilibrium at the interface of lignin and ion-containing effluent. A number of kinetic Monte Carlo simulations were performed for the analysis of the surface kinetics of ion adsorption. It was found that affinity of lignin with metal ions follows the order: Pb>Cu>Cd >Zn>Ni which is in agree with experimental observations. The stability of ions follows the order: Pb>Cd>Zn>Ni>Cu indicating that the adsorption affinity does not demand same order of stability on ions. In addition, it was found that while the adsorption of heavy metal ions on the lignin is accessible, however, the adsorbed heavy metal ions are less stable than the adsorbed water molecules so used lignin must be replaced by fresh ones in cyclic manner. While lignin provides desirable adsorption performance for single ion removal, it failed in processing of practical heavy metal ions solutions expected in environmental issues.

**Keywords**: wastewater; adsorption; lignin; metal ions; molecular modeling; quantum modeling

1. Introduction

Serious environmental and ecological pollutions are caused by today’s industrial activities in water and wastewater cycles [[1-3](#_ENREF_1)]. The presence of heavy metal ions in water streams would affect living organisms and particularly human health [[4](#_ENREF_4)] leading to demand of higher regulation and health standards [[5-7](#_ENREF_5),[2](#_ENREF_2)]. Intense investigations have been conducted for development of reliable treatment and remediation techniques [[8-10](#_ENREF_8)] where adsorption has found great attentions in last decades as is capable of processing a wide variety of wastewater streams [[11-16](#_ENREF_11)]. To get better understanding of processes and influencing parameters, mathematical modeling is valuable tool [[17-22](#_ENREF_17)] to reduce costs of conducting an experiment, set-up preparation and maintenance. In addition, using modeling, one may examine the effect of various operating parameters and evaluate design scenarios for industrial applications [[2](#_ENREF_2),[3](#_ENREF_3),[23](#_ENREF_23),[18](#_ENREF_18)].

For adsorption process, (1) equilibrium models (isotherms) [[24](#_ENREF_24),[25](#_ENREF_25)] descripting the equilibrium capacity of sorbate adsorption, (2) kinetic models [[26-29](#_ENREF_26)] describing the time dependent trend of adsorption and, (3) reaction and diffusion rate models [[30-33](#_ENREF_30)] describing the evaluation of sorbate adsorption into sorbent considering various controlling transport mechanisms are reported. The predictive ability of adsorption models is critically and practically of highest interest [[18](#_ENREF_18)], because the isotherms and kinetic equations have correlative properties that demand the prior experimental data availability which restricts their application. Thus, predictive methods that do not demand for experimental data are needed [[34-36](#_ENREF_34)].

Therefore, in this work, the predictive ability of molecular computational modeling techniques for description of adsorption of heavy metal ions on lignin is presented. For detailed comparison, the experimentally measured adsorption data of heavy metal ions (Pb, Cu, Cd, Zn, and Ni) adsorbed onto lignin [[37](#_ENREF_37)] were used. The source simulation files are provided as supplementary information and can be used for reproduction of results or extension of investigations by interested readers.

1. Outline of simulations
   1. Adsorption site analysis

In order to analyze the possible and potential interactions of heavy metal ions, water, and lignin, the adsorption locator module of Materials Studio software package was used [[38](#_ENREF_38)]. In this module, a substrate loaded with an adsorbate or an adsorbates mixture of a fixed composition would be simulated to find low energy adsorption sites and to investigate the preferential adsorption of mixtures of adsorbate components [[39-41](#_ENREF_39)]. In this method, the candidate substrate-adsorbate configurations are sampled from a canonical ensemble in which the loading of all adsorbate components on the substrate as well as the temperature are fixed [[39-41](#_ENREF_39)]. First, the constructed compounds must be optimized geometrically and minimized energetically. For this purpose, the Forcite module was used with the same energy and minimization settings as intended to be used in adsorption locator runs as recommended by software documentations [[39-41](#_ENREF_39)]. For both Forcite module and adsorption locator module, a rule-based force field (Universal) was employed as recommended [[39-41](#_ENREF_39)]. Following this simulations, a number of substrate-adsorbate configuration energies would be generated that are used for assessment and evaluations.

* 1. Adsorption capacity analysis

The adsorption of heavy metal ions by lignin from water effluents can be predicted following the use of equilibrium calculations at the interface of two contacting phases as described in Ref. [[1](#_ENREF_1)] and given in Eq. 1 where *x* denotes the mole fraction of heavy metal ions in each phase and *γ* denotes the activity coefficient of heavy metal ion and superscripts *C* and *W* denotes the lignin and water phases respectively.

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The activity coefficients were calculated employing the conductor-like screening models with segmented activity coefficients model [[42](#_ENREF_42),[34-36](#_ENREF_34)]. For the application of COSMO-based activity coefficients models, molecular and quantum calculations are required to obtain the charge and energy density distributions using the Dmol3 Module of the Materials Studio software package [[1](#_ENREF_1)] where it has been recommended that density functional theory of generalized gradient approximate (GGA) and Volsko-Wilk-Nusair functional (VWN) must be employed for calculations which is implemented in Dmol3 Module by GGA/VWN-BP and DNP v.4.0.0 basis options [[43](#_ENREF_43),[44](#_ENREF_44)]. Upon performing simulations, the obtained “.cosmo” files then were used for activity calculations by using the scripts retrieved from Ref. [[1](#_ENREF_1)]. It must be noted that the mole fractions (*x*) can be converted to concentrations (*c*) as illustrated in App. A.

* 1. Adsorption surface kinetic

For the analysis of the kinetics of ion adsorption onto surface, a number of kinetic Monte Carlo (kMC) simulations were performed by using Kinetix module in material studio software package. This module allows us to investigate reaction rates of complex chemical processes on surfaces under different external conditions [[38](#_ENREF_38)]. The adsorption kinetic as shown in Eq. 2 was implemented into the kMC simulations using the built submenu of Kinetix module.

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The details of considered mechanism presented in Eq. 2 were retrieved from our recent work (submitted) and listed in Table 1.

Table 1. parameters of considered mechanism

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | ***α*** | ***β*** | ***γ*** | ***k1***  **(g/mmol/min)** | ***k2***  **(g/mmol/min)** |  |
| ***Ion*** |  |  |  |  |  |  |
| Ni | 1.0169 | 0.25 | 1.000001 | 10-4 | 6.5×10-9 |  |
| Zn | 1.021 | 0.023 | 1.000001 | 5×10-5 | 7×10-9 |  |
| Cd | 1.022 | 0.03 | 1.000001 | 10-4 | 8×10-9 |  |
| Cu | 1.025 | 0.01 | 1.00001 | 3×10-4 | 10-8 |  |
| Pb | 1.312 | 0.01 | 1.00007 | 0.001 | 10-8 |  |

Practically, the kMC simulations are performed to examine the suitability of lignin for adsorptive removal heavy metal ions from effluent samples containing all ions which is expected to be found practically in environmental issues. The laboratory samples for which the adsorption tests are carried out are almost one-ion containing effluents. Therefore, these simulations can easily show the performance of lignin for such cases.

1. Computation facility

For all the aforementioned simulations, a personal computer of Fujitsu brand, model AH531/GFO, with a core-i7 x64-bit architecture CPU with base speed of 2.7 GHz (boasting up to 3.6 GHz) and 8 GB of installed memory (RAM) and by implementation of a USB flash disk of HP brand, model v160w, with 16 GB capacity utilized as virtual memory through ReadyBoost option in Windows 10 professional OS (64-bit OS) were used. All unwanted services and programs in OS were disabled manually to enhance the performance.

1. Collected data

In this work, experimental data of heavy metal ions (Pb, Cu, Cd, Zn, and Ni) adsorbed onto lignin were collected from literature [[37](#_ENREF_37)]. The collected adsorption kinetic and isotherm data of metal ions on lignin are listed in Table 2 and Table 3 respectively.

Table 2. collected adsorption kinetic data of ions on lignin (initial metal concentration = 0.8 mM) [[37](#_ENREF_37)]

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Ni** |  | **Zn** |  | **Cd** |  | **Cu** |  | **Pb** |  |
| ***t*** | ***qe*** | ***t*** | ***qe*** | ***t*** | ***qe*** | ***t*** | ***qe*** | ***t*** | ***qe*** |
| 2.9 | 0.01250 | 2.8 | 0.01500 | 4.8 | 0.06325 | 2.8 | 0.15925 | 1.7 | 0.23200 |
| 5.8 | 0.01975 | 6.9 | 0.03625 | 7.8 | 0.06825 | 4.7 | 0.18625 | 3.7 | 0.25300 |
| 9.8 | 0.02475 | 9.8 | 0.05125 | 10.9 | 0.07100 | 6.8 | 0.20975 | 6.9 | 0.26675 |
| 14.9 | 0.03225 | 12.9 | 0.05175 | 14.9 | 0.08425 | 9.8 | 0.23150 | 9.7 | 0.27825 |
| 19.9 | 0.03400 | 15.9 | 0.05825 | 19.9 | 0.08450 | 19.7 | 0.25125 | 12.7 | 0.28950 |
| 32.8 | 0.04650 | 19.9 | 0.05825 | 24.7 | 0.09075 | 24.9 | 0.25250 | 15.9 | 0.29050 |
| 39.9 | 0.04925 | 24.8 | 0.06575 | 29.8 | 0.09500 | 34.8 | 0.25675 | 19.9 | 0.30175 |
| 49.9 | 0.05125 | 29.9 | 0.07075 | 39.9 | 0.10050 | 49.8 | 0.25750 | 24.7 | 0.30175 |
| 59.8 | 0.05450 | 34.9 | 0.06575 | 49.9 | 0.10850 | 64.9 | 0.25850 | 29.9 | 0.30300 |
| 79.9 | 0.05600 | 39.9 | 0.07350 | 59.8 | 0.11925 | 79.7 | 0.26600 | 34.9 | 0.30350 |
| 99.9 | 0.06075 | 49.8 | 0.07900 | 79.8 | 0.12275 | 84.9 | 0.26675 | 39.8 | 0.30350 |
| 119.8 | 0.05850 | 59.9 | 0.08600 | 99.9 | 0.12200 | 119.7 | 0.26650 | 49.8 | 0.30425 |
| 155.8 | 0.06000 | 79.9 | 0.08725 | 119.9 | 0.12200 | 180.0 | 0.26700 | 59.8 | 0.30400 |
| 180.0 | 0.06075 | 99.9 | 0.08750 | 149.9 | 0.12375 |  |  | 89.8 | 0.30425 |
|  |  | 119.9 | 0.08850 | 180.0 | 0.12400 |  |  | 130.8 | 0.30400 |
|  |  | 149.9 | 0.08875 |  |  |  |  | 180.0 | 0.30425 |
|  |  | 180.0 | 0.08975 |  |  |  |  |  |  |
| * *t* in min and *qe* in mmol/gr. | | | | | | | | | |

Table 3. collected adsorption isotherm data of metal ions on lignin [[37](#_ENREF_37)]

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Ni** |  | **Zn** |  | **Cd** |  | **Cu** |  | **Pb** |  |
| ***Ce*** | ***qe*** | ***Ce*** | ***qe*** | ***Ce*** | ***qe*** | ***Ce*** | ***qe*** | ***Ce*** | ***qe*** |
| 0.06649 | 0.05192 | 0.01353 | 0.03409 | 0.02177 | 0.07055 | 0.01353 | 0.07253 | 0.00883 | 0.07570 |
| 0.21948 | 0.07174 | 0.04648 | 0.06025 | 0.08297 | 0.12644 | 0.02648 | 0.14863 | 0.01118 | 0.15418 |
| 0.38188 | 0.08680 | 0.13239 | 0.10622 | 0.21948 | 0.15141 | 0.06296 | 0.21324 | 0.01824 | 0.23187 |
| 0.56311 | 0.09433 | 0.27714 | 0.12842 | 0.33480 | 0.18589 | 0.09356 | 0.28220 | 0.05825 | 0.29568 |
| 0.77729 | 0.08839 | 0.41600 | 0.15299 | 0.46778 | 0.21284 | 0.19947 | 0.31946 | 0.12651 | 0.34919 |
| 0.98794 | 0.08363 | 0.63607 | 0.15379 | 0.58664 | 0.20769 | 0.38541 | 0.32541 | 0.26655 | 0.37218 |
| 1.25390 | 0.09711 | 0.80435 | 0.15735 | 0.98441 | 0.20491 | 0.63607 | 0.34443 | 0.47367 | 0.41062 |
| 1.72698 | 0.10741 | 1.10327 | 0.15735 | 1.44101 | 0.22315 | 1.15387 | 0.33769 | 0.92086 | 0.43123 |
|  |  | 1.58223 | 0.16607 |  |  | 1.63636 | 0.34364 | 1.38335 | 0.44590 |
| * *Ce* in mM and *qe* in mmol/gr | | | | | | | | | |

1. Results and discussion

The detailed results of all simulations are included in the source library created in Material Studio software package which are provided in the ***supplementary information***. The chemical structures of optimized lignin, heavy metal ions and water that are shown in Fig. 1 and Fig. 2 respectively where hydrogen, oxygen, and carbon atoms are shown in white, red, and grey colors respectively.

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| Fig. 1. Chemical structure of lignin |

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| Fig. 2. Structure of heavy metal ions; left to right: Cd, Cu, Ni, Pb, Zn and water | | | | |  |

The surface of lignin colored by charged groups is shown in Fig. 3.

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| Fig. 3. Chemical structure of lignin colored by charge groups |

* 1. Adsorption site analysis

The results of individual energies of substrate-adsorbate configurations for heavy metal ions adsorption on lignin are summarized in supplementary files. The total energy of the substrate-adsorbate configuration is the sum of the energies of the adsorbate components, the rigid adsorption energy, and the deformation energy in kcal/mol. The adsorption energy is the energy released (or required) when the relaxed adsorbate components are adsorbed on the substrate which itself is the sum of the rigid adsorption energy and the deformation energy for the adsorbate components in kcal/mol. The rigid adsorption energy is the energy released (or required) when the unrelaxed adsorbate components are adsorbed on the substrate in kcal/mol. The deformation energy is the energy released when the adsorbed adsorbate components are relaxed on the substrate surface in kcal/mol. The dEad/dNi’s are energies of substrate-adsorbate configurations in kcal/mol where one of the adsorbate components has been removed. The obtained energy values indicating that the adsorbed heavy metal ions are less stable than the adsorbed water molecules, so used lignin must be replaced by fresh ones in cyclic manner. The optimal adsorption substrate-adsorbate configurations of lignin and heavy metal ions are shown in supplementary files.

The averaged adsorption energies of heavy metal ions on lignin are shown in Fig. 4 which clearly shows that affinity of lignin with metal ions follows the order: Pb>Cu>Cd >Zn>Ni which is in agree with experimental observations [[37](#_ENREF_37)].

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| Fig. 4. Comparison of adsorption energies of heavy metal ions on lignin |

The required energy for removal of adsorbed ions from lignin which shows the stability of adsorbed ions on lignin is shown in Fig. 5. The comparison of results shows that higher energy requirements are needed to remove adsorbed Pb ions from lignin surface rather than other heavy metal ions indicating that the adsorbed Pb ions have high stability on the adsorbent surface. The results showed the stability of ions follows the order: Pb>Cd>Zn>Ni>Cu. While adsorption affinity of lignin with metal ions follows the order: Pb>Cu>Cd >Zn>Ni, however the stability results indicate that this affinity does not demand same order of stability on ions.

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| Fig. 5. Comparison of stability of adsorbed heavy metal ions on lignin |

* 1. Adsorption capacity analysis

The details of cosmo calculations are listed in Table 4.

Table 4. details of cosmo calculations

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| --- | --- | --- | --- |
| **Compound** | **Volume of cavity**  **(A3)** | **Surface area of cavity**  **(A2)** | **total number of segments** |
|
| Lignin | 26141.12 | 9288.67 | 11275 |
| Water | 25.73454 | 43.26923 | 136 |
| Cd | 50.965010 | 66.476101 | 50 |
| Cu | 45.829755 | 61.932101 | 50 |
| Ni | 45.829755 | 61.932101 | 50 |
| Pb | 57.905836 | 72.382295 | 50 |
| Zn | 45.829755 | 61.932101 | 50 |

The sigma profiles of constructed heavy metal ions, water and lignin are shown in Fig. 6.

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| **Cd** |
| **Cu** |
| **Ni** |
| **Pb** |
| **Zn** |
| **Water** |
| **Lignin** |
| Fig. 6. Compounds sigma profiles |

Sigma profile, *p*(*σ*), are mainly used to represent the probability distribution of surface area having charge density *σ* [[1](#_ENREF_1)]. Commonly, histograms of segment surface are reported over a charge density range of −0.025 to 0.025 e/Å2 as ideal screening charge density for most of the molecules are in this range [[44](#_ENREF_44)]. It must be noted that due to sign inversion of the polarization charge density, σ, the peak from the negative lone-pairs is located on the right side of the σ-profile and vice versa [[45](#_ENREF_45)].

The results of equilibrium adsorption capacities of each ion are shown in Fig. 7. Desirable agreement between calculated and experimental data was found.

|  |  |
| --- | --- |
| **Cd** | |
| **Cu** | | | |
| **Ni** |
| **Pb** | |
| **Zn** | | |
| Fig. 7. Adsorption data of heavy metal ions on lignin; solid lines show model calculations and solid bullets show experimental data | | |

* 1. Adsorption surface kinetic

The kMC simulations are performed to examine the suitability of lignin for adsorptive removal heavy metal ions from effluent samples containing all ions which is expected to be found practically in environmental issues. The laboratory samples for which the adsorption tests are carried out are almost one-ion containing effluents. Therefore, these simulations can easily show the performance of lignin for such cases. The computed adsorption of heavy metal ions (gr/mmol) onto lignin from an effluent containing all ions is shown in Fig. 8.

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| Fig. 8. Computed adsorption of heavy metal ions (gr/mmol) onto lignin from an effluent containing all ions |

The competition of ions for adsorption in an effluent containing all ions makes the adsorption process longer than the adsorption from one-ion effluent as can be seen in Fig. 8. The final surface covered by adsorbed ions is shown in Fig. 9. For evolution of surface coverage see supplementary file ***SurCov.MP4*** or refer to the provided source library.

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|  |
| Fig. 9. Covered surface by adsorbed ions; color legends same as Fig. 8 |

The slowed down adsorption of heavy metal ions makes it hard to recommend lignin as an adsorbent for practical adsorption heavy metal ions from polluted effluents in wastewater treatments. In addition, the necessity of lignin replacement during the process as demanded by the adsorption affinity revealed in aforementioned sections, is another drawback for lignin as adsorbent. Therefore, while lignin provides desirable adsorption performance for single ion removal, it failed in processing of practical heavy metal ions solutions expected in environmental issues. One remedy for this drawback could be the use of blend of lignin and another adsorbent which will be investigated in a future work.

1. Conclusion

Simulations were performed in this work to investigate the molecular mechanism of heavy metal ions removal from wastewater using lignin. These simulations revealed that having the chemical structure of compounds in considered system, with no need to further data, one can proceed to calculation of various compounds properties and their interactions using quantum chemical and molecular modeling approaches. Thanks to developments in current computing facilities and computational packages, with little of computational cost and time, we are able to analysis and investigate a wide variety of compounds and their properties. From simulations, it was found that the kinetic data clearly shows the affinity of lignin with metal ions follows the order: Pb>Cu>Cd >Zn>Ni which is in agree with experimental observations. The stability of ions follows the order: Pb>Cd>Zn>Ni>Cu indicating that the adsorption affinity of lignin with metal ions does not demand same order of stability on ions. In addition, it was found that while the adsorption of heavy metal ions on the lignin is accessible, however, the adsorbed heavy metal ions are less stable than the adsorbed water molecules so used lignin must be replaced by fresh ones in cyclic manner. While lignin provides desirable adsorption performance for single ion removal, it failed in processing of practical heavy metal ions solutions expected in environmental issues.

1. Supplementary files info

The source library of present work created in Material Studio software package is provided as supplementary file and can be freely downloaded from associated links on online version of article. The compressed “.rar” file has a size of **938 MB** and needs a disk space of about **2.42 GB** upon extraction. The link bellow also can be used to access all the supplementary files.

<https://www.mediafire.com/folder/444nklrtuwjsy/Lignin-Ion-MD>

1. Appendix

The mole fractions (*z*) can be converted to concentrations (*c*) using following expression.

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where *M* denotes molecular weight () and *ρ* is density ().

The mole fractions (*z*) can be related to amount of adsorbed adsorbate (*qA*) as *z*=εusing following expression.

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|  | 4 |
|  | 5 |
|  | 6 |

Unit of is mol/gr, thus, to give mmol/gr, both side of Eq. 6 is multiplied by 10-3.

**References**

1. Ghasemi A, Asgarpour Khansary M, Marjani A, Shirazian S (2017) Using quantum chemical modeling and calculations for evaluation of cellulose potential for estrogen micropollutants removal from water effluents. Chemosphere 178:411-423. doi:10.1016/j.chemosphere.2017.02.152

2. Asgarpour Khansary M, Shirazian S, Asadollahzadeh M (2017) Polymer-water partition coefficients in polymeric passive samplers. Environ Sci Pollut Res Int 24 (3):2627-2631. doi:10.1007/s11356-016-8029-7

3. Khansary MA, Mellat M, Saadat SH, Fasihi-Ramandi M, Kamali M, Taheri RA (2017) An enquiry on appropriate selection of polymers for preparation of polymeric nanosorbents and nanofiltration/ultrafiltration membranes for hormone micropollutants removal from water effluents. Chemosphere 168:91-99. doi:10.1016/j.chemosphere.2016.10.049

4. Worch E (2008) Fixed-bed adsorption in drinking water treatment: a critical review on models and parameter estimation. Journal of Water Supply: Research and Technology—AQUA 57 (3):171. doi:10.2166/aqua.2008.100

5. Gido B, Friedler E, Broday DM (2016) Assessment of atmospheric moisture harvesting by direct cooling. Atmospheric Research 182:156-162. doi:<http://dx.doi.org/10.1016/j.atmosres.2016.07.029>

6. Bergmair D, Metz SJ, de Lange HC, van Steenhoven AA (2015) A low pressure recirculated sweep stream for energy efficient membrane facilitated humidity harvesting. Separation and Purification Technology 150:112-118. doi:<http://dx.doi.org/10.1016/j.seppur.2015.06.042>

7. Trapani F, Polyzoidis A, Loebbecke S, Piscopo CG (2016) On the general water harvesting capability of metal-organic frameworks under well-defined climatic conditions. Microporous and Mesoporous Materials 230:20-24. doi:<http://dx.doi.org/10.1016/j.micromeso.2016.04.040>

8. Xu M, Bai X, Pei L, Pan H (2016) A research on application of water treatment technology for reclaimed water irrigation. International Journal of Hydrogen Energy 41 (35):15930-15937. doi:<http://dx.doi.org/10.1016/j.ijhydene.2016.05.020>

9. Zanacic E, Stavrinides J, McMartin DW (2016) Field-analysis of potable water quality and ozone efficiency in ozone-assisted biological filtration systems for surface water treatment. Water research 104:397-407. doi:<http://dx.doi.org/10.1016/j.watres.2016.08.043>

10. Mahmoud B, Yosra M, Nadia A (2016) Effects of magnetic treatment on scaling power of hard waters. Separation and Purification Technology 171:88-92. doi:<http://dx.doi.org/10.1016/j.seppur.2016.07.027>

11. Weber WJ, Smith EH (1987) Simulation and design models for adsorption processes. Environmental Science & Technology 21 (11):1040-1050. doi:10.1021/es00164a002

12. Aksu Z, Kabasakal E (2004) Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon. Separation and Purification Technology 35 (3):223-240. doi:10.1016/s1383-5866(03)00144-8

13. Babu BV, Gupta S (2007) Adsorption of Cr(VI) using activated neem leaves: kinetic studies. Adsorption 14 (1):85-92. doi:10.1007/s10450-007-9057-x

14. Borba CE, Guirardello R, Silva EA, Veit MT, Tavares CRG (2006) Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: Experimental and theoretical breakthrough curves. Biochemical Engineering Journal 30 (2):184-191. doi:10.1016/j.bej.2006.04.001

15. Brauch V, Schlünder EU (1975) The scale-up of activated carbon columns for water purification, based on results from batch tests—II. Chemical Engineering Science 30 (5-6):539-548. doi:10.1016/0009-2509(75)80024-8

16. Hashemi F, Parham H (2006) Heavy Metal Removal from Effluents using Adsorption. Iranian Chemical Engineering Journal (Persian) 5 (23):45-52

17. Ali Aroon M, Khansary MA (2017) Generalized similarity transformation method applied to partial differential equations (PDEs) in falling film mass transfer. Computers & Chemical Engineering 101:73-80. doi:10.1016/j.compchemeng.2017.02.047

18. Khansary MA, Joogh FKQ, Hosseini A, Safari J, Allahyari E, Zadeh NS, Sani AH (2014) Modeling Drying of a Coated Paper. International Journal of Modeling, Simulation, and Scientific Computing 05 (01):1350019. doi:10.1142/s1793962313500190

19. Costa C, Rodrigues A (1985) Design of cyclic fixed-bed adsorption processes. Part I: Phenol adsorption on polymeric adsorbents. AIChE Journal 31 (10):1645-1654. doi:10.1002/aic.690311008

20. Ko DCK, Porter JF, McKay G (2003) Mass Transport Model for the Fixed Bed Sorption of Metal Ions on Bone Char. Industrial & Engineering Chemistry Research 42 (14):3458-3469. doi:10.1021/ie020505t

21. Do DD, Mayfield PLJ (1987) A new simplified model for adsorption in a single particle. AIChE Journal 33 (8):1397-1400. doi:10.1002/aic.690330819

22. Gholami M, Talaie MR (2010) Investigation of Simplifying Assumptions in Mathematical Modeling of Natural Gas Dehydration Using Adsorption Process and Introduction of a New Accurate LDF Model. Industrial & Engineering Chemistry Research 49 (2):838-846. doi:10.1021/ie901183q

23. Tosun I (2007) Modeling in Transport Phenomena : A Conceptual Approach. 2 edn. Elsevier,

24. Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal 156 (1):2-10. doi:10.1016/j.cej.2009.09.013

25. Limousin G, Gaudet JP, Charlet L, Szenknect S, Barthès V, Krimissa M (2007) Sorption isotherms: A review on physical bases, modeling and measurement. Applied Geochemistry 22 (2):249-275. doi:10.1016/j.apgeochem.2006.09.010

26. Ho Y (2006) Review of second-order models for adsorption systems. Journal of Hazardous Materials 136 (3):681-689. doi:10.1016/j.jhazmat.2005.12.043

27. Ho YS, McKay G (1999) Pseudo-second order model for sorption processes. Process Biochemistry 34 (5):451-465. doi:10.1016/s0032-9592(98)00112-5

28. Liu Y (2008) New insights into pseudo-second-order kinetic equation for adsorption. Colloids and Surfaces A: Physicochemical and Engineering Aspects 320 (1-3):275-278. doi:10.1016/j.colsurfa.2008.01.032

29. Wu F-C, Tseng R-L, Huang S-C, Juang R-S (2009) Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review. Chemical Engineering Journal 151 (1-3):1-9. doi:10.1016/j.cej.2009.02.024

30. Berninger JA, Whitley RD, Zhang X, Wang NHL (1991) A versatile model for simulation of reaction and nonequilibrium dynamics in multicomponent fixed-bed adsorption processes. Computers & Chemical Engineering 15 (11):749-768. doi:<http://dx.doi.org/10.1016/0098-1354(91)85020-U>

31. Kaczmarski K, Mazzotti M, Storti G, Morbidelli M (1997) Modeling fixed-bed adsorption columns through orthogonal collocations on moving finite elements. Computers & Chemical Engineering 21 (6):641-660. doi:<http://dx.doi.org/10.1016/S0098-1354(96)00300-6>

32. Xu Z, Cai J-g, Pan B-c (2013) Mathematically modeling fixed-bed adsorption in aqueous systems. Journal of Zhejiang University SCIENCE A 14 (3):155-176. doi:10.1631/jzus.A1300029

33. Shafeeyan MS, Wan Daud WMA, Shamiri A (2014) A review of mathematical modeling of fixed-bed columns for carbon dioxide adsorption. Chemical Engineering Research and Design 92 (5):961-988. doi:<http://dx.doi.org/10.1016/j.cherd.2013.08.018>

34. Klamt A (2005) COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design. Elsevier Science,

35. Klamt A, Krooshof GJP, Taylor R (2002) COSMOSPACE: Alternative to conventional activity-coefficient models. AIChE Journal 48 (10):2332-2349. doi:10.1002/aic.690481023

36. Toure O, Audonnet F, Lebert A, Dussap C-G (2014) COSMO-RS-PDHS: A new predictive model for aqueous electrolytes solutions. Chemical Engineering Research and Design 92 (12):2873-2883. doi:10.1016/j.cherd.2014.06.020

37. Guo X, Zhang S, Shan XQ (2008) Adsorption of metal ions on lignin. J Hazard Mater 151 (1):134-142. doi:10.1016/j.jhazmat.2007.05.065

38. Dassault Systemes Materials Studio Tutorials (2017). BIOVIA Support, 5005 Wateridge Vista Drive, San Diego, CA 92121 USA

39. Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E (1953) Equation of State Calculations by Fast Computing Machines. The Journal of Chemical Physics 21 (6):1087-1092. doi:doi:<http://dx.doi.org/10.1063/1.1699114>

40. Kirkpatrick S, Gelatt CD, Vecchi MP (1983) Optimization by Simulated Annealing. Science 220 (4598):671-680. doi:10.1126/science.220.4598.671

41. Černý V (1985) Thermodynamical approach to the traveling salesman problem: An efficient simulation algorithm. Journal of Optimization Theory and Applications 45 (1):41-51. doi:10.1007/bf00940812

42. Islam MR, Chen C-C (2015) COSMO-SAC Sigma Profile Generation with Conceptual Segment Concept. Industrial & Engineering Chemistry Research 54 (16):4441-4454. doi:10.1021/ie503829b

43. Shah MR, Yadav GD (2013) Prediction of sorption in polymers using quantum chemical calculations: Application to polymer membranes. Journal of Membrane Science 427:108-117. doi:10.1016/j.memsci.2012.09.037

44. Islam MR, Chen C-C (2014) COSMO-SAC Sigma Profile Generation with Conceptual Segment Concept. Industrial & Engineering Chemistry Research:141209090605008. doi:10.1021/ie503829b

45. Klamt A (2005) COSMO-RS From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design. Elsevier