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学位論文全文に代わる要約
Extended Summary in Lieu of Dissertation

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学位論文題目：
Title of Dissertation

ADSORPTION MECHANISM AND SELECTIVITY OF HEAVY METALS AND PESTICIDES ON ZEOLITES AND MONTMORILLONITE
（重金属及び殺虫剤のゼオライト及びモンモリロナイトへの吸着選択性と吸着機構）

学位論文要約：
Dissertation Summary

The adsorption mechanism and selectivity of heavy metals and an organophosphate pesticide on zeolites and montmorillonite was studied with the objective of assessing the capacity of zeolites and montmorillonite to remove heavy metals (Cu, Pb and Cd) and pesticides (Diazinon). The selectivity sequence of the removal and the factors affecting the removal capacity were studied in detail. The study further analyzed the mechanism of pollutant removal by the aforementioned adsorbents. Various types of zeolites, with variations in their cation exchange capacities (CEC), pore structures, Si/Al ratio and surface area were used in the study. Zeolite A4, faujasite X, faujasite Y, mordenite, Na-P1, clinoptilolite and montmorillonite were used for the heavy metal adsorption experiments. For the diazinon adsorption experiments, iron-modified montmorillonite was used.

The adsorption of Cu onto zeolites and montmorillonite as a reference was conducted at an initial Cu concentration range of 0-0.60 mM in the presence of 100 mM NH_4NO_3 at an initial pH of 5. The zeolites used were A4, Faujasite X, Faujasite Y, mordenite, Na-P1 and clinoptilolite. The samples were analyzed before commencement of the adsorption experiments: CEC measurement, Si/Al ratio determination, and XRD analysis. Table 1 is an illustration of the CEC and Si/Al ratio of the samples. Zeolite A4 was the sample with the highest CEC of 6150 mmol kg^{-1} followed by the rest of the samples.

Table 1: CEC and Si/Al ratio of the samples

Sample	**CEC (mmol kg-1)**	**Si/Al ratio**
A4	6150	1.00
Faujasite X	5560	1.24
Faujasite Y	3470	2.66
Na-P1	4500	1.67
Modernite	2457	4.88
Montmorillonite	1200	-
Clinoptilolite	2112	5.04

The samples for the experiments were then saturated with Na in order to obtain samples that had uniform exchangeable cations. Langmuir and Freundlich models were used in analyzing the equilibrium data and a selectivity sequence derived from the Langmuir calculation was A4 > faujasite X > modernite > Na-P1 ≈ montmorillonite ≈ faujasite Y > clinoptilolite. Zeolites A4 and faujasite X had high adsorptive capacities of 1429 mmol kg^{-1} and 909 mmol kg^{-1}, respectively. Zeolite A4 has the highest CEC among all the samples (6150 mmol kg^{-1}), and the adsorption capacity of Cu was largely influenced by the CEC of the samples.

The adsorption mechanism was based on the exchange of Cu from solution with mostly Na which was the main exchangeable cation available. Figure 1 shows the adsorption isotherms of copper on the studied zeolite samples. The adsorption isotherm for A4 was very steep in the lower concentration range compared to the other samples. This resulted in A4 having the highest Langmuir *K* constant compared to all other samples. The steep nature of the isotherm further indicated that Cu was more strongly attached to zeolite A4 than the rest of the samples, indicating that A4 would be used efficiently for the adsorption of Cu in nature at low concentrations. This was followed by faujasite X and the rest of the samples.

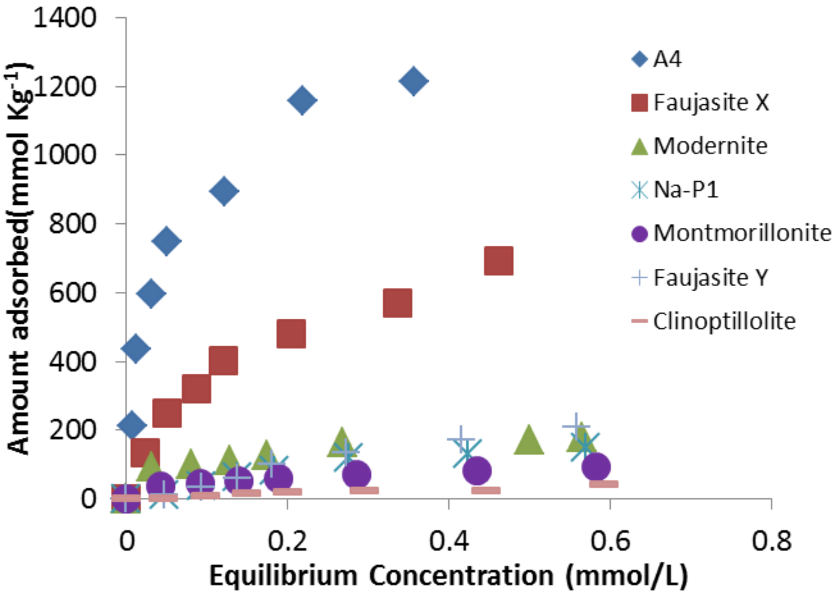
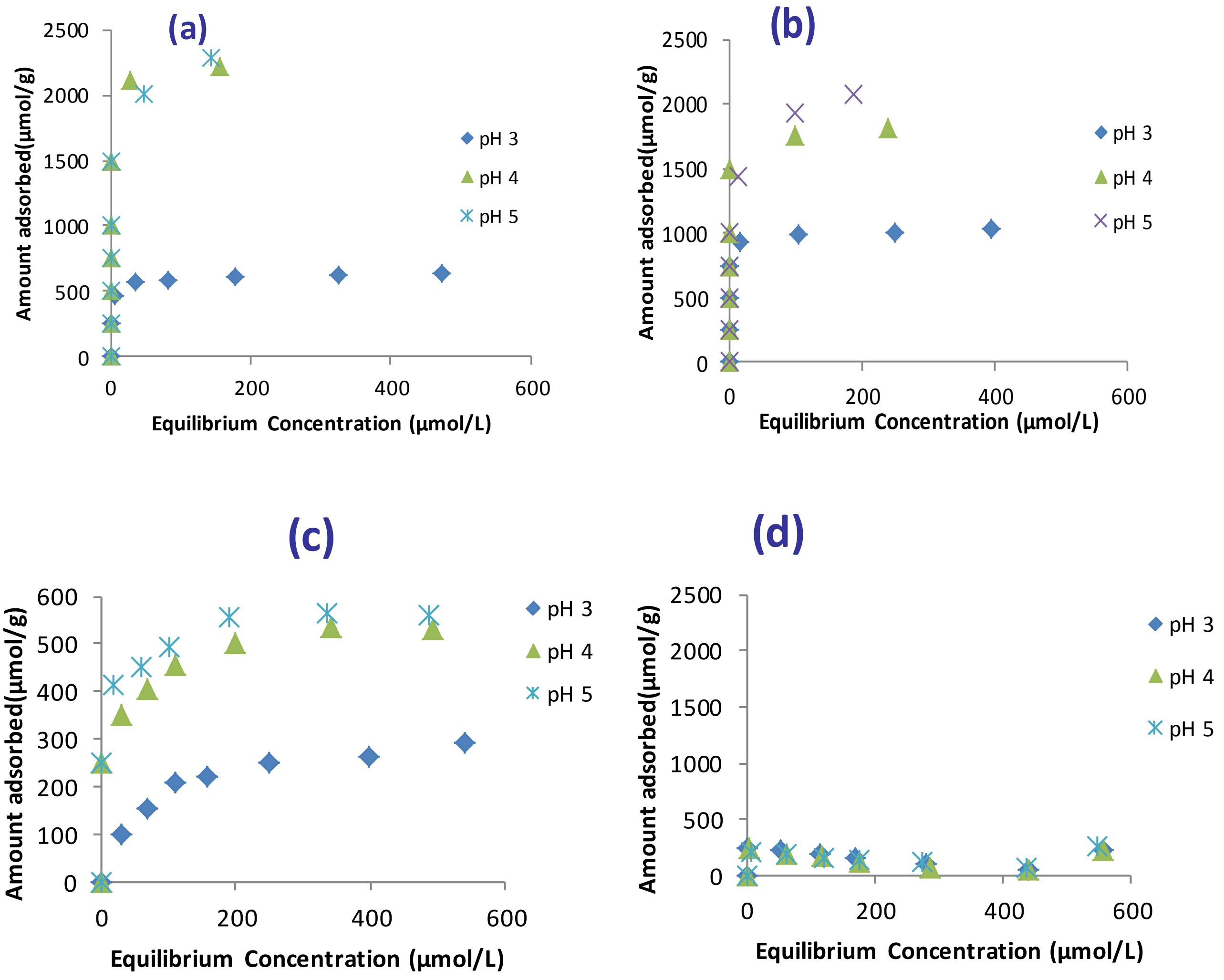


Figure 1: Copper adsorption isotherms on zeolites A4, faujasite X, modernite, Na-P1, montmorillonite, faujasite Y and clinoptilolite.

Following the Cu adsorption experiments, Pb adsorption experiments were conducted. The adsorption of Pb on zeolites A4, faujasite X, faujasite Y and mordenite was studied at various initial pH with the purpose of assessing the pH dependence of Pb adsorption. The samples were also saturated with Na as a uniform exchangeable cation. The adsorption was conducted using 0-0.6 mM $PbNO_3$ in the presence of 100 mM NH_4NO_3 and pH adjustment done using HNO_3. The coexisting NH_4NO_3 served as a representative of other cations available in nature. The study was conducted at initial solution pH ranging from 3-5. Adsorption results were analyzed using Langmuir isotherm analysis.

Figure 2 shows the Lead adsorption isotherms on the studied samples. Adsorption was noted to be dependent on pH with increasing adsorption as pH increased from 3-5 for zeolites A4, faujasite X and faujasite Y. It was observed that adsorption was highest at an initial pH of 5 among the samples except mordenite whose adsorption was almost constant across this pH range. The uptake capacity of metal ions and the adsorption mechanism involved are known to be dependent on the pH of the solution, which affects the degree of ionization, surface charge of the adsorbent and the speciation of the adsorbate (Hasan, 2008 and Stefanova, 2000). As the pH increased, more negatively charged surfaces became available, therefore leading to a greater metal uptake.



Figures 2 : Lead adsorption isotherms on (a)A4, (b)Faujasite X ,(c) Faujasite Y and (d) Mordenite

It is conceivable that at low pH values, there were more H_3O^+ ions in the solution, and competition existed between the positively charged hydrogen ions and metal ions for the available adsorption sites on the zeolite surface. As the pH increased, more of the positively charged metal ions in solution were adsorbed on the negative surface and thus the percentage removal of the metal ions increased. The adsorptive capacities were 2500, 2000, 588 and 179 mmol kg^{-1} for A4, faujasite X, faujasite Y and mordenite, respectively.

Figure 3 is the plot of the amount adsorbed and equilibrium pH at initial concentration of 600 μmol L^{-1}. Zeolite A4 and faujasite X have steep isotherms which are spread over a narrow range of pH compared to faujasite Y and modernite whose isotherm is spread over a wider pH range. The figure highlighted the high dependence on pH, of the adsorption of Pb within this pH region. In the pH range of 2–6, the sorption percentage increases gradually with increasing pH. Adsorption is mainly dominated by ion exchange as H^+ ions are competitive to Pb ions for ion exchange sites. The figure

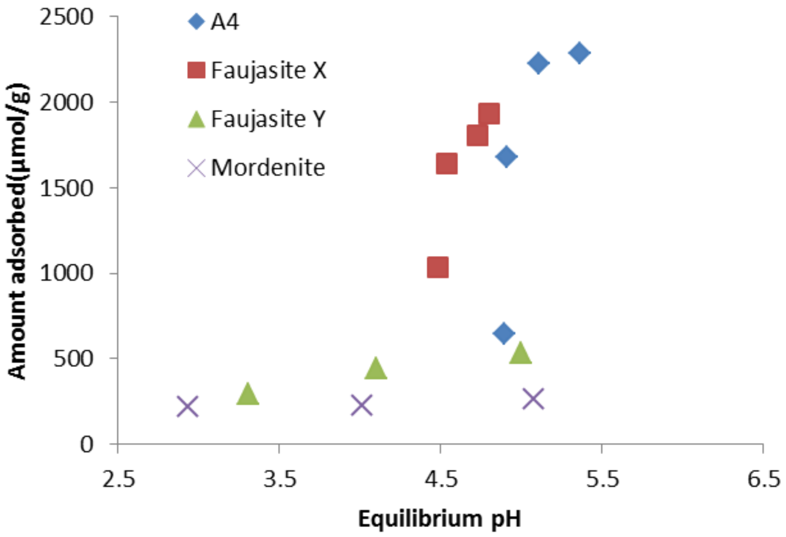


Figure 3: pH dependence of the samples for Pb adsorption at initial Pb concentration of 600 μmol L-1 and pH of 5.

further highlights the fact that the adsorption of Pb is strongly affected by the increasing concentration of proton (H^+), in other words, decreasing pH.

In the subsequent experiments, the adsorption of Cd onto zeolites A4, faujasite X, faujasite Y and mordenite was conducted at an initial Cd concentration range of 0-0.60 mM in the presence of 100 mM NH_4NO_3 at initial pH of 5. The samples for the experiments were initially saturated with Na in order to obtain samples that had uniform exchangeable cations. Similar to the experiments mentioned above, the selectivity sequence was A4 > faujasite X > faujasite Y > modernite. Cation exchange was also the main factor that influenced adsorption. Figure 4 indicates the adsorption isotherms of Cd on the studies zeolite samples.

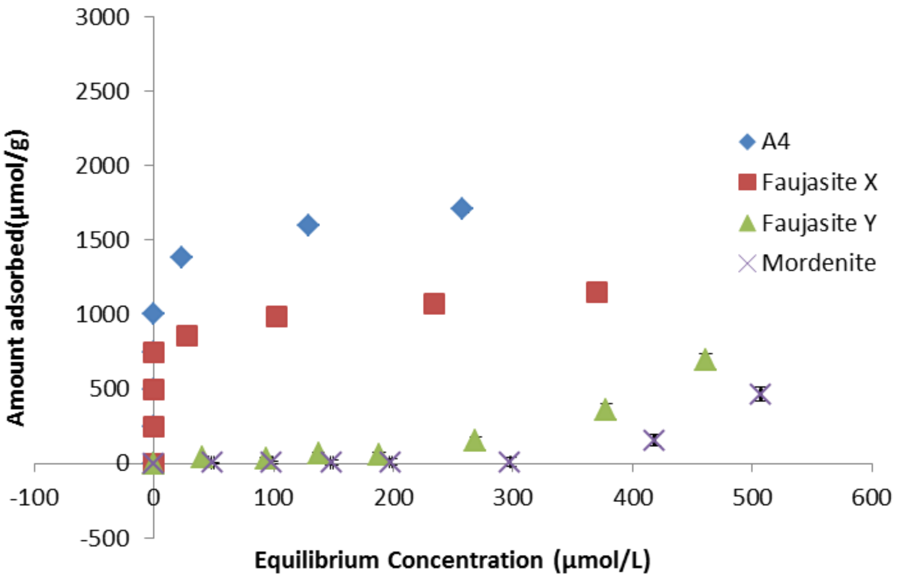


Figure 4: Adsorption isotherms of Cd on Zeolites A4, Faujasite X,Y ad Mordenite at initial pH of 5.

Lastly, the adsorption of Diazinon, and organophosphate pesticide was conducted using montmorillonite as an adsorbent. Montmorillonite modified with iron was used. Two different types of iron-modified montmorillonite, each having different contents of iron and synthesized with different pH and levels of Fe hydrolysis were used. One was denoted “Fe-modified” and the other denoted as “FeOH- modified”. The color of the samples changed from greyish green to light-reddish brown after the modification. X-ray diffraction and physical observations were used for characterization of the samples. The d-spacing of the samples was greater than 15Å, indicating the formation of iron hydroxides in the interlayer space of montmorillonite. The amount of adsorption was calculated from the difference between the initial and final concentration of diazinon. The adsorption data were analyzed using the Langmuir adsorption isotherms. Figure 5 indicates the adsorption isotherms of diazinon on the studied samples.

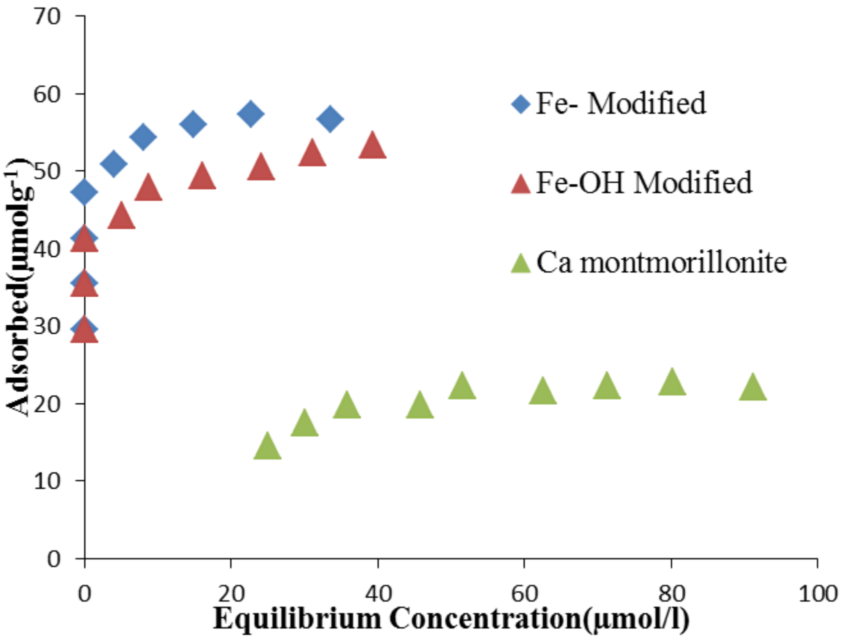


Figure 5: Adsorption isotherms of Diazinon on Fe modified, FeOH modified and Ca montmorillonite

The amounts of diazinon adsorbed were 58.8 and 54.1 mmol kg^{-1} for Fe-modified and FeOH-modified respectively. The steep rise in their adsorption isotherms indicated the possibility of adsorption for low levels of diazinon in polluted water.

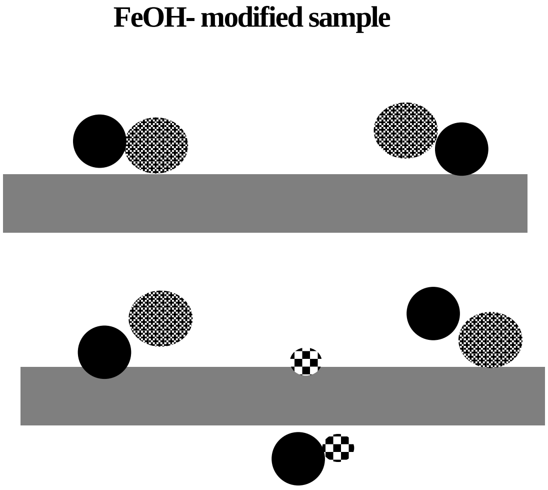


Figure 6: Mechanism for diazinon adsorption on FeOH-modifies sample

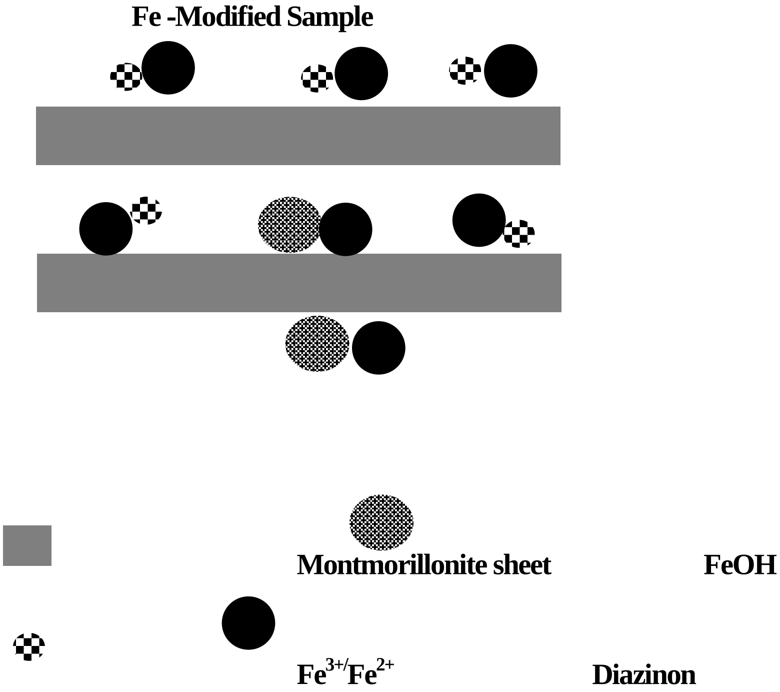


Figure 7: Mechanism for diazinon adsorption on Fe-modified sample

Figures 6 and 7 are the mechanisms of diazinon adsorption by the samples. The degree of polymerization had a significant contribution to the adsorptive properties of the samples. Figures 6 and 7 are illustrations of the mechanism for diazinon adsorption. The Fe-modified sample, which was prepared at a lower pH than the FeOH-modified sample was less polymerized and had a comparatively larger available room within its structure for diazinon adsorption. On the contrary, the FeOH-modified sample whose preparation pH was slightly higher, had a higher degree of polymerization. This implied that the available room for adsorption of diazinon was less hence lower adsorption. In other studies, FeOH-montmorillonite prepared at OH/Fe= 2 (similar to current study), practically all original exchangeable cations in the montmorillonite sample were replaced by ferric ions with a majority of the total present outside the interlayer space (Grygar, 2007). This was due to the large size of the polymerized Fe species which could into easily penetrate into the interlayer space. This is unlike the Fe-modified sample whose Fe species could easily penetrate the interlayer space.

The results of this study can be used in designing or planning for the clean-up of polluted water using adsorption techniques. An important attribute of these findings was that the samples studied were shown to have the capacity of removing even a very low concentration of the studied pollutants, a property which is hardly achievable by most adsorbents. The results of this study are also important is assisting decision makers in choosing the most efficient, cost effective and environmentally friendly method of removing Cu, Pb, Cd and diazinon from polluted environments. These results can as well apply to other heavy metals and some organophosphate pesticides.

Key words: Heavy metals; Pesticides; Cu adsorption; Pb adsorption, Cd adsorption, Selectivity; Cation exchange Capacity, Langmuir isotherm analysis; Freundlich isotherm analysis.

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