RESEARCH ARTICLE

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Removal of 2,4-dichlorophenoxyacetic acid from water by modified zeolite adsorbents

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ABSTRACT: The removal of 2,4-dichlorophenoxyacetic acid (2,4-D) by zeolites (ZY, ZY-10, and ZY-200 with Si/Al ratios of 6.07, 14.68, and 207.25, respectively) and modified zeolites with hexadecyltrimethyl ammonuium (HDTMA) were investigated. The influence of HDTMA concentration, modification methodology, and 2,4-D initial concentration were evaluated for 24 h at room temperature (30 °C). The results showed that the best adsorption capacity was obtained from 15 mM HDTMA using a dropwise method and 10 mg/l 2,4-D solution. The best adsorption capacities of the unmodified and modified zeolites were 20.80 ± 0.23, 27.90 ± 0.45, 18.02 ± 0.27, 10.32 ± 0.40, 71.01 ± 0.51, and 99.61 ± 0.36% for ZY, ZY-10, ZY-200, 15MZY, 15MZY-10, and 15MZY-200, respectively. Compared with the unmodified zeolites, the adsorption efficiency of 2,4-D of the modified zeolites was higher except for the MZY, which was due to the steric hindrance caused by blocking of zeolite pores by large HDTMA molecules. The adsorption isotherms of ZY, ZY-10, 15MZY, and 15MZY-10 corresponded to the Freundlich model with the R^2 values in the range of 0.7922–0.9752. The ZY-200 and 15MZY-200 corresponded to the Langmuir model and showed the R^2 values of 0.9091 and 0.9589, respectively. The XRD characterization results showed that all unmodified and modified zeolites were similar in crystallinity and the structural framework of zeolite Y. The BET surface area, micropore surface area, and micropore volume of unmodified and modified zeolites were on a downward trend, while external surface area, pore volume, and pore diameter increased.

KEYWORDS: zeolite, 2,4-dichlorophenoxyacetic acid, HDTMA, adsorption isotherm, adsorbents

INTRODUCTION

2,4-D or 2,4-dichlorophenoxyacetic acid ($C_8H_6Cl_2O_3$) is an organic herbicide used to prevent, destroy, and control broad-leaf weed in rice, wheat, maize, and many other crops [1]. 2,4-D, when sprayed on dicotyledonous plants, functions as plant growth regulator which increases agricultural productivity [2]. Both 2,4-D and its derivative are imported in large amounts into Thailand [3]. The 2,4-D herbicide causes contamination of soil, ground water, as well as agricultural products. The health effects from 2,4-D include liver necrosis; destruction of the liver, kidneys, and central nervous system; and carcinogenicity [4]. Despite a half-life of degradation in soil between 10–50 days (less than other herbicides), 2,4-D is still detected in water resources because of its high solubility in water of up to 900 mg/l. According to USEPA quality control of drinking water, a concentration up to 0.07 mg/l of 2,4-D indicates contamination [5]. Several methods can be employed to remove residues of 2,4-D from water including biodegradation, photodegradation, hydrolysis, evaporation, and oxidation [6–9]. However, the adsorption process, widely used for the treatment of wastewater containing organic and inorganic pollutants, has advantages over other methods because of its simple design and low level investment [10].

Most adsorbents of heavy metal movement to the biosystem are coal fly ash, activated carbon, and clay minerals (zeolite, sepiolite, and diatomite) [11]. Zeolites are good adsorbents because they have large enough pore sizes to adsorb organic and inorganic compounds. The zeolite Y is used as an adsorbent in extraction process for the determination of pesticide residues in water and agricultural products. It is also used as a sorbent for pesticide, herbicide, and hydrocarbon (such as paraquat, linuron, and ethylene) [12, 13]. According to the structure of zeolite Y, which contains large channels and negative oxygen sites, it is interesting that the zeolite Y and 2,4-dichlorophenolixyacetic acid

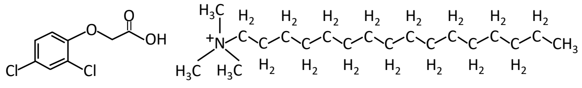
(a) (b)

Fig. 1 Structures of 2,4-D (a) and HDTMA surfactant (b).

might interact with each other by hydrogen bond and intermolecular forces. In addition, the modification of zeolite Y with HDTMA might enhance the adsorption capacity via hydrogen bond (CH-π interaction) between CH of HDTMA and the π of 2,4-D. The CH—O interaction might be one of the weak hydrogen bonds that also enhance the adsorption capability. Other than the fact that modified zeolites are cheaper than granular activated carbon and synthetic ion exchange resins [14], the specific gravity of high porosity zeolite is very low. For example, zeolite modified with HDTMA surfactant increases absorption capacities of Cr^{3+}, As^{5+}, and compound aromatic hydrocarbon [15, 16]. The increase in absorption capacities of Cr^{6+}, linuron, and atrazine by zeolite modified with HDPB, HDTMA, and SDBAC surfactants has been reported [17–19].

In order to reduce the 2,4-D contamination of water sources and prevent the spread and its toxicity to the environment, this research aims to remove the herbicide (2,4-D) (Fig. 1a) using zeolite Y with different Si/Al ratios and to increase adsorption capacity with HDTMA (Fig. 1b) modification. This research investigates the effect of modified zeolite adsorbent for 2,4-D adsorption from water in an attempt to further apply for the removal of the pollutant from wastewater in the environment.

MATERIALS AND METHODS

Synthesis of zeolite

The absorbent used in this research is zeolite Y with three different Si/Al ratios: ZY, ZY-10, and ZY-200. Zeolite Y was synthesized hydrothermally [20] using mole ratio of reagent: $4.62\,Na_2O{:}Al_2O_3{:}10\,SiO_2{:}180\,H_2O$. Seed gel and feed stock gel were prepared. Seed gel was prepared by mixing together sodium aluminate, sodium hydroxide, DI water, and sodium silicate solution. The mixture was stirred for 10 min and kept at room temperature (30 °C) for 24 h. Feed stock gel was prepared by mixing together sodium aluminate, sodium hydroxide, and DI water; and the mixture was stirred until smooth. Then sodium silicate solution was added and stirred for 25 min. For the overall gel preparation, seed gel and feed stock gel were mixed, stirred with overhead stirrer of 1300 rpm for 20 min, aged at room temperature (30 °C) for 24 h, crystallized at 100 °C for 7 h, and washed with deionized water until the pH of the filtrate turned to be neutral. The neutral filtrate was dried overnight at 110 °C to obtain a synthesized zeolite ZY (Si/Al ratio = 6.07). The other zeolites, ZY-10 and ZY-200, were purchased from Tosoh Corporation, Japan.

Characterization

The Si/Al ratio of adsorbents were analyzed by X-Ray Fluorescence Spectrometry (XRF); and the determination of SiO_2, Al_2O_3, Na_2O, MgO, K_2O, CaO, TiO_2, and Fe_2O_3 was done using Horiba 5200, XGT diameter 100 µm, X-ray tube 30 kV, current 1.00 mA.

The structural analysis and mineral identification of the zeolite samples were done by X-ray diffraction technique (XRD) using Bruker D5005 Powder. X-ray diffractometer with Ni-filtered Cu Kα radiation was used to record all of the diffraction spectra in 5–50 range of 2θ.

The surface area, pore volume, and pore diameter of the zeolites were analyzed by N_2 adsorption and Brunauer-Emmett-Teller (BET) technique, measured at 77.3 K of liquid nitrogen Autosorp-1-C instrument, and degassed at 573 K for 3 h.

Modification of zeolite with HDTMA surfactant

Three zeolites: ZY, ZY-10, and ZY-200, were modified with cationic HDTMA surfactant based on two methods of adding 100 ml of HDTMA surfactant solution of various concentrations (5, 10, 15, and 20 mM) onto 1 g zeolite. In the first method (stirred method), the surfactant was added onto the zeolite at once and stirred for 48 h. In the second method, (dropwise method), the surfactant was added dropwise (about 1 drop per 30 s) onto the zeolite and stirred for 48 h. The solid phase was separated by filtration and washed with distilled water until free of Cl^- and, then, dried at 110 °C for 3 h to make the modified zeolites: MZY, MZY-10, and MZY-200.

Adsorption of 2,4-D

The adsorption of 2,4-D was performed by adding 25 ml of 2, 4, 6, 8, and 10 mg/l of 2,4-D to 0.1 g of individual adsorbents in a 100 ml flask. The mixture was shaken at 150 rpm for 24 h, centrifuged at 3000 rpm for 20 min, and filtered with a 45 µ filter paper. The obtained filtrate was used to analyze adsorption capacities with HPLC, and the

Table 1 Composition of some chemical elements in zeolites.

Composition (wt %)	Zeolite		
	ZY	ZY-10	ZY-200
SiO_2	73.63	86.34	99.48
Al_2O_3	12.13	5.88	0.48
Na_2O	12.78	6.15	0.00
MgO	1.25	1.56	0.00
K_2O	0.03	0.00	0.00
CaO	0.08	0.02	0.01
TiO_2	0.03	0.02	0.02
Fe_2O_3	0.04	0.01	0.00
Si/Al	6.07	14.68	207.25

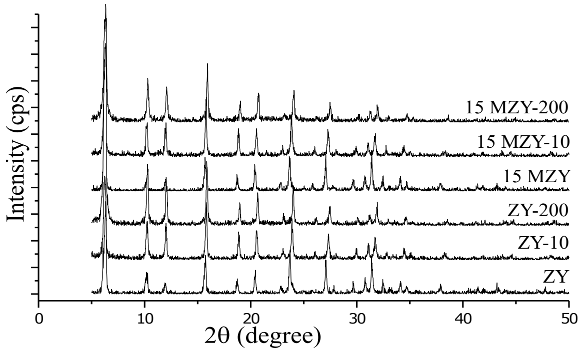

Fig. 2 X-ray diffraction pattern of unmodified and modified zeolites.

adsorption experiment was repeated four times for each concentration.

RESULTS AND DISCUSSION

Characterization

X-ray fluorescence (XRF) technique analysis revealed the composition of some elements in the three zeolites (Table 1). The main elements were silica, alumina, alkali, and alkaline earth metals. The Si/Al ratios were 6.07, 14.68, and 207.25; and the Na_2O compositions were 12.78, 6.15, and 0.00% for ZY, ZY-10, and ZY-200, respectively.

The X-ray diffraction (XRD) pattern of adsorbents (Fig. 2) showed that the intense lines at 2θ of the modified zeolites 15MZY, 15MZY-10, and 15MZY-200 were similar to those of the unmodified zeolites. This means that the structure of modified zeolites with HDTMA surfactant maintained the crystallinity and structural framework of their relevant unmodified zeolites ZY, ZY-10, and ZY-200. This is in agreement with the crystalline percentage (Fig. 3), which was calculated from strong area of sample per area of standard, of unmodified and modified zeolites [21]. The molecule of HDTMA surfactant is too large to pass through the pore size of the zeolite. Therefore, it was exchanged for Na^+ on the external surface without altering the original structure of the modified zeolites [22].

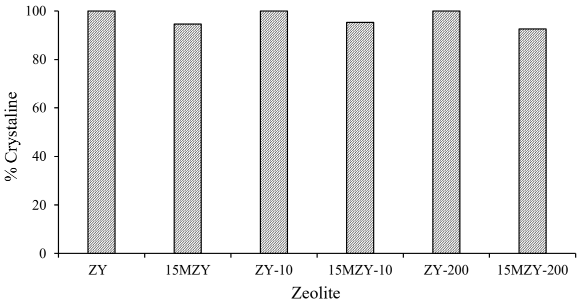

Fig. 3 Crystalline percentage of unmodified and modified zeolites.

Table 2 summarizes the BET analyzer results such as BET surface area, micro pore surface area, external surface area, pore volume, micro pore volume, and average pore diameter. Considering unmodified zeolites, it was found that BET surface area of ZY, ZY-10, and ZY-200 decreased by 765.21, 712.24, and 703.80 m^2/g, and the external surface area by 4.56, 16.41, and 19.85%, respectively, due to the effects of Si atomic size and framework defect [23]. When compared the modified zeolites with the unmodified zeolites, BET surface area decreased by 636.26, 657.17, and 541.90 m^2/g for 15MZY, 15MZY-10, and 15MZY-200, respectively. This could be explained by the fact that the surface of zeolite was covered with bulk HDTMA surfactant.

Correlation between BET surface area and micropore surface area of ZY-200 and 15MZY-200, decreased from 703.80 to 541.90 m^2/g and 609.43 to 390.83 m^2/g, respectively. This might be attributed to the occurrence of Van der Waals forces between HDTMA surfactant with pore opening super cages of zeolite structure [24]. BET surface area of MZY decreased 83.13% when compared with ZY. This might be due to the fact that NH_4^+ (from HDTMA head) replaced Na^+ at external zeolite surface with columbic force.

Pore volume of all the modified zeolites dropped because the HDTMA surfactant overlaid the channels of zeolite. The large surfactant blocked the smaller pores; thus, the average pore diameter increased [23].

Table 2 Surface analysis of unmodified and modified zeolites.

Adsorbent	BET surface area (m^2/g)	Micropore surface area (m^2/g)	External surface area (m^2/g)	Total pore volume (cm^3/g)	Micro pore volume (cm^3/g)	Average pore diameter Å
ZY	765.21	731.82	33.46	0.45	0.37	23.42
ZY-10	712.24	611.87	100.43	0.61	0.32	33.23
ZY-200	703.80	609.43	121.07	0.74	0.31	40.27
15 MZY	636.26	596.45	39.87	0.44	0.30	27.42
15 MZY-10	657.17	580.28	76.92	0.55	0.29	34.61
15 MZY-200	541.90	390.83	151.17	0.56	0.20	41.90

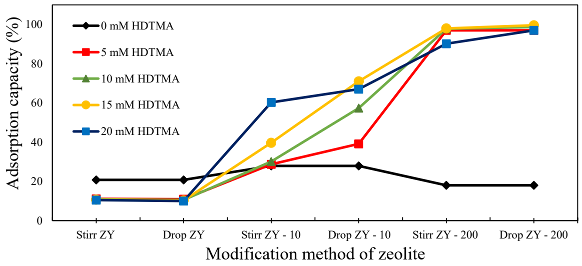

Fig. 4 2,4-D adsorptions of unmodified and modified zeolites prepared by stirred and dropwise methods at various HDTMA concentrations.

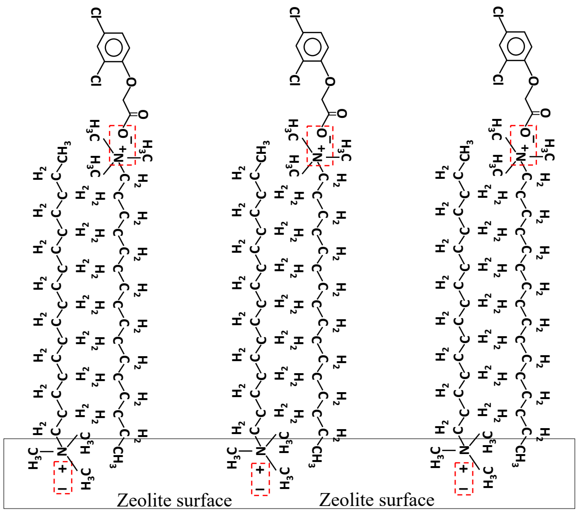

Fig. 5 Adsorption of 2,4-D on the surface of zeolite.

Adsorption of 2,4-D

The adsorption capacity at 10 mg/l of 2,4-D displayed in Fig. 4 revealed that unmodified zeolite ZY-10 (0 mM HDTMA) had the best adsorption capacity of 27.90 ± 0.45%, and the modified ZY and ZY-200 showed adsorption capacities of 20.80 ± 0.23 and 18.02 ± 0.27%, respectively. This is because 2,4-D is an anionic herbicide and well attracted to the zeolites' cationic surface; however, at the same time, it may contribute steric effects on the ZY. Moreover, the structure of unmodified zeolite Y composes of Si and Al linked together by sharing oxygen atom. Hence, the negative charge occurred in the framework structure and decreased when the Si/Al ratio increased. The presence of oxygen atoms led to the intermolecular force as hydrogen bond formed between zeolite framework and 2,4-D. It is found that the 2.4-D adsorption capability onto zeolite Y was related to the polarity of zeolites.

For the modified zeolite with cationic HDTMA surfactant experiment, we varied methods and HDTMA concentration. The results showed that adsorption capacity at 15 mM HDTMA surfactant and dropwise method could adsorb 2,4-D better than the others by 10.32 ± 0.40, 71.02 ± 0.51, and 99.61 ± 0.36% for 15MZY, 15MZY-10, and 15MZY-200, respectively. This might be caused by the surfactant gets into and is slowly arranged on the zeolite's surface. Only the 15MZY could adsorb 2,4-D less than the unmodified zeolites because the pore sizes of zeolite were blocked with large HDTMA molecule causing steric hindrance. When modified zeolite with HDTMA concentration higher than CMC (0.9 mM) was used, there was a bilayer arrangement on the zeolite's surface. The second layer, NH_4^+, was outside the surface and adsorbed with the anionic 2,4-D. The mechanism and the adsorption on zeolite's surface are shown in Fig. 5.

In Fig. 5, the interaction of HDTMA on zeolite Y surface enhanced the 2,4-D adsorption capability due to the dipole-dipole force between the positive charge of HDTMA (arranged in a bilayer) and the negative charge of 2,4-D (deprotonated by dehydration). As a result, the modified zeolite can adsorb 2,4-D better than the unmodified.

Effects of initial 2,4-D concentrations

The effects of initial concentrations of 2,4-D (2, 4, 6, 8, and 10 mg/l) showed that as the concentration

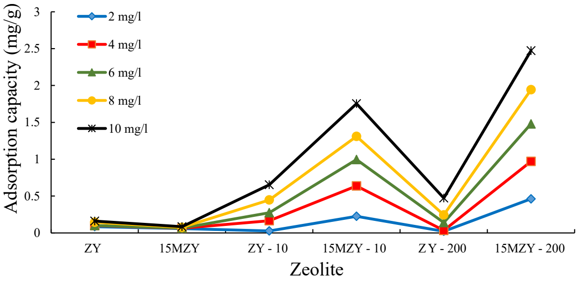

Fig. 6 Effect of 2,4-D initial concentrations on 2,4-D adsorption of the unmodified and modified zeolites.

of 2,4-D increased, the ability to adsorb 2,4-D of the zeolites increased (Fig. 6). At 10 mg/l, the ability of 2,4-D to adsorb was maximum at 0.16, 0.65, 0.47, 0.08, 1.75, and 2.47 mg/g for ZY, ZY-10, ZY-200, 15MZY, 15MZY-10, and 15MZY-200, respectively. The increased concentration of 2,4-D allowed the greater difference of concentrations of the solution and at the surface. As a result, it caused repulsion and more adsorption of 2,4-D.

Adsorption isotherm

Adsorption isotherm is the relationship between concentration at equilibrium and the amount adsorbed at constant room temperature. The Langmuir and the Freundlich Isotherms were investigated in this study. The Langmuir adsorption isotherm is based on the assumption that adsorbent molecules adsorb at the exact location, and each molecule adsorbs on the surface in monolayer. The Langmuir equation is shown in Eq. (1) and the transformation to linear in Eq. (2).

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m}\frac{1}{C_e} \tag{2}$$

where q_e is 2,4-D adsorption equilibrium (mg/g); Q_m refers to the maximum absorption that can be adsorbed monolayer (mg/g); C_e refers to equilibrium concentration of 2,4-D (mg/l); and K_L refers to Langmuir constant (l/mg).

The Freundlich adsorption isotherm is based on the assumption that the surface of the adsorbents is not homogeneous. This isotherm evaluates both chemical and physical adsorptions. The Freundlich equation and the linear transformation are shown in Eqs. (3) and (4), respectively. The Freundlich adsorption isotherm of 2,4-D is shown in Fig. 7.

$$q_e = K_F C_e^{1/n} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

where q_e is 2,4-D adsorption equilibrium (mg/g); C_e is equilibrium concentrations of 2,4-D (mg/l); K_F is the Freundlich constant (l/mg), and n refers to unlisted factors homogeneity.

In Fig. 7, the adsorption of 2,4-D by ZY, ZY-10, 15MZY, and 15MZY-10 corresponds to the Freundlich isotherm, based on the correlation coefficient (R^2). R^2 reveals a heterogeneous adsorption in a continuous process. Considering the K_F constant (Table 3), which represents the adsorption capacity (mg/g), the 15MZY-10 showed a higher value than the others. The n values of ZY, ZY-10, 15MZY, and 15MZY-10 were found to be lower than one needed to adsorb 2,4-D. This shows that adsorption occurs at high concentrations, or the concentrations influence the ability to adsorb a lot of 2,4-D.

The extremely high values of the correlation coefficients confirm that both the Langmuir and the Freundlich equations were suitable for describing the adsorption isotherms of ZY-200 and 15MZY-200. This explains that the adsorbent molecules adsorb at the exact location, and each sorbent molecule adsorbs on the surface in monolayer. The value of Q_m and R^2: 0.4743 mg/g ZY-200 ($R^2 = 0.9091$) and 2.4726 mg/g 15MZY-200 ($R^2 = 0.9589$), indicate that 15MZY-200 could adsorb more 2,4-D than ZY-200 (Table 3 and Fig. S1). The K_L values showed the attraction between 2,4-D ions on the surface of the adsorbents, i.e., the higher the K_L value, the higher the attraction; and the adsorption and the equilibrium are faster. The results show that K_L of the 15MZY-200 was higher than that of the ZY-200.

CONCLUSION

This study of three zeolites with different Si/Al ratios of about 6.07–207.25 represents the characterization of unmodified and modified zeolites which were similar in crystallinity and structural framework. To modify the zeolites, we varied both the concentration of cationic surfactant and the methodology. The effects of these variations on the efficiency to remove anionic 2,4-D herbicide in water were observed. The adsorption capacity at 15 mM HDTMA surfactant in a dropwise method was the best to adsorb 2,4-D. Because the surface of the surfactant was slowly modified into a bilayer arrangement which increased the ability to adsorb

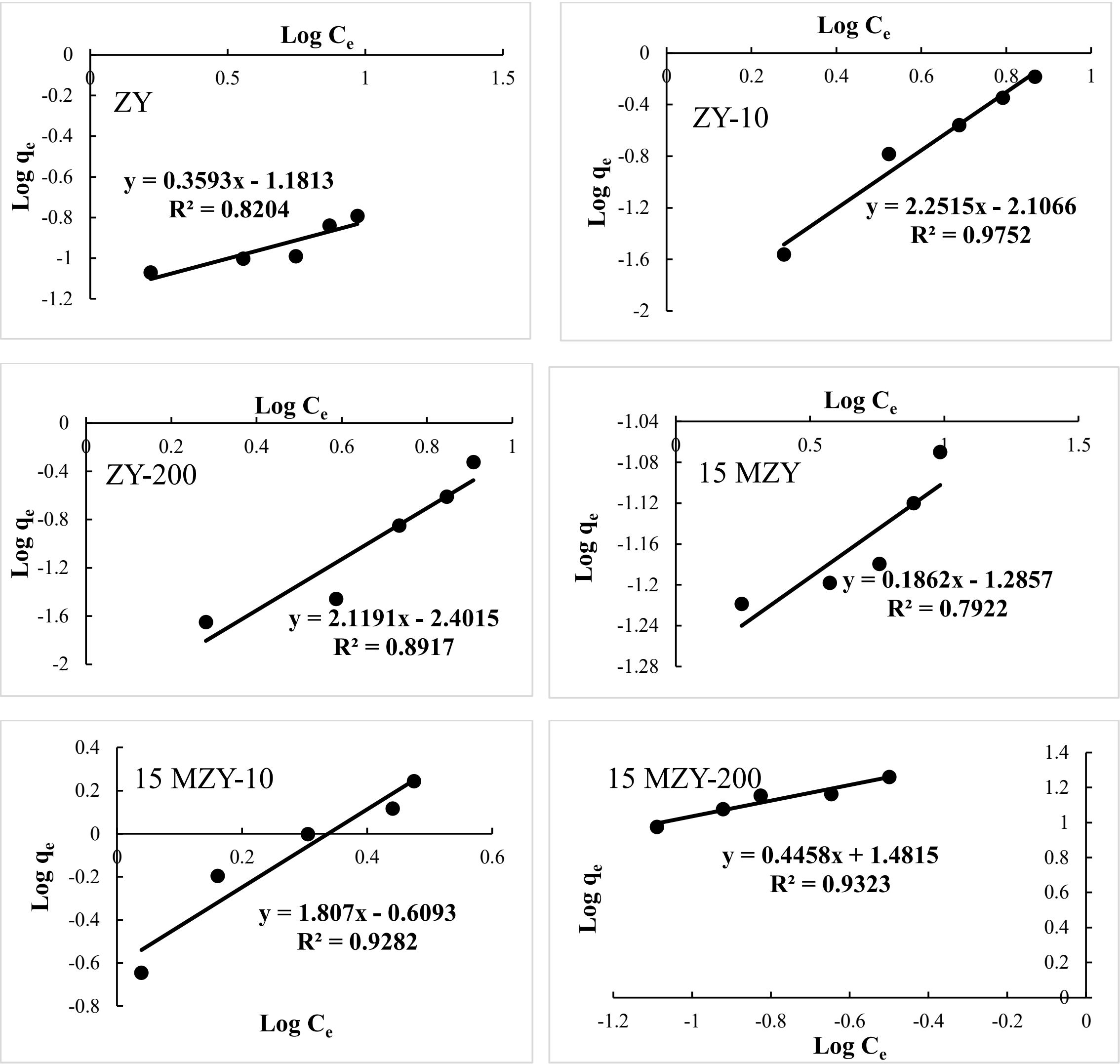

Fig. 7 Freundlich adsorption isotherms of unmodified and modified zeolites.

Table 3 Constants of the Langmuir and the Freundlich adsorption isotherms.

Adsorbent	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	Q_m	K_L	R^2	K_F	n	R^2
ZY	0.1628	0.6289	0.7202	0.0723	0.0720	0.8204
ZY-10	0.6553	0.0170	0.9211	0.0073	0.0073	0.9752
ZY-200	0.4743	0.0193	0.9091	0.0056	0.0056	0.8917
15 MZY	0.0861	1.4011	0.6339	0.0567	0.0565	0.7922
15 MZY-10	1.8512	0.0894	0.8618	0.2298	0.2294	0.9282
15 MZY-200	2.4726	76.3052	0.9589	6.6353	6.6352	0.9323

2,4-D. The adsorption efficacy of 2,4-D was higher in the modified zeolites compared with the unmodified, and the adsorption efficiency of 15MZY-200 was higher than that of the 15MZY-10. However, modified zeolite MZY showed less adsorption of 2,4-D compared with unmodified zeolite as the zeolite pores were blocked with large HDTMA molecules causing steric hindrance. The adsorption isotherms of ZY, ZY-10, 15MZY, and 15MZY-10 fitted the Freundlich isotherm; while those of ZY-200 and 15MZY-

200 fitted the Langmuir isotherm. In terms of the Freundlich isotherm, the zeolites were ranked ZY-10 > 15MZY-10 > ZY and > 15MZY, while for the Langmuir, the zeolites were ranked 15MZY-200 > ZY-200.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found at http://dx.doi.org/10.2306/scienceasia1513-1874.2021.077.

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Appendix A. Supplementary data

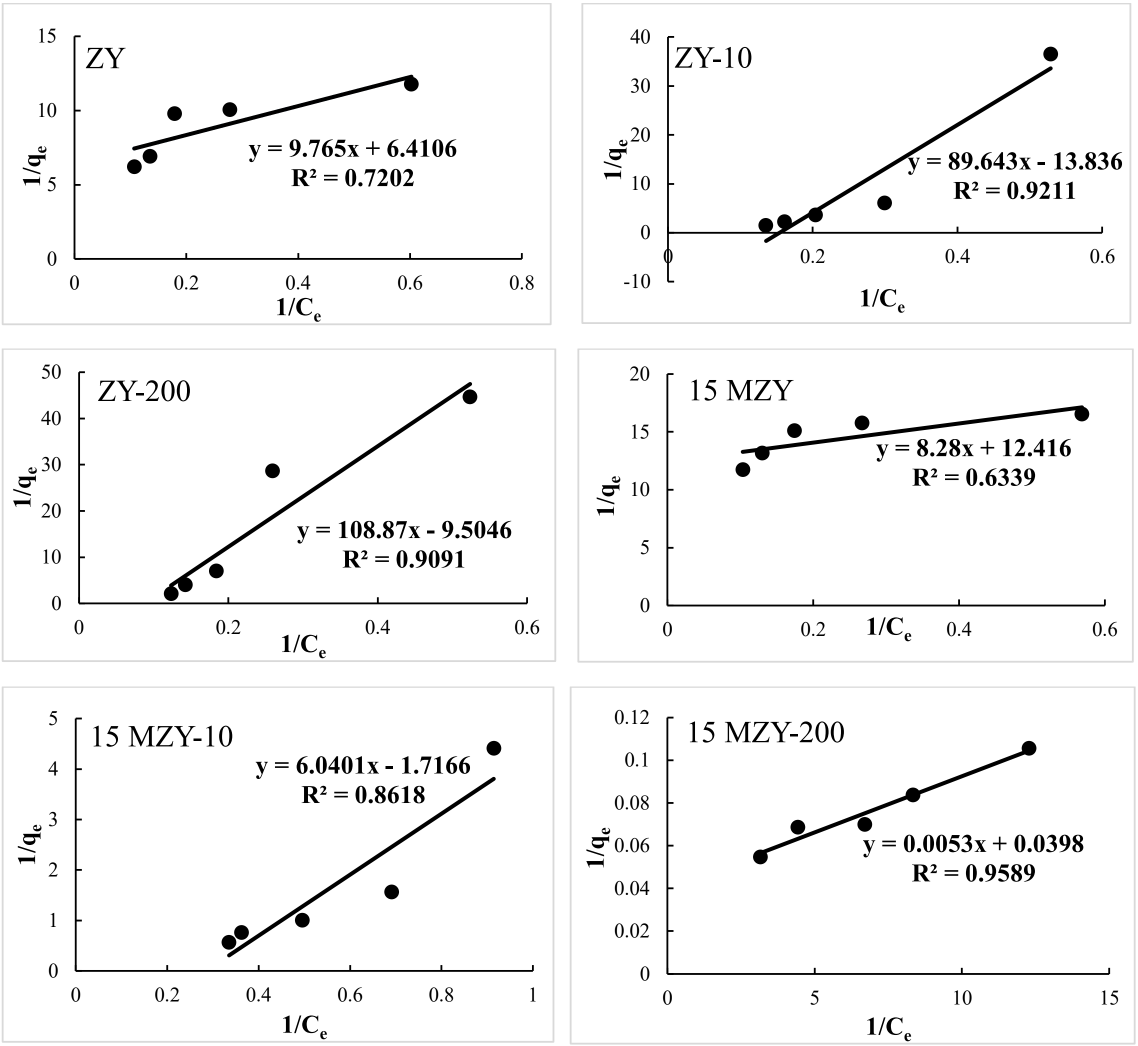

Fig. S1 The Langmuir adsorption isotherms of unmodified and modified zeolites.