Clays and Clay Minerals

removal of water-soluble polymers (PVP, PEG, PAM, and PVA).

EXPERIMENTAL

Materials

Suspension of a sample from the Tsunagi mine (2 wt.% in deionized water) sample gave a pH of 5. The cation exchange capacity (CEC) was determined by the ammonium acetate method (Schollenberger and Simon, 1945). Interlayer cation sites were saturated with ammonium ions through reaction with aqueous ammonium acetate. The eluent was analyzed using atomic absorption spectroscopy (AAS) to determine the types of interlayer cation. Then, the ammonium ion was desorbed by reaction with excess potassium chloride and the amount of ammonium ion eluted was determined by the Kjeldahl (1883) method. The CEC of the acidic clay was 83 meq/100 g clay and the eluted cations and their concentrations were Na^+: 0.4, K^+: 0.8, Ca^{2+}: 4.4, and Mg^+: 8.7 meq/100 g. By subtracting the amounts of metal ions $(0.4+0.8+4.4+8.7 = 14.3$ meq/100 g clay) from the CEC (83 meq/100 g clay), the amount of exchangeable H^+ was estimated to be 68.7 meq/100 g of clay.

Poly(vinylpyrrolidone) with average molecular weights of 10,000 and 160,000 (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), polyacrylamide with an average molecular weight of 150,000 (Sigma-Aldrich, St. Louis, Missouri, USA), poly(vinyl alcohol) with an average of 2000 monomer units and a degree of saponification of 80% (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), poly(ethylene glycol) with an average molecular weight of 500,000 (Wako Pure Chemical Industries Ltd., Osaka, Japan), and NaCl (Daejung Co., Ltd., Busan, Korea) were used without further purification.

PVP adsorption from an aqueous solution

Adsorption of PVP onto acidic clay was examined as follows: the acidic clay (50 mg) was mixed with 50 mL of aqueous PVP solution (average molecular weights of 10,000 and 160,000, designated as PVP_{10} and PVP_{160}, respectively) by sonication for 30 min. Then, the solid was collected by centrifugation at $78 \times g$ (Kubota model 2420, Tokyo, Japan) for 10 min and was dried at 60ºC for 12 h. The amount of the PVP adsorbed was determined by CHNS analysis of the adsorbents collected and dried.

Adsorption of PVP from aqueous NaCl solution onto the acidic clay was examined as follows: PVP_{160} was dissolved in 0.468 M NaCl solution (50 mL). The acidic clay (50 mg) was mixed with the solution by sonication for 30 min. The solid was collected by centrifugation at $78 \times g$ for 10 min and dried at 60ºC for 12 h. The amount of the PVP adsorbed was determined by CHNS analysis of the adsorbents which were collected and dried.

Characterization

Powder X-ray diffraction (XRD) patterns were collected using a NEW D8 ADVANCE instrument (from Bruker, Karlsruhe, Germany) with monochromatic CuKα radiation, operated at 40 kV and 40 mA. The amount of interlayer cation was determined by AAS (Shimadzu atomic absorption spectrometer AA-7000, Shimadzu Co., Kyoto, Japan). Images from scanning electron microscopy (SEM) were obtained using a JEOL JSM-7610F field emission scanning electron microscope (Tokyo, Japan). Prior to the measurements, the samples were coated with platinum. The amount of PVP adsorbed was determined by elemental chemical microanalysis using a LECO TruSpec Micro CHNS analyzer (St Joseph, Michigan, USA) and calculated using the following equations:

Amount of the PVP adsorbed (g/g clay)

$$= \frac{\text{MW of monomer unit (111)}}{\text{Amount of carbon in a monomer unit (72)}}\text{(carbon content in PVP)}$$
$$\times \text{carbon content after adsorption (\%)} \qquad (1)$$

where MW = molecular weight

Equilibrium concentration (g/L) =
Amount of PVP in the initial solution (g) − Amount of PVP adsorbed by the clay (g)/50 L   (2)

Langmuir model

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (3)$$

where q_e (g/g clay) is the amount of PVP adsorbed at equilibrium, C_e (g/L) is the equilibrium solution concentration of PVP, q_m (g/g clay) is the adsorption capacity, and K_L (L/g) is the Langmuir constant.

RESULTS AND DISCUSSION

Collection of the acidic clay from the aqueous suspension after adsorption of PVP was achieved easily by centrifugation at $78 \times g$ for 10 min (Figure 1). Straightforward collection of the solid is an advantage of the acidic clay over analogous natural adsorbents such as Na-type bentonite (Israel *et al.*, 2008) and kaolinite (Bhatti *et al.*, 2012), where centrifugation at $17,609 \times g$ was used to collect the adsorbents from the aqueous PVP solution. The advantage of easy collection may be a result of the poor swelling ability of the acidic clay compared to Na-type bentonite. This is confirmed by the fact that the acidic clay showed no interlayer expansion after intercalation of the PVP (Figure 3). The particle size is another key parameter affecting precipitation of the adsorbent where the acidic clay particles may have a larger particle size than kaolinite.

The amount of PVP adsorbed and the equilibrium concentration of PVP (Table1) were calculated from equations 1 and 2 using the carbon content of the
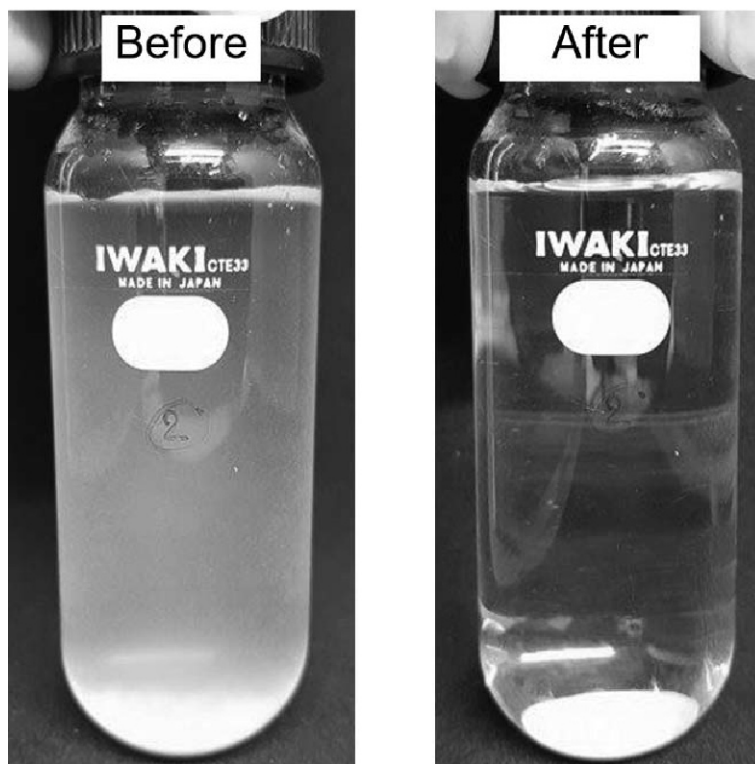
Figure 1. Suspension after adsorption of PVP_{160} on acidic clay (left) before and (right) after centrifugation at $78 \times g$ for 10 min.

adsorbent after reaction with PVP, as obtained by CHNS analysis. The adsorption isotherms of PVP_{10} and PVP_{160} onto the acidic clay from the aqueous solutions (Figure 2a) were classified as type L according to the classification by Giles *et al.* (1974), suggesting a strong affinity between the acidic clay and the PVP. The amount of the PVP adsorbed was greater for the larger-molecular-weight PVP_{160} because of the poor solubility of the longer-chain PVP. The effect of molecular weight on the adsorption of PVP onto adsorbents such as montmorillonite and kaolinite was reported previously (Israel *et al.*, 2001, 2008; Bhatti *et al.*, 2012) and the present result is consistent with those findings. The maximum amount of PVP_{160} adsorbed onto the acidic clay was 0.061 g/g of clay when the equilibrium concentration was 0.94 g/L. The amounts of PVP adsorbed by several other inorganic adsorbents are summarized in Table 2 and the value obtained in the present study (0.061 g/g clay) is comparable to those reported figures.

Table 1. Data from CHNS measurements, calculation of the amount of PVP adsorbed, and equilibrium concentration of PVP.

Initial amount of PVP (g)	Data from CHNS measurements			Calculation		
	Sample mass (g)	Carbon content (%)	PVP adsorbed (g)	Acidic clay (g)	Amount of PVP adsorbed (g/g clay)	Equilibrium concentration of PVP (g/L)
0.5	1.004	0.316	0.005	0.999	0.005	0.005
1	1.023	0.388	0.006	1.017	0.006	0.014
2	1.026	0.837	0.013	1.013	0.013	0.027
5	1.019	1.212	0.019	1.000	0.019	0.081
10	1.008	1.550	0.024	0.984	0.025	0.176
20	1.019	1.666	0.026	0.992	0.026	0.374
30	1.024	2.429	0.038	0.985	0.039	0.561
50	1.029	3.723	0.059	0.970	0.061	0.939
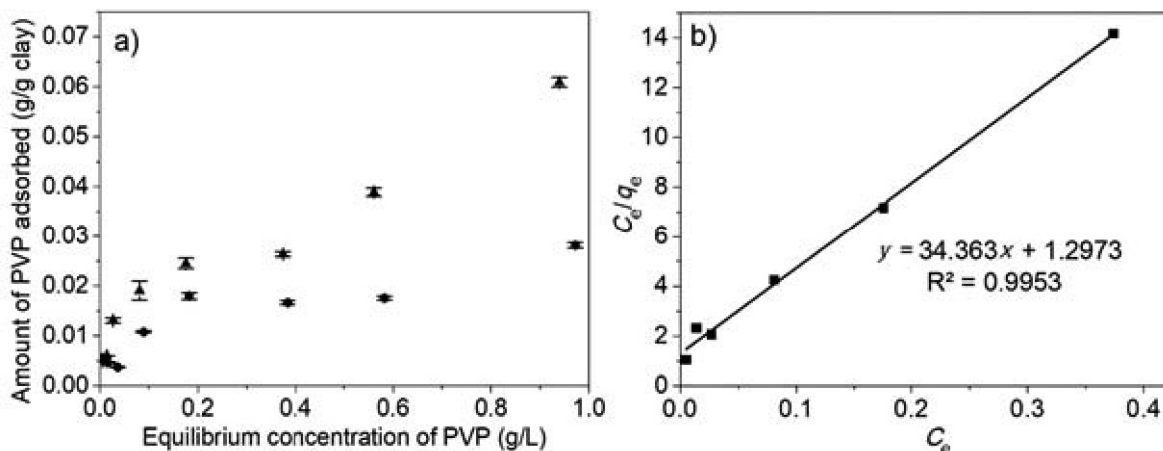
Figure 2. (a) Adsorption isotherms of PVP_{10} (circles) and PVP_{160} (triangles) onto the acidic clay from the aqueous solution from the plot of the amount of PVP adsorbed *vs.* the equilibrium concentration of PVP; and (b) Langmuir plot of the adsorption of PVP_{160} onto the acidic clay from the aqueous solution, C_e/q_e *vs.* C_e.

Using the surface area of smectites (750 m^2/g clay according to van Olphen and Fripiat, 1979) and the density of PVP (1.2 g/cm^3), the amount of PVP as a monolayer on each silicate layer is calculated roughly as 0.28 g/g clay. When the PVP adsorbed forms a densely packed monolayer in the interlayer space, the amount of the PVP is expected to be 0.14 g/g of clay (half of the 0.28 g/g clay value of the monolayer on each silicate layer). The value determined experimentally (0.061 g/g clay) was smaller than the calculated value (0.14 g/g clay), suggesting that the PVP adsorbed was a monolayer where the packing was not dense, keeping some of the layer surface occupied by the adsorbed water. The adsorption of PVP under various conditions such as adsorption from alcohols or at various temperatures may lead to larger degrees of adsorption (denser packing). Further study of this aspect using various conditions for

the adsorption are needed to achieve greater degrees of adsorption (dense packing of the adsorbed polymer).

In order to discuss the location of the PVP adsorbed, the acidic clays before and after the adsorption of PVP_{160} were characterized by XRD (Figure 3). The basal spacing of the acidic clay (Figure 3a) was determined by Bragg's equation, from the reflection in the lowest °2θ region (5.77°2θ), to be 1.53 nm, which suggested bilayer hydration in the interlayer space, as reported previously (Hayakawa *et al.*, 2016). The basal spacing did not change significantly following reaction with PVP to give a value of ~1.5 nm after adsorption of PVP from the aqueous solution (Figure 3b,c). The interlayer spacing was estimated, by subtracting the thickness of the silicate layer from the observed basal spacing, to be 0.5 nm, which is capable of accommodating PVP as a monolayer according to the size of the
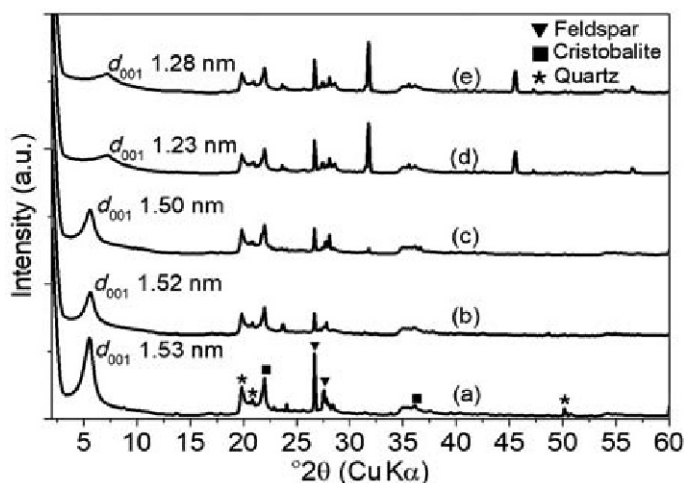
Figure 3. Powder XRD patterns of the acidic clay (a); and the acidic clay after the adsorption of PVP_{160} from aqueous solution (b, c) and from 0.468 M NaCl solution (d,e); using a PVP concentration of 0.004 wt.% (b, d) and 0.06 wt.% (c,e).

Table 2. Comparison of maximum amounts of PVP adsorbed by various adsorbents under specified conditions (data from the literature and the present study).

Adsorbents	Molecular weight of PVP	Solvents	Centrifugation	Maximum adsorption amount (g/g adsorbent)	References
Acidic clay	160,000	Water	$78 \times g$ 10 min	0.061	Present study
Pyrogenic silica	933,000	Water	$17,609 \times g$ 20 min	0.20	(Cohen Stuart *et al.*, 1982)
TiO_2	58,000	MeOH/Water 75%	–	0.003	(Sato *et al.*, 1998)
TiO_2	50,000	EtOH:Hexane (4:6)	–	0.015	(Esumi *et al.*, 1996)
Graphite	50,000	EtOH	–	0.018	
Fuller's earth	12,000	0.001 M KNO_3, pH 4.2	–	0.00055	(Bajpai and Vishwakarma, 2000)
Kaolinite	1,430,000	Water	$34,513 \times g$ 15 min	0.017	(Bhatti *et al.*, 2012)
Kaolinite	245,000	0.01 M NaCl pH 5.5	$31,304 \times g$ 30 min	0.02	(Hild *et al.*, 1997)
Kaolinite	40,000	NaCl	$3,835 \times g$ 90 min	0.88	(Israel *et al.*, 2001)
Na-montmorillonite	44,000	0.01 M NaCl pH 5.6	$31,304 \times g$ 30 min	0.077	(Baβmann *et al.*, 1999)
Na-montmorillonite	10,000	0.001 NaCl	$17,609 \times g$ 30 min	0.20	(Israel *et al.*, 2008)
Na-montmorillonite	44,000	10 mM NaCl pH 5.5	$31,304 \times g$ 30 min	0.60	(Sèquaris *et al.*, 2000)
Li-montmorillonite	400,000	0.1 mM LiCl	$31,304 \times g$ 30 min	0.75	(Sèquaris *et al.*, 2002)

polymer chain as well as previous publications on the intercalation of PVP (Ogawa *et al.*, 1993, 2000; Sohmiya *et al.*, 2012; Theng, 2012). Judging from the basal spacing observed, bilayer coverage of PVP in the interlayer space is not possible. The PVP was adsorbed as an intercalated monolayer in the interlayer space of the acidic clay, therefore, and an increase in the amount of PVP which might be adsorbed might be achieved by adjusting the conditions.

The Langmuir (1916) model (equation 3) was used to examine the adsorption of PVP_{160} from the aqueous solution and a linear plot of the relationship between C_e/q_e and C_e is shown in Figure 2b. The model was applied to the isotherm into two separate parts; with low (0.005−0.40 g/L) and high (0.40−0.94 g/L) equilibrium concentrations. The adsorption isotherm at the low equilibrium concentration of 0.005−0.40 g/L fitted the Langmuir model to give $R^2 = 0.9953$, $q_m = 0.029$ g/g clay, and $K_L = 26.50$ g/L, suggesting that interactions occurred between the polymer and the acidic clay surface and the adsorption as a monolayer. The isotherm of the reaction at high equilibrium concentrations (0.40−0.94 g/L) did not fit the Langmuir model, suggesting that the adsorption of PVP was affected by other interactions including polymer−polymer interactions in addition to the interactions between the polymer and the acidic clay surface.

Adsorption of PVP from aqueous NaCl solutions

The adsorption of PVP_{160} from aqueous NaCl solutions (simulated seawater) was also investigated with environmental protection in mind. The adsorption isotherm is shown in Figure 4a together with the isotherm obtained in the absence of NaCl solution. Although the concentration of PVP from the aqueous NaCl solutions was possible, the amount of the PVP adsorbed was slightly less than that of the PVP adsorbed from the aqueous solutions in the absence of NaCl. At low equilibrium concentrations (0.005−0.20 g/L), the shape of the adsorption isotherm was not type L and the isotherm did not fit with the Langmuir model ($R^2 = 0.8870$, Figure 4b), reflecting more complex interactions of PVP with the clay surface through the interlayer cations. The addition of NaCl led to interactions of PVP with Na^+ and Cl^- in the NaCl solution, which may have affected adsorption. The XRD patterns of the acidic clay after adsorption of PVP_{160} from the aqueous NaCl solution (Figure 3, traces d and e) showed that the basal spacing of the acidic clay became 1.3 nm after the adsorption experiment. A similar basal spacing was observed for Na-type smectites with monolayer interlayer hydration. The protons in the interlayer space of the acidic clay were thus exchanged with Na^+ ions during the PVP adsorption experiment. Because of the size of the PVP chain (Sohmiya *et al.*, 2012; Theng,
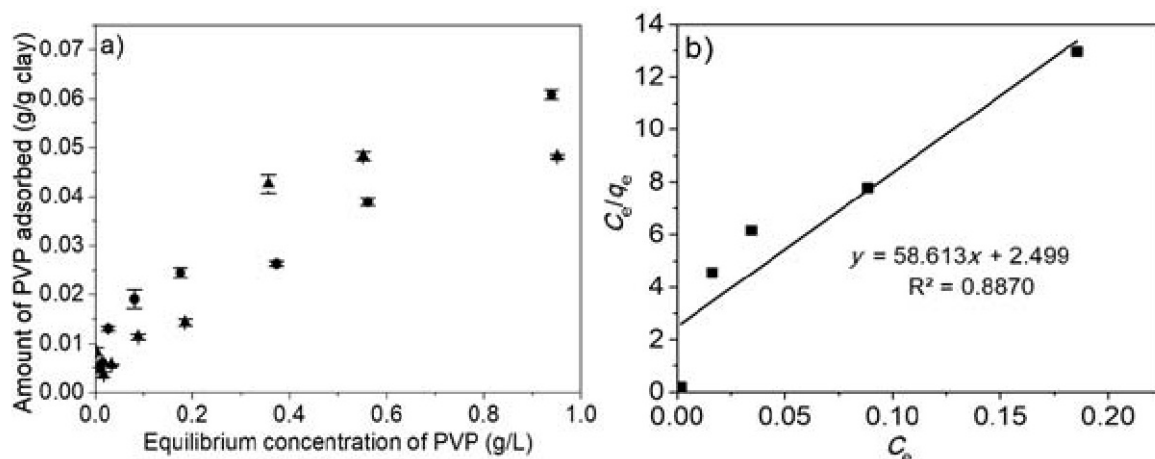
Figure 4. (a) Adsorption isotherms of PVP_{160} onto the acidic clay from the aqueous NaCl solutions of 0.468 M (triangles) compared with the aqueous solutions (circles) from the plot of the amount of PVP adsorbed *vs.* the equilibrium concentration of PVP; (b) Langmuir plot of the adsorption of PVP_{160} onto the acidic clay from the NaCl solution, C_e/q_e *vs.* C_e.

2012), the interlayer spacing was not large enough to accommodate it; PVP is thought, therefore, to adsorb only on the external surfaces of the acidic clay. The PVP was adsorbed on both the external surfaces and in the interlayer space when the adsorption was conducted in the absence of NaCl. Even though the interlayer cation was replaced with Na^+ ions to some extent, collection of the adsorbent was possible by the same procedure (centrifugation at $78 \times g$ for 10 min).

Effect of co-existing minerals

In the XRD pattern of the acidic clay (Figure 3a), reflections from co-existing minerals such as quartz, cristobalite, and feldspar were observed. The crystal sizes of the minerals were determined, using Scherrer's equation (Patterson, 1939), to be 20–40 nm. The presence of the co-existing minerals was also indicated by SEM images of the acidic clay before and after adsorption of PVP_{160} (Figure 5). In addition to the platy

particles, the main component of the acidic clay – other smaller, amorphous aggregates composed of finite particles 20–40 nm in size were noted – *i.e.* consistent with the Scherrer-equation data. These co-existing minerals may also adsorb PVP and so the co-existing minerals should be removed to enable more quantitative discussions about the acidic clay.

Possible removal of PVP from aqueous environments

In order to demonstrate the purification of the water contaminated by polymers, adsorption of PVP_{160} onto acidic clay was evaluated by assessing the concentration of the polymer remaining in water after adsorption. Using the aqueous PVP_{160} solution with a concentration of 0.004 wt.% with varied amounts of the acidic clay, the removal of PVP_{160} was evaluated (50 mL of PVP solution and 50, 100, and 200 mg of the acidic clay). The removal of PVP was reported as a percentage of the PVP initial concentration. As expected, the percentage of
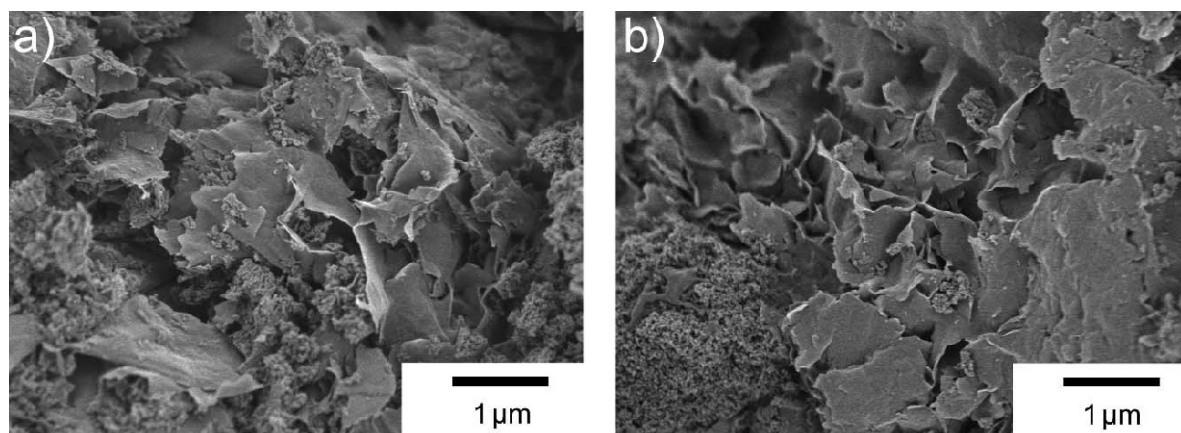

Figure 5. SEM images of the acidic clay before (a) and after (b) adsorption of PVP_{160} solution (0.004 wt.%).

PVP$_{160}$ removal increased from 33% to 64% and to 80% when using 50, 100, and 200 mg of the acidic clay, respectively. More efficient removal (>90%) was also achieved for the PVP$_{160}$ solution with a concentration of 0.001 wt.% using 200 mg of the acidic clay. The results indicate that the applicability of the acidic clay in water purification is potentially very favorable.

Adsorption of PAM, PVA, and PEG was also assessed using similar conditions; the amount of adsorbent at 200 mg and 50 mL of the aqueous solution (at a concentration of 0.004 wt.%). The percentage removed was 75, 38, and 35% for PAM, PVA, and PEG, respectively. The PVP and PAM were removed more efficiently than were PVA and PEG, reflecting the difference in the interactions between the polymers and the acidic clays. Further systematic study is certainly worthwhile, both so that interactions can be understood better and because of the practical application in terms of purification of water-containing, water-soluble polymers.

CONCLUSIONS

The acidic clay obtained from Tsunagi mine, Niigata, Japan, was applied successfully as an adsorbent of poly(vinylpyrrolidone) (PVP) from aqueous solutions. After adsorption, the acidic clay was collected easily by centrifugation. The adsorption isotherm of PVP of molecular weight 160,000 (PVP$_{160}$) on the acidic clay at a low equilibrium concentration was of type L, demonstrating high affinity between the clay mineral and the PVP. The maximum amount of PVP$_{160}$ adsorbed from water was 0.061 g/g clay which did not fit with the adsorption capacity derived from the Langmuir model (0.029 g/g). The values were smaller than those based on the ideal surface area of smectite, the density of the polymer, and assuming monolayer coverage, while it is comparable to the values reported for the adsorption of water-soluble polymers onto various adsorbents. In terms of water purification, >90% of the polymer (of molecular weight 160,000) was removed from solution by using 200 mg of the acidic clay per 50 mL of aqueous solution. The acidic clay was used to collect other water-soluble polymers such as polyacrylamide, poly(vinyl alcohol), and poly(ethylene glycol) from aqueous solution. All these results suggested the possible application of the acidic clay in the removal of water-soluble polymers from aqueous environments.

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