Mechanism of Copper(II) Adsorption by Polyvinyl Polyacrylate

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ABSTRACT: The mechanism of copper adsorption by polyvinyl polyacrylate (PVPA) was examined using ESR and magnetic measurements. The copper adsorption by PVPA obeyed Langmuir adsorption isotherm with the maximum adsorption amounts of 4.17 mmol g^{-1} adsorbent, being larger than those of uranium adsorption. Though copper in the solution was completely adsorbed by the resin above pH 4, the ESR intensity was remained low level and only increased above pH 8. The ESR spectrum of Cu(II) ion in PVPA are axial type with tetragonally distorted octahedral symmetry, having parameters of $g_{//}$ = 2.361, $g_{\perp}$ = 2.057, $|A_{//}|$ = 14.0 m cm^{-1} (pH 5), and $g_{//}$ = 2.329, $g_{\perp}$ = 2.058, $|A_{//}|$ = 16.2 m cm^{-1}, $|A_{\perp}|$ = 2.7 m cm^{-1} (pH 9). The absorption peaks originated from Cu(II)–Cu(II) dimer was also observed (pH 5). The paramagnetic susceptibility of PVPA adsorbed Cu(II) ion at pH 5 explained by the dimer model with $|J|$ = 220 K. These results suggested that most of copper was adsorbed and formed dimer in PVPA, being similar to that in Cu(II)-acetate monohydrate. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5372–5377, 2006

Key words: copper adsorption; polyvinyl polyacrylate; ESR; magnetic susceptibility; copper dimer

INTRODUCTION

The removal of toxic heavy metals, such as copper, cadmium, lead, and mercury, in water resources is in the center of wide interest on the standpoint of environmental pollution. One of most possible techniques for the removal of heavy metals in the environment is the adsorption using suitable adsorbents. Much effort has, therefore, been concentrated to remove copper by using various adsorbents, such as chelating resins,[1–4] activated carbon,[5–7] and biosorbents.[8–12] One of the present authors developed a new adsorbent, polyvinyl polyacrylate (PVPA), an ester of polyvinyl alcohol (PVA) and polyacrylic acid (PAA), which has a high ability to adsorb uranium from seawater.[13]

Both PVA and PAA have a spiral structure in aqueous solution.[14,15] In the PAA–Cu(II) solution, Cu(II) ion is free below pH 4, and forms dimer in the pH range from 4 to 9. Above pH 9, Cu(II) hydroxide incorporate into the spiral structure of PAA and are held in the structure by hydrophobic interaction, so called soft interaction.[15] On the other hand, in the PVA–Cu(II) solution, Cu(II) ion is free below pH 6, and Cu(II) hydroxide incorporate into the spiral structure of PVA above

pH 6 in similar as PAA–Cu(II) solution.[14] Present adsorbent, PVPA, being prepared by the esterification of PVA and PAA, have a high ability to adsorb heavy metal ions, such as uranium and copper.[13] It is very interesting that above-mentioned characteristics of each monomer affect the mechanism of heavy metal adsorption by the new adsorbent, PVPA. In this article, therefore, the aspects of copper adsorption by PVPA are examined, and its adsorption mechanism is also discussed by the analysis of magnetic properties of Cu(II) ion in the adsorbent.

EXPERIMENTAL

Reagents

Polyvinylalcohol (PVA, molecular weight 88,000) and 25% of polyacrylic acid (PAA) solution were obtained from Wako Pure Chemicals Industries (Osaka, Japan), Arsenazo III from DOJINDO Laboratories (Kumamoto, Japan), uranyl nitrate hexahydrate, UO_2 $(NO_3)_2 \cdot 6H_2O$, from Merck Chemical Industries (Darmstadt, Germany), and other chemicals used in this study were obtained from Nacarai Tesque (Kyoto, Japan).

Preparation of polyvinyl polyacrylate

Polyvinyl polyacrylate (PVPA) was prepared according to the method described previously.[13] PVA (50 g)

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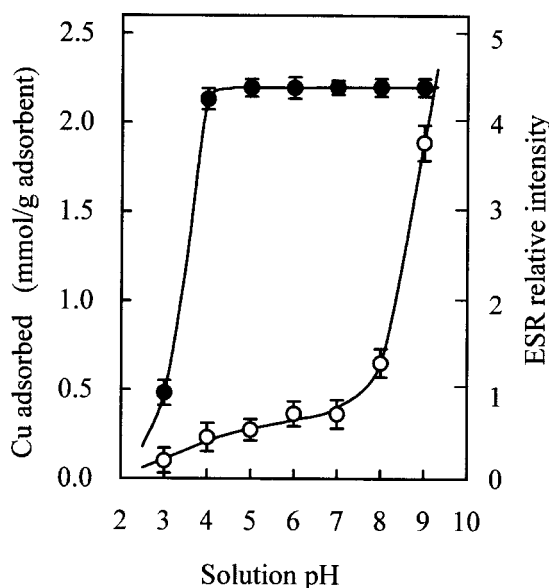
Figure 1 Effect of solution pH on the adsorption of copper by PVPA (●) and the ESR signal intensity (○).

were dissolved in 375 mL of deionized water. 100 g of 25% PAA solution and 210 mL of concentrated sulfuric acid were added to the PVA solution. The mixture solution was made up to 1000 mL with deionized water, and then reacted at 40°C for 24 h. After adding the reaction mixture to acetone, the resulting precipitate, the polymer ester, was collected and washed thoroughly with deionized water. The adsorbents with particle size from 32 to 60 mesh were used for the adsorption experiments. The amounts of carboxyl group in the resulted polymer ester (PVPA) was determined to be 6.44×10^{-3} mol g^{-1} by the conductmetric titration.[13,16] These results indicated that about 7% of carboxyl group in PAA were used for the esterification.

Adsorption experiments

Copper adsorption experiments by PVPA were conducted in 100 mL of the solution containing $CuSO_4 \cdot 5H_2O$ at 30°C using magnetic stirrer (250 rpm). After copper adsorption, the adsorbent was filtered off using a membrane filter (0.45 μm). Resultant adsorbents were air-dried and used for ESR measurements. The experiment for the pH effect was conducted by suspending 20 mg of the adsorbent in the solution containing 0.2 mM of Cu(II) ion at pH range 3–9 for 1 h. The pH of the solution was adjusted to desired values with $0.1N$ HCl and $0.1N$ NaOH. The time course experiment was conducted by suspending 20 mg of the adsorbent in the solution containing 0.2 mM of Cu(II) at pH 5 for 0.5–14 h. The copper concentration effect was conducted by suspending 20 mg of the adsorbent in the solution containing 0.2–1 mM of copper at pH 5 for 1 h.

The adsorption experiments were conducted three times and averaged.

Uranium adsorption experiments by PVPA were conducted as similar manner as copper adsorption using $UO_2(NO_3)_2 \cdot 6H_2O$.

Measurements

The metal contents in the supernatant were measured with the inductively coupled plasma quantometer (Shimadzu ICPQ-1000II). The amounts of metal adsorbed by PVPA was estimated as follows: $Q = (Cini - Cres) \times W/m$; where Cini and Cres are the initial and the residual metal concentrations; W, the volume of the metal solution; and m, the weight of adsorbent used.

Electron spin resonance measurements were conducted as follows: 5 mg of the freeze-dried powder samples were put into a quartz sample tube of 5 mm diameter, and recorded their ESR spectra using X-band ESR spectrometer (JES TE-100, JEOL, Tokyo, Japan) controlled by an WIN-RAD ESR data analyzer (Radical Research, Tokyo, Japan). The ordinal measurements conditions were as follows: microwave frequency, 9.44 GHz; magnetic field, 310 mT; field amplitude, ± 75 mT; field modulation, 100 kHz; modulation width, 0.32 mT; microwave power 5 mW, and the time constant, 0.1 s. For the wide magnetic range measurements, ESR spectra were recorded under the conditions of magnetic field, 250 mT; field amplitude, ± 250 mT, and modulation width, 1 mT.

Magnetic susceptibility data were collected in the temperature range 2–300 K in an applied field 0.6 T using a magnetometer (Model MPMS2, Quantum Design, Japan, Tokyo).

RESULTS AND DISCUSSION

Aspects of copper adsorption by PVPA

PVPA can adsorb copper highly effectively from aqueous solutions containing $CuSO_4$. As shown in Figure 1, the amounts of copper adsorbed by PVPA was increased from pH 3 to 4, and almost constant (2.2 mmol g^{-1}) above pH 4. However, the relative intensity of ESR signal gradually increased from pH 3 to 7, following its sudden increase above pH 7. The

TABLE I
Kinetic and Adsorption Isotherm Parameters of Langmuir Equation for PVPA-Metal Adsorption

Constants	Cu	U
Time course		
Qe (mmol g^{-1})	0.728	1.04
j (h^{-1})	0.97	2.92
Adsorption isotherm		
Qm (mmol g^{-1})	4.17	1.77
k (mM^{-1})	0.00273	0.0381
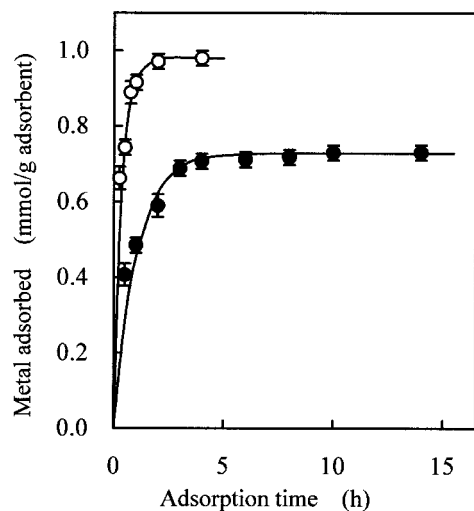
Figure 2 Time course of copper (●) and uranium (○) adsorptions by PVPA. Solid lines indicate the Langmuir model for the pseudofirst-order kinetics.

color of the resin which adsorbed copper shows blue–green in the pH range from 4 to 7, while light blue above pH 8. These results suggested that PVPA adsorbed copper through different mechanisms between that below pH 7 and above pH 8. In the case of uranium adsorption by PVPA from seawater, stable complex ion, $UO_2(CO_3)_3^{4-}$, prevented the uranium adsorption.[13] On the other hand, in the present case, there exists no dominant Cu(II) complex ion, preventing the copper adsorption, in the solution.

Copper adsorption by PVPA was reached to plateau within 4 h after adsorption was started, while uranium adsorption was reached within 2 h. The results were fitted by a time-dependent adsorption equation according to the Langmuir model for the pseudo-first-order kinetics,[17]

$$Q = Qe[1 - \exp(-j\,t)] \qquad j = ka + kd \qquad (1)$$

where Qe is the equilibrium adsorption amounts; ka, the adsorption rate constant; and kd is the desorption rate constant.

The estimated constants, Qe and j, are listed in Table I. Simulated results using these values are shown in Figure 2. The j values of Cu(II) is about one-third of that of uranium (Table I).

As shown in Figure 3, both copper and uranium adsorptions by PVPA were obeyed the Langmuir equilibrium isotherm.[17]

$$Qe = Qm \cdot k \cdot Ce/(1 + k \cdot Ce) \qquad (2)$$

where Qe is the equilibrium adsorption amounts; Qm, the maximum adsorption amount; Ce, the residual copper concentration; and k is the constant.

The estimated constants, Qm and k, are also listed in Table I. Simulated results using these values are shown in Figure 3. When one carboxyl group will couple with one Cu(II) ion, about 65% of free carboxyl ones coupled with Cu(II) ion. The amounts of uranium adsorbed by PVPA in the similar conditions are smaller than that of Cu(II). The ionic radius of Cu(II) ion is 72 pm,[18] while O=U=O length of uranyl ion is 175 pm.[19] These results suggested that Cu(II) ion can couple with carboxyl groups both surface and inside of PVPA, while uranyl ion can couple only functional groups on the surface. These consideration will be assisted by the faster adsorption rate mentioned above. The amounts of uranium adsorbed by PVPA from seawater were up to be 0.38 mmol g^{-1}.[13] In this case, carbonate ion in seawater kept the uranium adsorption in very low level.

Electron paramagnetic resonance study of Cu(II) adsorbed on PVPA

The ESR spectrum of Cu(II) ion is an axial type, having a major absorption to higher field at $g_{\perp}$ and lesser absorption to lower field at $g_{//}$ with four lines of $|A_{//}|$, which indicates that Cu(II) ion in the adsorbent will be under a ligand field with tetragonally distorted octahedral symmetry (Fig. 4). The ESR parameters of Cu(II) ion in PVPA are $g_{//}$ = 2.361, $g_{\perp}$ = 2.057, $|A_{//}|$ = 14.0 m cm^{-1} (pH 5), and $g_{//}$ = 2.329, $g_{\perp}$ = 2.058, $|A_{//}|$ = 16.2 m cm^{-1}, $|A_{\perp}|$ = 2.7 m cm^{-1} (pH 9). These values suggested that Cu(II) ion in PVPA will be surrounded by ligands with four oxygen atoms.[20] A simple spin Hamiltonian assuming an axial field and taking account only
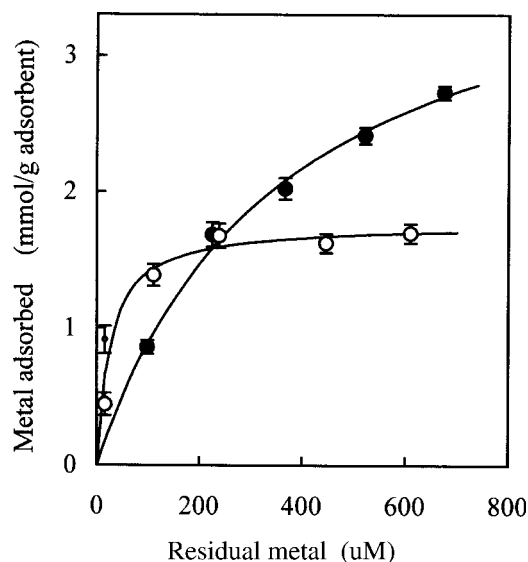
Figure 3 Adsorption isotherm of copper (●) and uranium (○) on PVPA. Solid lines indicate the Langmuir isotherm.
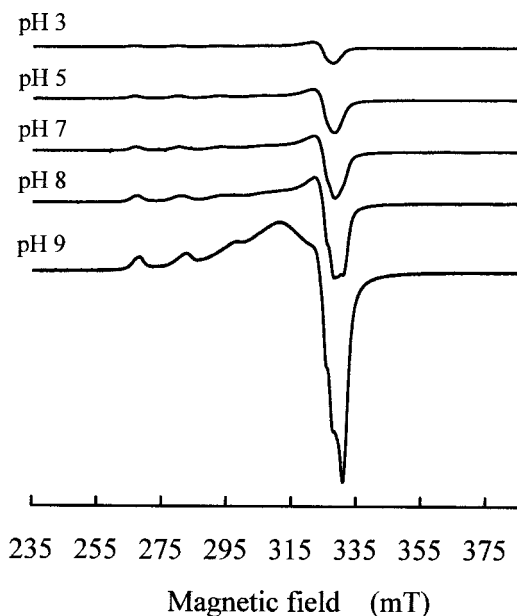
Figure 4 ESR spectra of Cu(II) ion in PVPA at pH 3 (a), 5 (b), 7 (c), 8 (d), and 9 (e).

the Zeeman term with an anisotropy in g ($g_{//}$, $g_\perp$), and the hyperfine term with its anisotropies ($A_{//}$, $A_\perp$) is as follows:[8,21,22]

$$H = g_{//}\mu_B HzSz + g_\perp\mu_B(HxSx + HySy) \\ + A_{//}SzIz + A_\perp(SxIx + SyIy) \quad (3)$$

Hx, Hy, Hz: magnetic field components, Sx, Sy, Sz: electron spin components, Ix, Iy, Iz: nuclear spin components, μ_B: the Bohr magneton. The d-electron density of Cu(II) ion is[8,21,22]

$$\alpha^2 = -(A_{//}/P) + (g_{//} - ge) + (3/7)(g_\perp - ge) + P \quad (4)$$

where P is the dipole term (3.6×10^{-2} cm^{-1} for free Cu(II)).

When $\alpha^2 = 1$, the coupling between Cu(II) ion and ligand is ionic, and $\alpha^2 = 0.5$, that is covalent. In ordinal Cu(II) complexes, α^2 is in the range of 0.7–0.9. The α^2 values of Cu(II) ion in PVPA are 0.81 (pH 5) and 0.84 (pH 9), respectively, which indicated that the coupling between Cu(II) ion and oxygen ligand atom at pH 9 was little bit ionic than that at pH 5.

The wide range ESR measurements were conducted in the magnetic field range from 0 to 500 mT. As shown in Figure 5, the adsorbent adsorbed copper at pH 5 indicated a couple of small peaks above and below the main peak. These peaks, being found in PVPA containing any amounts of Cu(II) ion examined, suggested the existence of Cu(II)–Cu(II) pairs

in the adsorbent. The following Hamiltonian can be used for the analysis of the spectrum.[21]

$$H = g_{//}\mu_B HzSz + g_\perp\mu_B(HxSx + HySy) \\ + DSz^2 + E(Sx^2 - Sy^2) \quad (5)$$

where D, E are the zero-field splitting parameters.

In the present spectrum [Fig. 5(a)], $D \cong 0.39$ and $E \cong 0$ cm^{-1}, being similar value ($D = 0.35–0.38$ cm^{-1}) estimated by Yokoi et al.[15] On the other hand, any D-splitting was not observed in ESR spectrum of the adsorbent adsorbed Cu(II) at pH 9 [Fig. 5(b)]. These results suggested that Cu(II) form dimers in PVPA adsorbed Cu(II) at pH 5. Similar D value was reported by Bleaney and Bowers in their early excellent work for Cu(II) acetate monohydrate ($D = 0.34$ and $E = 0.01$ cm^{-1}).[23] As reported by Pineri et al.,[24] and by one of the present authors,[25] ionic clusters, such as dimers, can easily form in polymers containing carboxylic acid group. In the present resin, PVPA, also contains carboxylic acid group, which is possible to form dimers.

Paramagnetic susceptibilities of Cu(II)–PVPA

The paramagnetic susceptibility (χ_m) of PVPA adsorbed Cu(II) ion at pH 9 obeyed the Curie' law in the temperature range from 2 to 300 K and its magnetic moments was 1.64 μ_B (Fig. 6). These results indicate that Cu(II) ion in the adsorbent at pH 9 is an isolated spin having little interaction with neighbored Cu(II) ion. In contrast, that at pH 5 had a small magnetic moment (about 0.2 μ_B) at room tem-
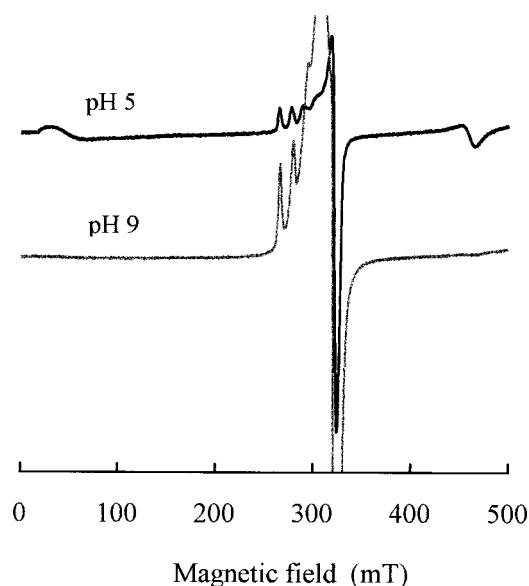
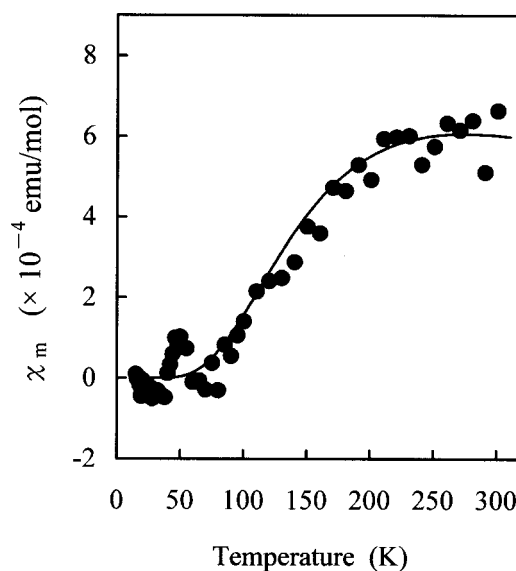**Figure 5** Wide range ESR spectra of Cu(II) ion in PVPA at pH 5 (a) and 9 (b).
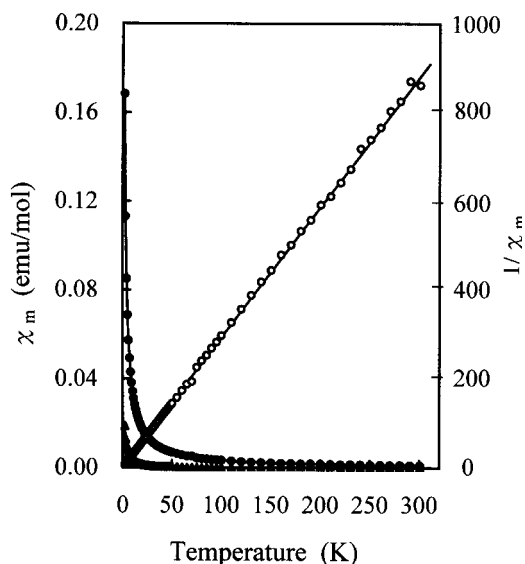
Figure 6 Paramagnetic susceptibilities (χ_m) (●, pH 5; ▲, pH 9) and its inverse ($1\;\chi_m^{-1}$) (○, pH 5) of Cu(II) ion in PVPA.

Figure 7 Paramagnetic susceptibilities of Cu(II) dimer in PVPA. Solid line indicates the paramagnetic susceptibility calculated using dimer model.

perature and very small paramagnetism in lower temperature (about 12% of that at pH 9). For further analysis, χ_m of PVPA adsorbed Cu(II) ion at pH 5 was redrawn in Figure 8, after taking away the contribution of the paramagnetic impurity, $0.116 \times \chi_m$ (pH 9), and the diamagnetic terms (5×10^{-4} emu mol^{-1}). Resulted paramagnetic susceptibility gradually increased with temperature (Fig. 7). Theoretical paramagnetic susceptibility of dimer of Heisenberg spin with negative spin exchange interaction ($J < 0$) was as follows:[26]

$$\chi_m = Ng^2\mu_B^2 S(S + 1)/kT(3 + e^{2|J|/kT}) \qquad (6)$$

where N is the Avogadro's number; g, g-factor; μ_B, the Bohr magneton; S, electron spin; J, exchange integral; k, the Boltzmann constant, T, is the absolute temperature.

In the present case, $S = 1$. The calculation data with $|J|\;k^{-1} = 220$ K indicated fairly good agreement with the experimental ones (Fig. 8). Foex, Karantissis and Perakis gave $|J|\;k^{-1} = 310$ K for Cu(II) acetate monohydrate, in which the Cu(II)—Cu(II) distance was given as 2.64 Å.[23] As the exchange integral, $|J|$, is related to the distance of two interacting metal ions,[27] the Cu(II)—Cu(II) distance in PVPA was roughly estimated to be 3–4 Å. These results indicated that about 88% of Cu(II) ion adsorbed on PVPA (pH 5) formed dimers, being corresponded to the results obtained in ESR measurements. In the previous section (Aspects of Copper Adsorption by PVPA), it was assumed that only 65% of free carboxyl groups were estimated to be used for copper adsorption.

Assumed structure of Cu(II) dimer in PVPA

From the results for ESR and paramagnetic susceptibility analyses, most of Cu(II) ion adsorbed in PVPA at pH 5 formed dimer. As the present D value (0.39 cm^{-1}) was similar as that of Cu(II)-acetate (0.345 cm^{-1}) rather than that of Cu(II)-formate (0.143 cm^{-1}),[25] the Cu(II) dimer structure in PVPA should be assumed similar as that in Cu(II) acetate (Fig. 8).[24,28] As shown in Figure 8(a), Cu(II) ion in the dimer has a possibility of having extra ligand molecules (H_2O). On the other hand, at pH 9, as shown in Figure 8(b), those water molecules should
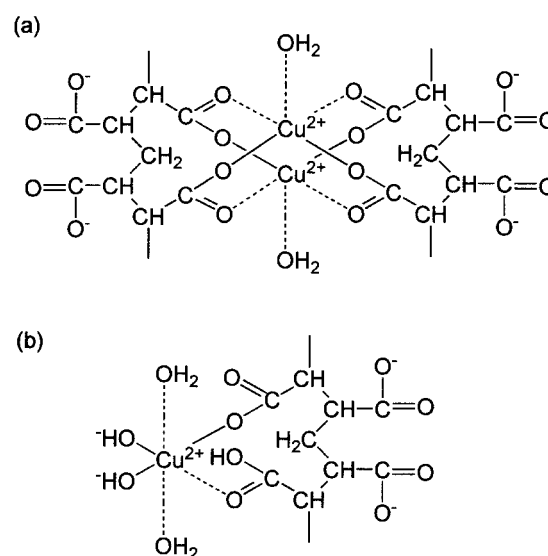
Figure 8 Assumed structures of Cu(II) dimer in PVPA at pH 5 (a) and Cu(II) monomer in PVPA at pH 9 (b).

be replaced by hydroxide ion, being more stronger ligand than water against for the Cu(II) dimer formation through carboxyl group, which is supported by the α^2 values estimated from ESR parameters.

CONCLUSIONS

The copper adsorption by PVPA was reached to plateau within 4 h and obeyed Langmuir adsorption isotherm with the maximum adsorption amounts of 4.17 mmol g^{-1} adsorbent. Its ESR and magnetic studies gave the following information: Cu(II) ion in PVPA are axial type with tetragonally distorted octahedral symmetry. Copper(II) ion forms dimer in PVPA at pH 4–7, while it forms isolated complex ion above pH 8. The Cu(II)–Cu(II) distance of dimer in PVPA was roughly estimated to be 3–4 Å, and should be assumed similar as that in Cu(II) acetate.

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