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Adsorptive removal of vinyl polymer tanning agents from aqueous solution using wastewater activated sludge

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ABSTRACT

Adsorptive studies were carried out on four synthetic vinyl polymer tanning agents removal from aqueous phase onto wastewater activated sludge (AS). Batch experiments investigated the effects of contact time, dosage of adsorbate, extracellular polymeric substances (EPS), coexisted cations, and physical property of sludge flocs on the four vinyl polymers removal by AS to evaluate the kinetics, isotherms, and mechanisms. Almost 96% of polydiallyldimethylammonium chloride-acrylic-acrylamide (PDM-AA-AM), 90% of polydiallyldimethylammonium chloride-acrylic (PDM-AA), 82% of polydiallyldimethylammonium chloride-acrylic-acrylamide-hydroxyethyl acrylate (PDM-AA-AM-HEA), and 56% of polydiallyldimethylammonium chloride (PDM) were removed from aqueous solutions. The kinetics process of adsorption can be described by the pseudo-second-order kinetic equation and the adsorption isotherms fitted to the Langmuir model very well. The adsorption capacity increases with the increase in initial vinyl polymers concentration. Coexisted cations (Ca^{2+}, Na^{+}) in aqueous solution restrained vinyl polymers adsorption on AS. The presence of Cr^{3+} ions slightly improved the PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA removal, whereas retarded the PDM removal in some extent. AS are more effective than inactivated sludge in the removal of vinyl polymers. All the four vinyl polymers showed a decrease in the degree of removal when EPS was partial extracted from the biomass. The adsorption mechanisms of AS for vinyl polymers included hydrophobic interaction, surface binding, and electrostatic force. Surface binding may play a major role in PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA adsorption, while electrostatic interaction may play a major role in PDM removal. This study provided strong evidence that AS can be employed for an effective solution for vinyl polymers syntans removal.

Keywords: Vinyl polymers; Activated sludge; Adsorption

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1. Introduction

Tanning is a process by which animal hides and skin are converted into a resistant, durable material that is useful for a wide range of applications. The collagen of various operations from the skin reacts with chemical materials containing vegetable tanning or chromium [1–3]. More than 90% of global leather production is through chrome-tanning process currently. Conventional chrome tanning in leather processing discharges a very large amount of chromium, which leads to significant material loss and serious environmental pollution [4]. Since the environmental protection has now become a global issue, a cleaner and greener technology is warranted for the abatement of the industrial pollution [5]. Tanners are looking for new product–process innovations towards low waste and high exhaust chrome tanning [6]. In fact, organic tanning agents such as syntans have been indispensably used in pretanning, tanning, and retanning processes since the utilization of them can remarkably improve the quality of leathers and would result in less time for its degradation or composting [7].

Therefore, our research group has been engaging in the study on environmental friendliness of leather chemicals. In our previous research [8–11], polydiallyldimethylammonium chloride (PDM) was synthesized via solution polymerization, polydiallyldimethylammonium chloride-acrylic (PDM-AA), polydiallyldimethylammonium chloride-acrylic-acrylamide (PDM-AA-AM), and polydiallyldimethylammonium chloride-acrylic-acrylamide-hydroxyethyl acrylate (PDM-AA-AM-HEA) were synthesized using PDM, acrylic acid, acrylamide (AM), 2-hydroxyethyl acrylate (HEA) as raw materials, and the four PDM vinyl polymers associated with chromate tannage were applied in leather making process separately. In contrast to traditional chrome tanned process, the application results showed the tanning properties were improved.

PDM and its copolymers have been extensively used in oilfields, papermaking, water treatment, leather making, textile printing and dyeing, medicine, cosmetics etc. [12–15]. For example, in leather making, the underused vinyl polymers inevitably discharged into wastewaters and leads to many problems associated with environmental pollution and wastewater treatment. The potential ecological risk of the vinyl polymers may vary greatly with its chemical composition and molecular structure. At present, many processes were carried out to treat tannery effluent such as biological process [16–17], oxidation process [18–19], and membrane filtration [20]. Adsorption processes to sludge are of special interest because the excess sludge extraction represents an important removal pathway and adsorption is often the first stage in biological [21]. In consideration of the potential environmental impact of vinyl polymers, it is necessary to evaluate vinyl polymers entering wastewater treatment plants, and methods are needed for the industry to assess the potential removal of them during wastewater treatment.

This is the first study to determine whether the four synthetic vinyl polymers tanning agents can be effectively removed by activated sludge (AS) biomass from aquatic solution and to provide clearer insight into the individual adsorption removal mechanisms. The removal of PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA in AS process were investigated through kinetic and isothermal tests. The dynamic behaviors of the adsorption were analyzed by the effects of contact time, initial adsorbate concentration, coexisted inorganic ions, extracellular polymeric substances (EPS), and textural properties of AS to further elucidate adsorption mechanisms. The accomplishment of these objectives will exploit potential pathways for evaluating different types of vinyl polymers syntans removal from wastewater and have important implications for the transformation and fate of vinyl polymers in the environment.

2. Materials and methods

2.1. Materials and analytical methods

Vinyl polymers syntans in the current investigation were provided by Key Laboratory of Chemistry and Technology for Light Chemical Industry of Ministry of Education and prepared as described in the literature [8–11]. Sodium azide (NaN_3) was purchased from Zhengzhou Paini Chemicals Co., Ltd. Other chemicals were purchased from Xi’an Chemical Co., China. All the other chemicals were of the analytical grade and used without further purification.

The AS was collected from a local municipal wastewater treatment plant (Xi’an, China). During the steady state, concentration of mixed liquid suspended solids (MLSS) was 4.2 g/L, pH 7.1. The AS was fed with nutrients consisting of glucose, NH_4Cl, and KH_2PO_4. This AS solution was employed as adsorbent and it was continuously aerated until use.

The concentrations of vinyl polymers syntans were expressed as chemical oxygen demand (COD). The COD concentration was determined using standard method and the absorbance was analyzed by a UV spectrophotometer (UV2300). The total organic carbon (TOC) was measured by TOC analyzer (elemental Y-Liqui TOC 35091009). Dehydrogenase concentration was measured using TTC methods. The surface morphologies of AS and inactivated sludge (IAS) were characterized by a scanning electron photomicrograph (SEM, Hitachi–S4800). FT-IR analysis of AS and IAS were carried out by a Fourier transform infrared spectrometer (Vector-22, Bruker). The samples were prepared by usual KBr pellet method. The textural parameters of AS and IAS were observed using brightfield by an epifluorescence microscope (OPTPro BK-FL). Zeta potentials were measured using a Malvern Zeta Potential Analyzer. The surface areas of AS and IAS were characterized by Quantachrome NovaWin instruments with N_2 adsorption.

2.2. Adsorption experiments

Adsorption experiments with AS and IAS were performed to investigate the effect of surface properties of the adsorbent. To make the AS inactivated, 1% NaN_3 was added to the AS as described by the previous studies [22]. After the addition of NaN_3, the microbial respiration in the water was found to be zero. This suggested that the addition of NaN_3 significantly inhibited microbial activities and also indicated that the biological activity of the sludge was completely inhibited by NaN_3.

For the adsorption kinetics, AS was added to a 250 mL conical flask at MLSS concentration 1,000 mg/L and receiving of vinyl polymer syntan with concentration approximately 500 mg/L, and the mixture was adjusted to pH 6.5 using 0.1 M HCl or 0.1 M NaOH. The flasks were placed in an incubator and operated at 120 rpm and 25˚C. Samples were withdrawn at regular time intervals and the solutions were filtrated in order to remove any adsorbent particles for COD determination. With respect to adsorption isotherms, similar procedures were used with initial vinyl polymers concentrations from 100 to 1,000 mg/L. The MLSS concentrations of sludge were 1,000 mg/L in all adsorption experiments. A blank test which contained only the absorbent and distilled water was run. The adsorption amounts of syntans were calculated according to Eq. (1) [23]:

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where q_e (mg/g) is the amount of syntans adsorbed at equilibrium, C_0 is the initial concentration of syntans (mg/L), C_e is the equilibrium syntans concentration (mg/L), V is the volume of syntans solution (L), and M is the adsorbent mass (g).

2.3. Effect of EPS, Cr^{3+}, Ca^{2+}, and Na^+ on adsorption

EPS-extracted biomass was processed as formaldehyde plus NaOH method [24]. The centrifuged supernatant containing separated and suspended EPS was discarded. Extracted EPS was characterized by dissolved organic carbon (DOC) analysis. DOC was measured by TOC analyzer. EPS-extracted biomass for this experiment had 25% reduction in DOC. The EPS-extracted AS biomass was stored at 4˚C until used in experiments. Effects of EPS, Cr^{3+}, Ca^{2+}, and Na^+ on adsorption were the same as the kinetics adsorption procedures. In the experiment utilizing 1,000 mg/L MLSS of biomass, Cr^{3+}, Ca^{2+}, and Na^+ were added to the solution with its concentration about 20 mg/L, 25, and 50 mmol/L, respectively. Na^+ or Ca^{2+} was added as chloride salts. AS suspensions were prepared at 1,000 mg/L containing different Na^+ or Ca^{2+} concentrations (1–100 mmol/L) for zeta potential measuring.

3. Results and discussion

3.1. Adsorption kinetics

The effect of contact time on the adsorption of PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA is shown in Fig. 1. As can be seen from Fig. 1, the adsorption increases rapidly at the beginning and then becomes slower until the attainment of equilibrium. Since the equilibrium is reached nearly within 30 min for all the adsorbate tested, subsequent adsorption experiments were performed for 30 min. The removal of all these vinyl polymers 96% of PDM-AA-AM, 90% of PDM-AA, 82% of PDM-AA-AM-HEA, and 56% of PDM were adsorbed on the AS. On the basis of these results, the adsorption removal capacity

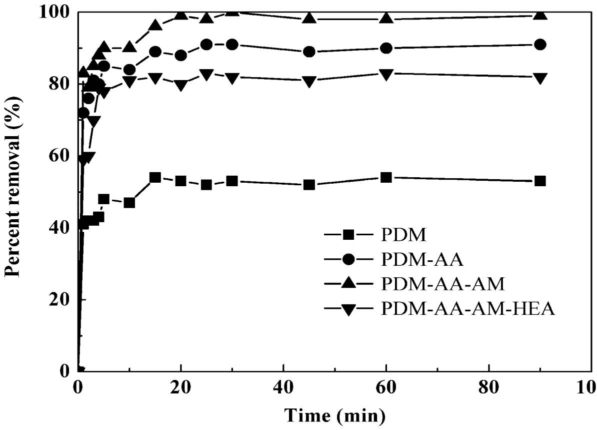

Fig. 1. Percent removal of four types of vinyl polymers from the liquid phase after exposure to 1,000 mg/L MLSS of whole wastewater AS biomass.

for different vinyl polymers by AS was in order PDM-AA-AM > PDM-AA > PDM-AA-AM-HEA > PDM.

In order to investigate the mechanisms of adsorption, kinetic models have been used to test experimental data. The pseudo-second-order model (Eq. (2)) was used [25].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where q_e (mg/g) is the adsorption amount, q_t (mg/g) is the adsorption amount at time t (min), k_2 (g/(mg min)) is the constant of pseudo-second-order adsorption rate.

Parameters based on pseudo-second-order kinetic equation are given in Table 1. The relative coefficients (R^2) values are in the range of 0.995–0.999, and the calculated equilibrium adsorption capacity ($q_{e,cal}$) are closer to the experiment data ($q_{e,exp}$). On the basis of these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the adsorption of vinyl polymers onto AS.

3.2. Adsorption isotherms

In order to determine the vinyl polymers adsorption characteristics and to evaluate the applicability of this adsorption process, Langmuir and Freundlich isotherm models were applied to analyze the experimental data [26].

Langmuir equation:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \tag{3}$$

Freundlich equation:

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

where q_e (mg/g) is the equilibrium adsorption amount, C_e (mg/L) is the equilibrium concentration, q_m (mg/g) is the maximum adsorption capacity corresponding to complete monolayer coverage, K_L (L/mg) is the equilibrium constant related to the energy of adsorption, K_F is Freundlich constant ($\mathrm{mg}^{1-1/n}\,\mathrm{L}^{1/n}/\mathrm{g}$), and $1/n$ is the heterogeneity factor.

The corresponding parameters for vinyl polymers adsorption isotherms based on Langmuir and Freundlich equations are presented in Table 2. The fitting results showed that the relative coefficient (R^2) of Langmuir model was higher than that of Freundlich model, indicating that vinyl polymers adsorption onto AS can be better fitted to Langmuir model than Freundlich model. The maximum adsorption capacity (q_m) were 384 mg/g for PDM, 909 mg/g for PDM-AA, 1,128 mg/g for PDM-AA-AM, and 769 mg/g for PDM-AA-AM-HEA, respectively. According to the Langmuir parameters, the theoretical maximum adsorption capacity for AS in this study follows the order PDM-AA-AM > PDM-AA > PDM-AA-AM-

Table 1
Pseudo-second-order kinetic model parameters of vinyl polymers onto AS

Vinyl polymers	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	K (g/(mg min^{-1}))	R^2
PDM	279	270	2.52×10^{-3}	0.995
PDM-AA	448	454	5.38×10^{-3}	0.999
PDM-AA-AM	482	490	4.00×10^{-3}	0.999
PDM-AA-AM-HEA	412	424	3.02×10^{-3}	0.999

Table 2
Langmuir and Freundlich model parameters of vinyl polymers onto AS

	Langmuir model parameters			Freundlich model parameters		
Vinyl polymers	q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
PDM	384	1.04×10^{-4}	0.994	16.420	2.486	0.930
PDM-AA	909	9.71×10^{-4}	0.995	4.039	1.190	0.961
PDM-AA-AM	1,128	2.33×10^{-3}	0.984	17.037	1.390	0.967
PDM-AA-AM-HEA	769	4.71×10^{-3}	0.982	16.680	1.450	0.957

HEA > PDM. The adsorption capacity of the AS for PDM is the lowest among the four polymers. This might be mainly due to PDM is a widely used antibacterial agent [27], the addition of PDM inhibited the activities of microorganisms in adsorption processes.

Separation factor constant (R_L) is the characteristic parameter of Langmuir isotherm, which was widely used to describe the adsorption intensity of a surface. R_L is defined as [28]:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

where C_0 (mg/L) is the initial concentration of vinyl polymers and K_L is the Langmuir constant described above. Adsorption process with $0 < R_L < 1$ is favorable, and that with $R_L > 1$ is unfavorable. When the initial concentration of each vinyl polymers was in the range of 100 to 1,000 mg/L at 25℃, the adsorption intensity R_L of PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA ranged from 0.49 to 0.088, from 0.91 to 0.53, from 0.83 to 0.30, and from 0.68 to 0.17, respectively. These parameters ($0 < R_L < 1$) indicate that the vinyl polymers adsorption on AS are favorable.

The R^2 values indicate that the adsorption data also followed the Freundlich isotherm well. It has been shown that n values between 1 and 10 represent good adsorption potential of the adsorbent [29]. The Freundlich constant n ranged from 1.19 to 2.48, indicating that the adsorption of vinyl polymers onto AS was favorable under the study conditions. From the results, the equilibrium adsorption data present good agreement with both Langmuir and Freundlich models. This may be attributed to both the homogeneous and heterogeneous distributions on the adsorption sites on the surface of the AS. Therefore, the adsorption properties of the vinyl polymers are likely to involve more than one mechanism [25].

3.3. Effect of initial concentration on the removal of vinyl polymers

Five different initial concentrations (100, 300, 500, 700, and 900 mg/L) of vinyl polymers were studied for their effect on the adsorption capacity of AS are illustrated in Fig. 2. The equilibrium adsorption capacity of PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA with initial vinyl polymers concentrations at 100 mg/L were found as 68, 87, 96, and 76 mg/g, respectively. At higher initial vinyl polymers concentrations (900 mg/L), the equilibrium adsorption capacity of PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA were 365, 611, 645, and 532 mg/g, respectively. The results show that at higher initial concentrations of vinyl polymers, the removal of vinyl polymers at equilibrium on AS are higher. This may be due to initial concentration provides an important driving force to overcome all mass transfer resistances of the vinyl polymers between the aqueous and solid phases [30].

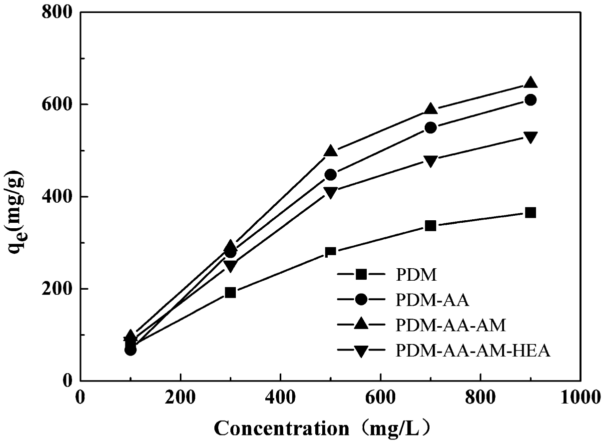

Fig. 2. Effect of initial vinyl polymers concentration on adsorption by AS.

3.4. Comparison of vinyl polymers removal with AS and IAS

Adsorption tests with AS and IAS were performed with MLSS concentration 1,000 mg/l. Figs. 1 and 3

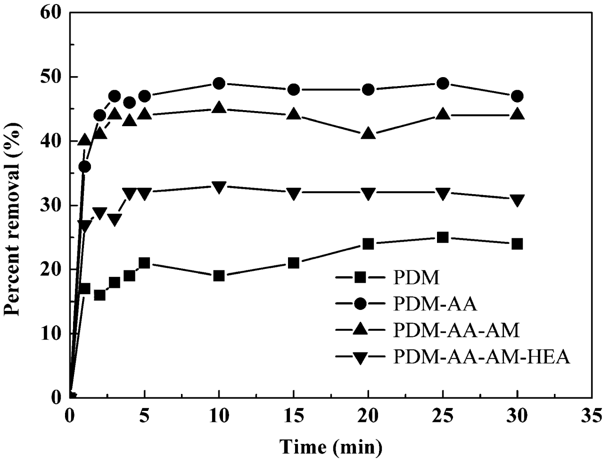

Fig. 3. Percent removal of four types of vinyl polymers from the liquid phase after exposure to 1,000 mg/L MLSS of whole wastewater IAS biomass.

show the percent removal of vinyl polymers for the two adsorbent agents separately. The percent removals by AS were 96, 90, 82, and 56% for the PDM-AA-AM, PDM-AA, PDM-AA-AM-HEA, and PDM, respectively. Whereas, for the IAS, the percent removals obtained from the experiment were 50, 45, 33, and 23% for the PDM-AA, PDM-AA-AM, PDM-AA-AM-HEA, and PDM, respectively. AS showed a significantly higher capacity for the removal of vinyl polymers. Studies showed that the adsorption experiments were performed with AS and IAS in order to distinguish pure adsorption processes and biosorption [21]. Interestingly, in this study, the adsorption processes were very quick and reached equilibrium within 30 min. The impacts of biodegradation were negligible. Thus, vinyl polymers adsorbed less to IAS than to AS might be due to the different surface properties of the two sludges.

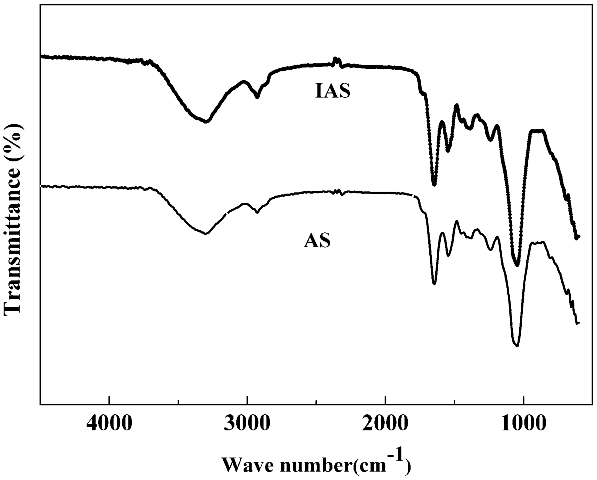

Fig. 4. FT-IR spectra of AS and IAS.

The FT-IR analysis of AS and IAS is given in Fig. 4. The results show that the two sludges have the same functional groups. The band at 3,400 cm^{-1} is O–H stretching of AS polymeric compounds. The peaks at 2,943, 1,770 and 1,674 cm^{-1} is ascribed to C–CH_3, –COOH, and –$CONH_2$ stretching vibration, respectively. The band at 1,430 cm^{-1} is of phenolic O–H and C–O stretching. The band at 1,237 is vibration of C–N– amines. The 1,082 band is vibration of C–O–C polysaccharides. FT-IR result showed that sludge has characteristic bands of proteins, lipids, polymeric compounds, and carboxylic acid groups.

Adsorptive properties of organic chemicals on adsorbents are generally determined by their physical and chemical interaction [31]. Due to the similarity in

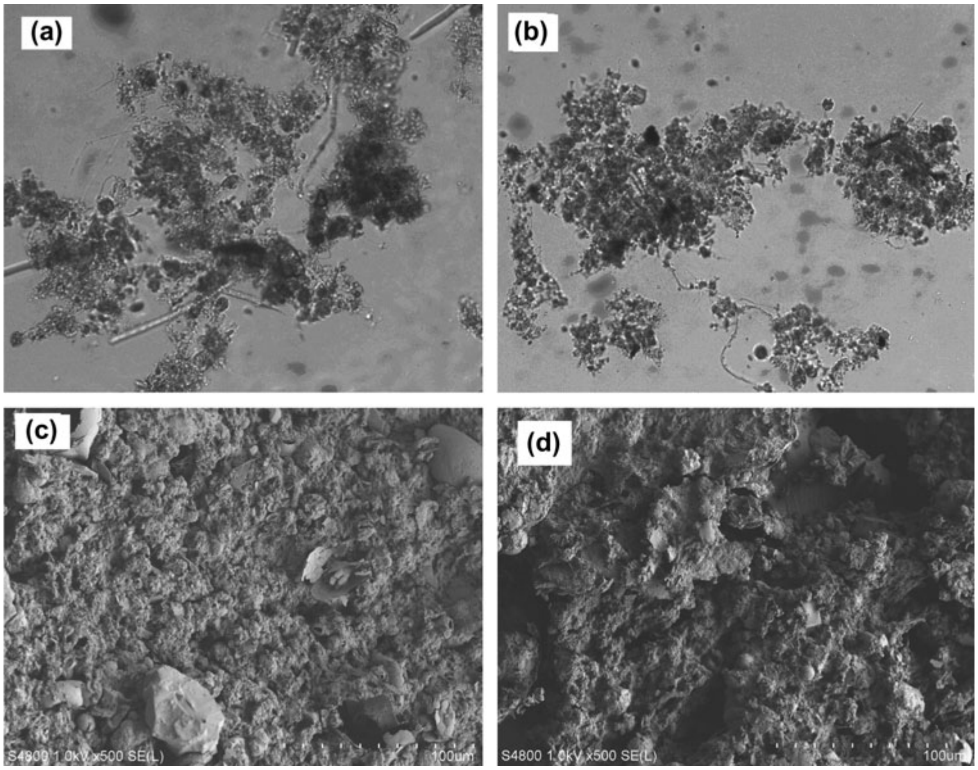

Fig. 5. Brightfield images of AS (a) and IAS (b). SEM photographs of AS (c) and IAS (d).

surface functional groups of the two sludges, surface area and pore volume may play a fundamental role in adsorption process. The BET surface area of AS and IAS were 106 and 15.8 m^2/g, respectively, indicating that the AS has more micropores and bigger surface areas than IAS. AS and IAS were qualitatively compared using brightfield images and SEM (Fig. 5). As can be seen from the brightfield images, the AS (Fig. 5(a)) has visible and clear surface morphology such as filaments and spheres of different sizes and loose volume. However, IAS (Fig. 5(b)) appears as amorphous clumps of matter and lacks distinct features. Compared with the SEM images of bare AS and IAS, the chemical activation was done on AS that has resulted in appearance of noticeably more pores than that on IAS. It could be observed in the experiments that AS with NaN_3 addition lead to a smaller floc size, which is in accordance with former study [32]. The AS has more pores and more surface area than IAS and molecules easily found the active adsorption sites [33], which is why the AS resulted in greater percent removal than IAS.

3.5. Comparison of adsorption of different types of vinyl polymers

Vinyl polymers adsorption experiments performed on AS and IAS reveal a removal sequence of PDM-AA-AM > PDM-AA > PDM-AA-AM-HEA > PDM and PDM-AA > PDM-AA-AM > PDM-AA-AM-HEA > PDM, respectively. PDM has the lowest percent removal onto both AS and IAS. PDM adsorption inhibition observed on AS might be attributed to the cationic quaternary (Fig. 6) of PDM with special biotoxicity leading to micro-organisms inactivation [34], thereby retarding the adsorption. The octanol–water partition coefficients (K_{OW}) value (Table 3) of PDM is lower than the rest of the vinyl polymers, taking into account the fact that hydrophilic interaction may also have a negative impact on PDM adsorption.

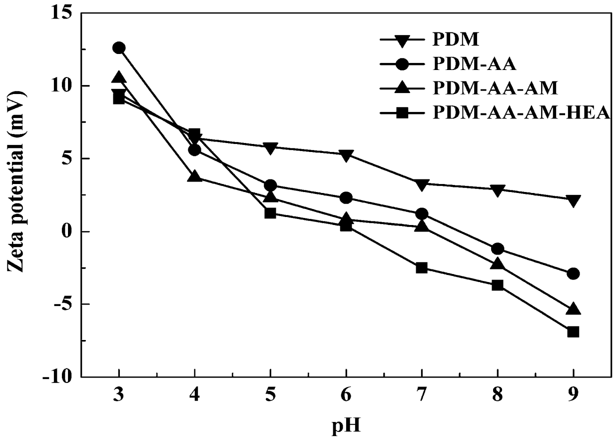

Fig. 6. Variation of zeta potentials of vinyl polymers.

Compared with the significant variation in functional groups of PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA, polydiallyldimethylammonium chloride (PDM) is the major constituent of a 5-membered nitrogen-containing ring. The zeta potentials of the four vinyl polymers are plotted in Fig. 6, which show that PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA are all amphoteric polymers. PDM-AA has greater zeta potential than PDM-AA-AM in the pH range of 3–9. The properties of the copolymer (PDM-AA) are dependent on the polyacrylic acid, the hydrophilic group (–COOH) of copolymer increases the polarity of the PDM-AA. The binding of both AM (–$CONH_2$) and polyacrylic acid in the PDM-AA-AM polymer chains decreased PDM-AA-AM molecular polarity. Compared with the zeta potential and molecular polarity of PDM-AA and PDM-AA-AM, the change trend coincides with the adsorption capacity in the case of the IAS. Thus, it can be said that the adsorption proceeds through the strongly polar effect which are characterized as unusually strong electrostatic attraction. The presence of –COOH, –$CONH_2$, and –OH groups in the PDM-AA-AM-HEA polymer chains increase PDM-AA-AM-HEA space steric hindrance. Increasing steric hindrance may result in increased electrostatic repulsive force, which may decrease the PDM-AA-AM-HEA adsorption.

The adsorption processes and mechanisms were also studied by octanol–water partition coefficients. The K_{OW} values (Table 3) obtained from the experimental were 18, 280, 53, and 41 for the PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA, respectively. PDM-AA has the highest percent removal on IAS, followed by PDM-AA-AM, PDM-AA-AM-HEA, and PDM, respectively. The adsorption efficiency increased noticeably with increasing K_{OW}; therefore,

Table 3
K_{OW} values of vinyl polymers

Vinyl polymers	PDM	PDM-AA	PDM-AA-AM	PDM-AA-AM-HEA
K_{OW}	18	280	53	41

adsorption phenomena of vinyl polymers on IAS can be explained on the basis of hydrophobic and dispersion effects.

In the case of the AS, the reversal of PDM-AA and PDM-AA-AM in the adsorption trend could probably be explained on the basis of surface behavior. The greatest overall removal of PDM-AA-AM on AS can be attributed to the strongly surface binding. The sludge surface binding plays an important mechanism on PDM-AA-AM uptake other more than hydrophobic and electrostatic attraction.

3.6. Effects of EPS, Cr^{3+}, Ca^{2+}, and Na^+ on adsorption of vinyl polymers

EPS in microbial aggregates involve active secretion from bacterial cells, sloughing of cell surface material, cell degradation, and adsorption of matter from the environment [30]. EPS have many available sites for the adsorption of metals and organic matter [35]. The adsorption of organic pollutants by microbial aggregates may be attributed to the fact that there are some hydrophobic regions in EPS [36]. In order to observe what roles EPS play in vinyl polymers adsorption, we conducted adsorption experiments in which EPS were partially extracted from AS biomass. As shown in Fig. 7, the partial extraction of EPS biomass decreased the removal of all the four vinyl polymers, indicating that these pollutants were adsorbed by EPS and a portion was adsorbed by cells. The effect of EPS was more significant in PDM removal, about 25% less to EPS-extracted AS biomass than to AS, this is mainly because EPS with negative charges is capable of binding with positively charged PDM via electrostatic interaction [35].

Cations such as Cr^{3+}, Ca^{2+}, and Na^+ are frequently found in tannery wastewater, which may affect vinyl polymers adsorption. As illustrated in Fig. 7, the addition of Cr^{3+} did not result in noticeable change in the degree of the four vinyl polymers removal. Studies have indicated that AS showed better adsorption capacity of Cr^{3+} [37,38]. The slight decrease in PDM removal by coexisting Cr^{3+} is likely attributed to PDM polymer chains which always contain positive charges, and the presence of a competitive cation in solution caused a reduction of the removal capacity. The presence of Cr^{3+} ions slightly improved the PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA adsorption probably because Cr^{3+} may directly combine with carboxyl group. Thus, the acrylic bounded to the Cr^{3+} leads to enhanced acrylic vinyl polymers removal.

Fig. 7 shows that the presence of Ca^{2+} and Na^+ cations hinder all the four vinyl polymers adsorption on AS. When the solution was added with Ca^{2+}, the percent removal of PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA were 37, 63, 54, and 65%, respectively. In the presence of Na^+, the percent removal of PDM, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA were 39, 66, 55, and 67%, respectively. Coexisting Ca^{2+} and Na^+ ions have negligible effect on the four vinyl polymers removal capacity, and the effect of Ca^{2+} and Na^+ nearly in the same degree of each target vinyl polymers.

The zeta potential variation of the AS studied with the addition of Na^+ and Ca^{2+} at pH 6.5 is presented in Fig. 8. Based on the plots, the zeta potential of AS increased with the increasing ionic concentration of Ca^{2+} and Na^+ at ionic concentration from 1 to 100 mmol/L. The inhibition of vinyl polymers adsorption on AS are probably because the cations in

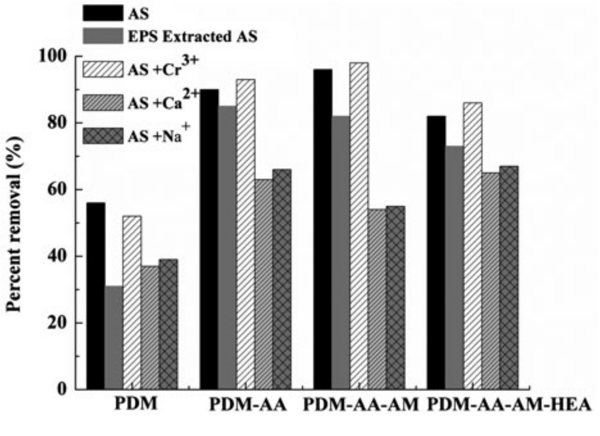

Fig. 7. Comparison of the effects of EPS extraction and Cr^{3+}, Ca^{2+}, and Na^+ addition on the percent removal of vinyl polymers.

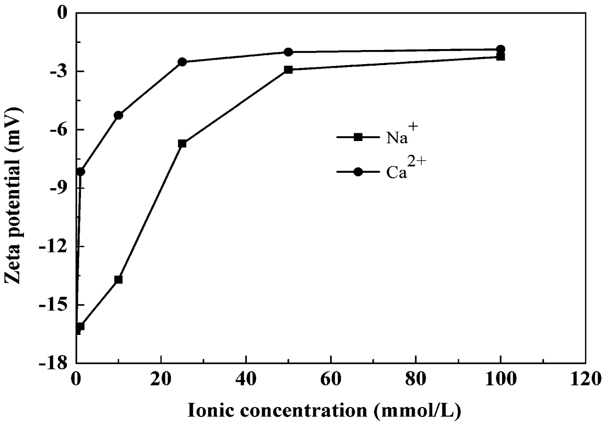

Fig. 8. Effects of Na^+ and Ca^{2+} on the zeta potential of AS.

solution may neutralize the negative charge carried by the AS flocs, then weaken the electrostatic force interaction between vinyl polymers molecules bounded to the surface of the AS. Studies showed that cations (Ca^{2+} and Na^{+}) addition leads to lower viscosity values [39] and higher compressibility [40]. A lower viscosity and higher compressibility indicate that there may be less surface binding of vinyl polymers on the surfaces of the sludge flocs. Moreover, the existed competitive effects might make the active sites fewer with the increasing of ion strength [41].

3.7. Possible mechanism of vinyl polymers adsorption

The images and data demonstrate that there are a number of mechanisms by which vinyl polymers were adsorbed to biomass surfaces from aqueous solutions. AS is more effective than IAS in the removal of vinyl polymers indicating that surface area and pore volume play significant roles in the removal process. Vinyl polymers adsorption amount onto IAS exhibited high affinity for K_{OW} and increasing K_{OW} result in enhanced vinyl polymers adsorption suggests that hydrophobic interaction also play an important role. The presence of Cr^{3+} ions slightly improved the PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA removal, whereas retarded the PDM removal to some extent, which is probably because Cr^{3+} may directly combine with carboxyl group. Coexisting Ca^{2+} and Na^{+} ions have negligible effect on the four vinyl polymers removal. Effects of coexisting Cr^{3+}, Ca^{2+}, and Na^{+} ions suggest that electrostatic attraction serves as another factor which influences vinyl polymers adsorption. All the four vinyl polymers showed a decrease in the degree of removal when EPS was partial extracted from the biomass, indicating that these pollutants were adsorbed by EPS and a portion adsorbed by cells. The effect of EPS was more significant for PDM removal mainly because EPS with negative charges is capable of binding with positively charged PDM via electrostatic interaction, which suggests that electrostatic interaction may play an important role in PDM removal.

3.8. Effect of vinyl polymers on bioactivity of the AS

The dehydrogenase activity was studied in order to estimate the effect of vinyl polymers on bioactivity of the AS. As shown in Fig. 9, the dehydrogenase concentrations of AS in all treatments declined after 30 min adsorption, indicating that these vinyl polymers have negligible effect on bioactivity of the AS. Clearly, PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA did not result in noticeable change in bioactivity of the AS, while PDM affected bioactivity of the AS significantly. The result further evidenced that PDM with special biotoxicity retarded adsorption.

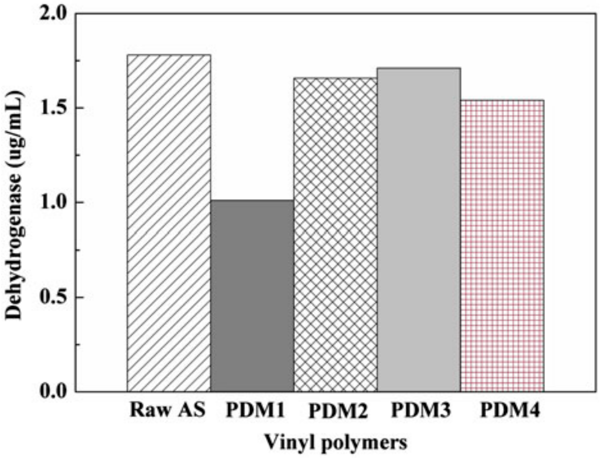

Fig. 9. Dehydrogenase concentrations of the raw AS and the AS adsorbed with vinyl polymers.

Based on the above results, AS is an inexpensive and easily available material that can be an alternative for more costly adsorbents used for the removal of vinyl polymers in wastewater treatment processes and which is a major removal process. Thus, further research emphasis is needed on vinyl polymers biodegradation in AS.

4. Conclusion

This study focuses on the feasibility of using AS biomass from wastewater as an adsorbent for the removal of vinyl polymer syntans. The adsorption rate is quick and adsorption equilibrium can be achieved within 30 min. The results showed that different types of vinyl polymer syntans adsorb to differing degrees. Kinetics data showed good correlation with the pseudo-second-order model. Vinyl polymers adsorption isotherms on AS can be fitted by Langmuir model rather than Freundlich model. The adsorption capacity increases with the increase in initial vinyl polymers concentration. The presence of Cr^{3+} ions slightly improved the PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA removal whereas hinder the PDM removal. Coexisting Ca^{2+} and Na^{+} ions and EPS-extracted biomass have negligible effect on all the four vinyl polymers removal. There are a number of mechanisms by which vinyl polymers were adsorbed onto wastewater biomass from aqueous solutions. They include hydrophobic interaction, surface binding, and electrostatic force. Surface binding may play a major role in PDM-AA, PDM-AA-AM, and PDM-AA-AM-HEA adsorption, while electrostatic interaction may play a major role in PDM removal. A better understanding of vinyl polymers adsorption to wastewater biomass is essential for improving predictions of the fate and transport of vinyl polymers in the environment.

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