

Research Article

TiO₂ Photocatalyst Nanoparticle Separation: Flocculation in Different Matrices and Use of Powdered Activated Carbon as a Precoat in Low-Cost Fabric Filtration

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Separation of photocatalyst nanoparticles is a problem impeding widespread application of photocatalytic oxidation. As sedimentation of photocatalyst particles is facilitated by their flocculation, the influence of common constituents of biologically pretreated wastewaters (NaCl, NaHCO₃, and their combination with humic acid sodium salt) on flocculation was tested by the pipet method. Results showed that the impact of these substances on TiO₂ nanoparticle flocculation is rather complex and strongly affected by pH. When humic acid was present, TiO₂ particles did not show efficient flocculation in the neutral and slightly basic pH range. As an alternative to photocatalyst separation by sedimentation, precoat vacuum filtration with powdered activated carbon (PAC) over low-cost spunbond polypropylene fabrics was tested in the presence of two PAC types in aqueous NaCl and NaHCO₃ solutions as well as in biologically treated greywater and in secondary municipal effluent. PAC concentrations of ≥ 2 g/L were required in order to achieve a retention of nearly 95% of the TiO₂ nanoparticles on the fabric filter when TiO₂ concentration was 1 g/L. Composition of the aqueous matrix and PAC type had a slight impact on precoat filtration. PAC precoat filtration represents a potential pretreatment for photocatalyst removal by micro- or ultrafiltration.

1. Introduction

Biological treatment of municipal wastewater does not remove all trace organics. For example, some pharmaceuticals such as carbamazepine are not susceptible to biodegradation. Therefore, ozonation is widely discussed as an oxidative tertiary treatment in municipal wastewater treatment [1]. Besides ozonation which is highly energy-consuming (6–10 kWh are required for the production of 1 kg O₃ in large-scale ozone generators), advanced oxidation processes (AOPs) are increasingly focused for this purpose [2]. An AOP which can be powered by the sun is heterogeneous photocatalytic oxidation (PCO). TiO₂ nanoparticles were most frequently investigated, because they represent absolutely stable photocatalysts. As an industrial bulk product, TiO₂ is easily available.

Although TiO₂ is looked at as nontoxic, a concentration of TiO₂ nanoparticles (diameter ≈ 100 nm) as small as 2 mg/L has recently been shown to inhibit the second molting of age-synchronized *Daphnia magna* neonates by about 90%, while the first molting was not affected [3]. At the end of a 96 h incubation period, around 70% of the organisms were immobilized due to TiO₂ nanoparticles. TiO₂ particles with diameters around 100 nm were significantly more toxic toward *D. magna* than 200 nm particles. These findings emphasize the need of a safe barrier for TiO₂ photocatalyst nanoparticles within the PCO process in order to prevent them from spreading into the aqueous environment.

Investigations with a laboratory-scale wastewater treatment plant resulted in considerable escape of nanoparticles with the effluent [4]. Sedimentation for separation of the photocatalyst subsequent to the accomplished PCO process

is usually insufficient. Even when the photocatalyst flocculates, there is often a residue of suspended photocatalyst as observed by the authors in settled samples from laboratory-scale PCO experiments with biologically pretreated greywater. Sometimes, turbidity was visible even after centrifugation of the sedimentation supernatants. Photocatalyst flocculation depends on the wastewater matrix [5] and is hardly predictable.

One option making photocatalyst separation unnecessary is photocatalyst immobilisation. However, data on long-term stability of immobilized photocatalysts is very scarce. Another drawback of photocatalyst immobilization on surfaces of larger particles such as powdered activated carbon (PAC), silica, or zeolite (which are more rapidly settling than nanoparticles) is that these composites have to be especially produced requiring special know-how and additional financial resources.

Alternatives to sedimentation and to photocatalyst immobilization on surfaces are sand filtration, hydrocyclones, or membrane filtration. Sand filtration is not a safe method for recovering TiO_2 nanoparticles, because only under conditions leading to TiO_2 agglomeration (pH 7), retention of photocatalyst particles in a sand filter was observed, while at pH 5 flocculation and also retention of particles were low [6]. In contrast, TiO_2 immobilized by sol-gel method on 20 to 200 μm diameter glass spheres could be removed by sand filtration subsequent to PCO [7].

There exists little experience with hydrocyclones for photocatalyst removal. However, as hydrocyclones are based on centrifugal forces, they might be similarly inefficient as laboratory centrifuges with several 1000 times gravitational acceleration, g , as frequently observed by the authors during particle removal from samples taken from PCO experiments utilizing TiO_2 "P25." Bickley et al. [8] have tested large particle size (1–100 μm) photocatalysts which were proven to be separated by means of hydrocyclones. However, such large photocatalyst particles exhibit low specific surfaces. The consequence is poor adsorption of organics and thus low reaction rates [9]. Additionally, microparticles do not show any "quantum size effect." This makes them also less efficient PCO catalysts than nanoparticles [10].

Membrane filtration processes are more successful in photocatalyst removal. Sopajaree et al. [11] found separation of nanosized photocatalyst TiO_2 "P25" to be complete with ultrafiltration membranes, but concentration polarisation increased with increasing photocatalyst concentration. Additionally, there is little to no experience with working life of organic membranes when the feed/retentate contains abrasive TiO_2 particles. Doll and Frimmel [12] gathered positive lab-scale experience combining heterogeneous PCO with a ceramic single channel microfiltration membrane made of α -aluminium oxide. Flocculation of nanoparticles is beneficial for their retention by microfiltration. Another disadvantage of membrane filtration is that it adds to power consumption of a PCO reactor (which is also the case for hydrocyclones due to the strong pumps necessary for their operation).

A more economically feasible solution for photocatalyst separation would be fabric filtration using cheap fabrics such as the raw material for disposable laboratory coats

(Wendland, personal communication) made from spunbond polypropylene. However, fabrics like this are not expected to be able to retain nanoparticles. Therefore, precoat filtration using powdered activated carbon (PAC) might be useful in combination with fabric filters. As the combination of particulate PAC types with PCO was shown to be advantageous for removal of phenol [13–16] and also other compounds, the precoat filtration of TiO_2 with PAC suggests itself.

For evaluating the feasibility of precoat filtration for nanoparticle separation, TiO_2 "P25" suspensions (1 g/L) were mixed with different amounts of two PAC types. A TiO_2 concentration of 1 g/L was chosen because it is very common in PCO studies. These mixtures were subjected to vacuum filtration over small pieces of spunbond polypropylene fabrics and the filtrates were analyzed for total solids. Another aim of the study was to investigate TiO_2 "P25" nanoparticle flocculation in model wastewaters containing different amounts of NaCl, NaHCO_3 , and humic acid sodium salt by means of the pipet method.

2. Materials and Methods

2.1. Flocculation Experiments. Flocculation of photocatalyst in different model wastewaters was investigated by the "pipet method" as described elsewhere [5] by allowing 1 g/L TiO_2 (Aeroxide P25, Evonik Industries AG, Hanau-Wolfgang, Germany) suspensions in aqueous solutions containing different NaCl or NaHCO_3 concentrations (0–1000 mg/L) and different concentrations (0–50 mg/L) of humic acid sodium salt (HANa, Carl Roth GmbH, Karlsruhe, Germany) to settle for 1 hour prior to taking a 50 mL sample with a pipet the tip of which was fixed exactly 10 cm below the liquid surface. These samples were subsequently membrane-filtered (0.45 μm pore width) and the TiO_2 mass retained on the filter was gravimetrically determined after drying at 105°C.

2.2. Precoat Fabric Filtration of TiO_2 . Circular pieces of 5 cm diameter were cut from 100 g/m² spunbond polypropylene fabrics used for disposable laboratory coats manufacture (Figure 1).

The fabric pieces were fixed in a vacuum filtration apparatus using a water-jet vacuum pump for creating the vacuum. For filtration over the fabrics, the following suspensions were prepared: 1 g/L TiO_2 "P25" suspension either in NaCl or NaHCO_3 solutions of different concentrations (0, 0.1, 0.5 or 1 g/L) in deionized water, in a matrix of biologically pretreated greywater (effluent of a constructed wetland for greywater treatment described in more detail elsewhere [17]) or in secondary municipal effluent. 100 mL of these suspensions were added to different amounts of two types of PAC (Merck article no. 102186 or Lurgi Hydrarfin WG; for properties of both PAC types, see Table 1) resulting in activated carbon concentrations in the range from 0 to 5000 mg/L.

Volumes of 50 mL of the stirred suspensions were pipetted on to the filter pieces and vacuum-filtered. The filtrates were collected in 100 mL beakers with exactly recorded tare weights. The beakers with the filtrate were heated in a furnace at 80°C until all the water was evaporated and dried at 105°C

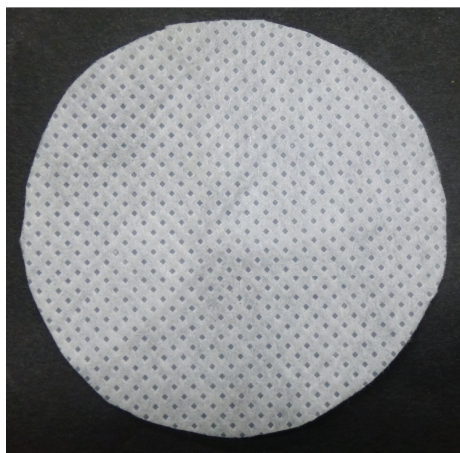


FIGURE 1: Circular piece of spunbond polypropylene fabric (5 cm diameter) used as filter medium for TiO_2 nanoparticles precoat filtration with PAC.

TABLE 1: Providers' information about properties of the investigated activated carbons.

	Merck 102186	Hydraffin WG
Ash content	<1	About 5
pH (in deionised water)	4–7	3–5
Particle size	About $60 \mu\text{m}^a$, 50% $\leq 30 \mu\text{m}$, 90% $\leq 100 \mu\text{m}$	85% $\leq 40 \mu\text{m}$
BET surface (m^2/g)	775 ^a	1100
Iodine uptake (mg/g)	888	1050

^a[16].

until weight constancy, cooled in a desiccator and weighed again for total solids (TS) determination. TS concentrations of the matrices (without TiO_2 and PAC) were recorded in the same way by drying 50 mL of each solution. These values representing total solids of the matrix ($\text{TS}_{\text{matrix}}$) were subtracted from the TS concentrations of the filtrates.

3. Results and Discussion

3.1. Aqueous Matrix Impact on TiO_2 Flocculation. In Figure 2, the influence of NaCl concentration on TiO_2 flocculation at different HANa concentrations is shown. When no humic acid was present, TiO_2 flocculation was increasing with increasing NaCl concentration (Figure 2(a)). At an NaCl concentration of 1 g/L, about 90% of TiO_2 settled from the top 10 cm of the suspension after 1 h indicating a high extent of flocculation, while in deionized water the concentration of suspended TiO_2 was only diminished by 10%. Enhanced flocculation with increasing NaCl concentration can be attributed to compression of the electric double layer around the photocatalyst particle. When 10 mg/L of humic acid sodium salt was present (Figure 2(b)), flocculation was very pronounced nearly irrespective of NaCl concentration. This can be referred to the influence of HANa on pH of the suspensions which was about 5.8 at this humic acid sodium

salt concentration (Figure 2(b)). It can be assumed that this pH is close to the point of zero charge (PZC) of TiO_2 "P25" in the given matrix. At PZC, maximum flocculation is achieved. This PZC was also found in another TiO_2 flocculation study in aqueous matrices containing the nondissociable organic tetraethyleneglycol dimethylether and different inorganic salts [5].

With 20 mg/L HANa (Figure 2(c)), flocculation increased with increasing NaCl concentration similar to experiments without humic acid, but not as pronounced. At this HANa concentration, the pH of the suspensions was 6.3 instead of 4.5 to 5 as determined in the absence of HANa. An HANa concentration of 50 mg/L (Figure 2(d)) led only to slight flocculation. This can be interpreted by efficient adsorption of humic acid anions to the photocatalyst surface [18] with the consequence of more negative surface charges leading to increased repulsion of particles.

It has to be noted that artifacts caused by the applied methodology for evaluating nanosized photocatalyst flocculation cannot be excluded. Nonflocculated nanoparticles might not have been retained by microfiltration. In this case, flocculation would have been overestimated. However, the study of Armanious et al. [5] clearly showed full retention of nonflocculated TiO_2 nanoparticles in a deionized water matrix by microfiltration.

The inorganic salt NaHCO_3 showed an influence on flocculation (Figure 3) different from that of NaCl. Concentrations of NaHCO_3 of 100 mg/L and more resulted in a pH above 8, irrespective of HANa concentration. The graphs in Figures 3(b), 3(c), and 3(d) clearly show that TiO_2 flocculation was increased in matrices containing humic acid when NaHCO_3 concentration was augmented from 100 to 200 mg/L. Further enhancement of bicarbonate concentration did not result in markedly intensified flocculation, probably due to efficient adsorption of humic acid anions which are predominantly negatively charged at $\text{pH} > 8$ (pK_a of humic acids is reported to be in the range of 3.5–5 [19]) leading to particle repulsion. When no humic acid sodium salt was present (Figure 3(a)), flocculation was much more pronounced. There was a sharp increase in flocculation for small NaHCO_3 concentrations of 10 and 20 mg/L obviously due to pH adjustment by these NaHCO_3 concentrations to PZC which may be around pH 7 when no humic acid anions were present. Compression of the electric double layer can be assumed to play an additional role at NaHCO_3 concentrations above 500 mg/L in the absence of humic acid (Figure 3(a)).

PZC in the presence of HANa can be assumed to be around 5–6 because the lowest TiO_2 concentration after 1 h sedimentation time in HANa-containing suspensions was recorded in this pH range (Figure 2(b)). When pH was elevated to around 7 by NaHCO_3 and further HANa addition, humic acids adsorbed to the photocatalyst surface were predominantly negatively charged leading to repulsion of photocatalyst particles (compare Figure 3(b) to Figure 2(b)). Elevating pH to more than 7.5 by adding NaHCO_3 (compare Figure 3(d) to Figure 2(d)) may lead to more negatively charged TiO_2 surfaces which may cause reduced adsorption of humic acid anions on the photocatalyst. A lower repulsion between photocatalyst particles because of less negative

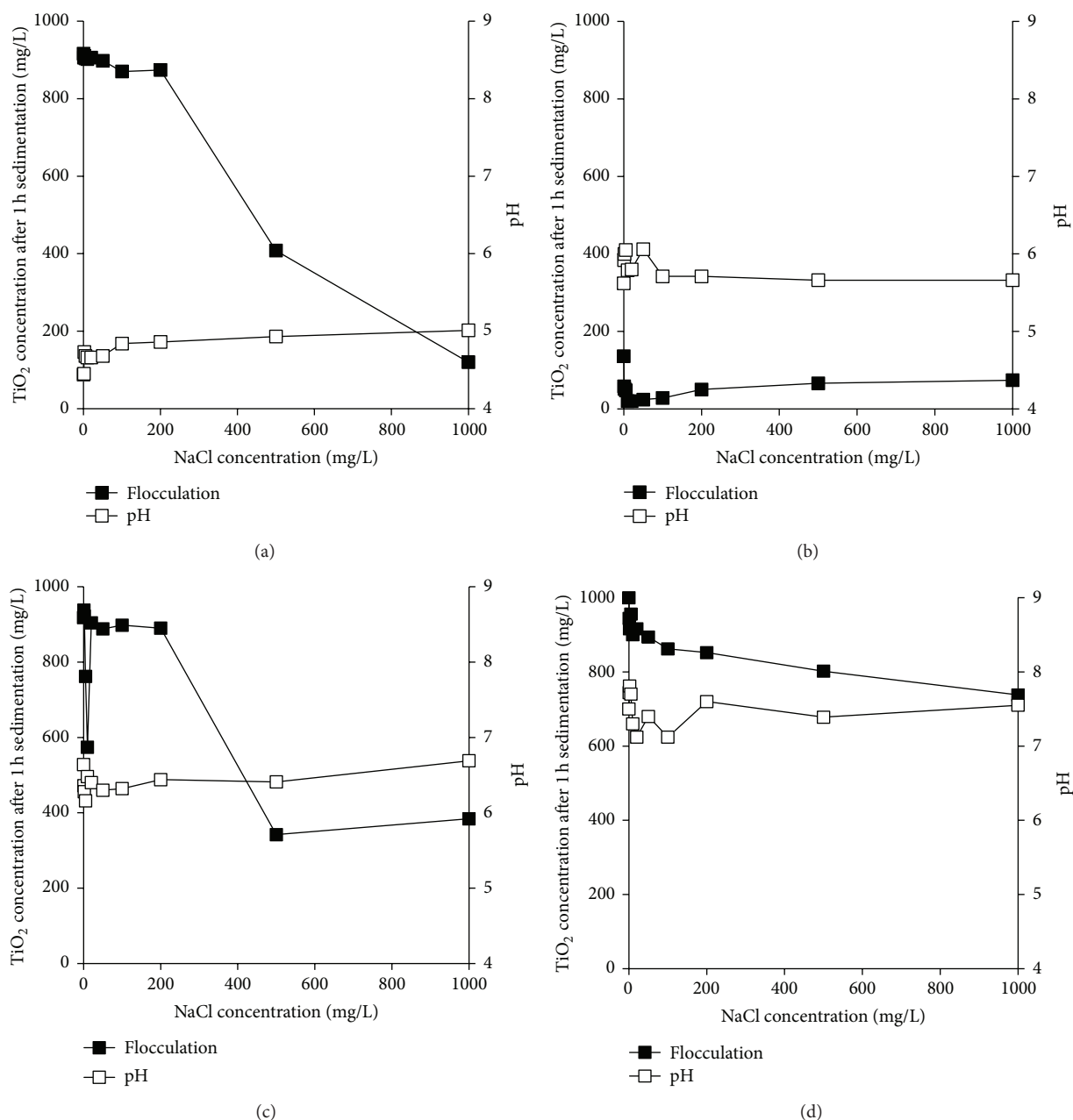


FIGURE 2: Photocatalyst flocculation and pH in 1 g/L TiO₂ "P25" suspensions in aqueous solutions with no (a), 10 (b), 20 (c), and 50 mg/L (d) humic acid sodium salt, HANA, at different NaCl concentrations.

charges on their surface due to less adsorbed humic acid anions might have been the consequence.

Only a few of the matrices tested in this study led to pronounced flocculation of TiO₂ nanoparticles; in the absence of HANA, only NaCl concentrations in the range of 1000 mg/L (pH \approx 5) and NaHCO₃ concentrations of 10 to 1000 mg/L (resulting in a pH range of 7–8.5) led to flocculation. HANA addition commonly deteriorated flocculation except in NaCl matrices (irrespective of NaCl concentration) when HANA concentrations did not exceed 10 mg/L (Figure 2). However, as PCO leads to removal of humic substances, repulsion of photocatalyst particles caused by humic or fulvic acid anions

adsorbed to the photocatalyst is no longer expected in PCO-treated wastewaters. The hydrogen carbonate formed by PCO might enhance flocculation when pH of the suspension is between 6.5 and 8 (Figure 3(a)).

Overall, the impact of organic and inorganic wastewater constituents on photocatalyst flocculation is very complicated and difficult to predict. Flocculation can be expected to affect photocatalyst sedimentation as well as PCO efficiency. A previous study [5] revealed that the relation of PCO rate constants to photocatalyst flocculation was not as unequivocal as the relationship between rate constants and pH. However, most intense flocculation was linked to

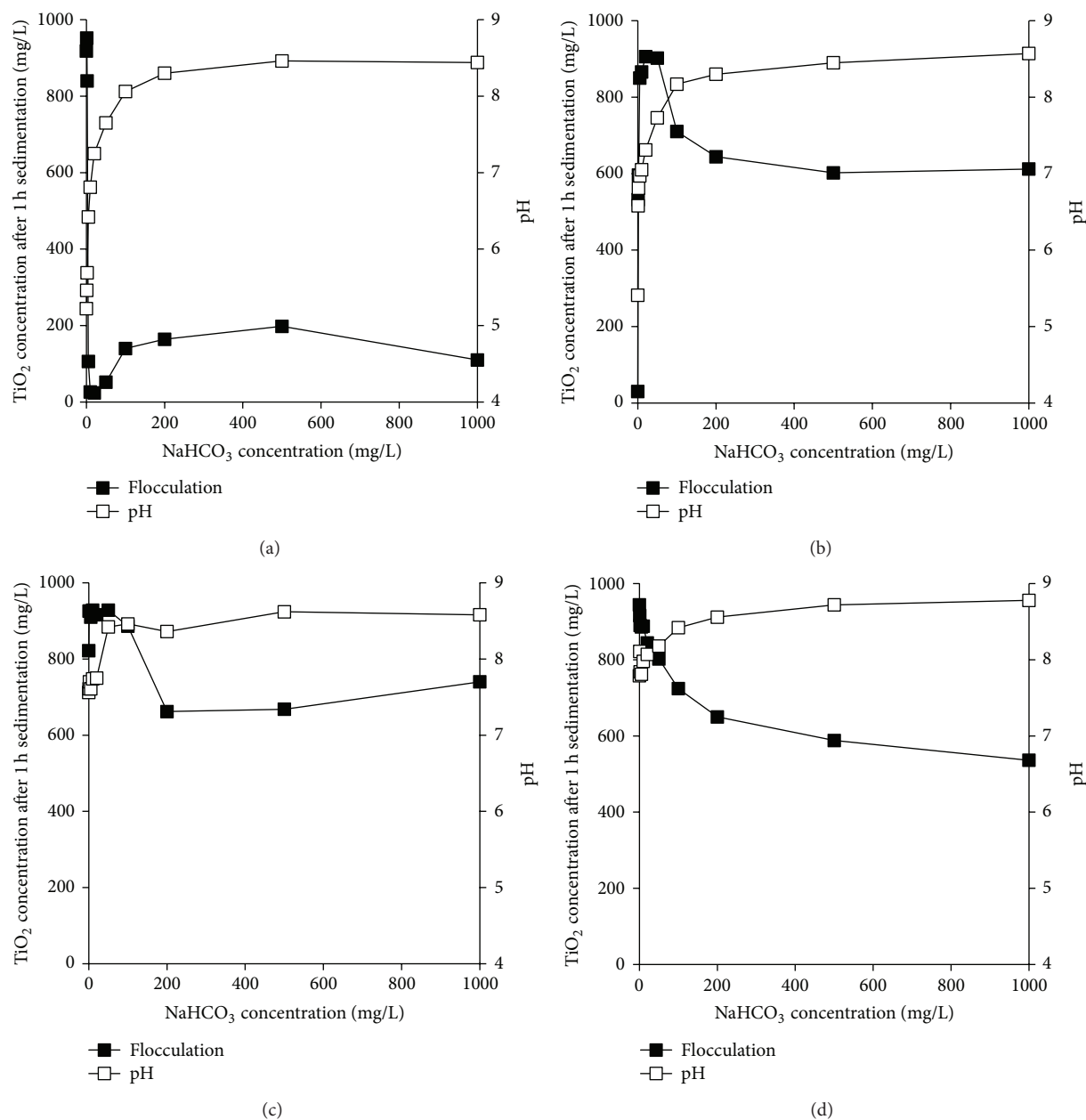


FIGURE 3: Photocatalyst flocculation and pH in 1 g/L TiO_2 “P25” suspensions in aqueous solutions with no (a), 10 (b), 20 (c), and 50 mg/L (d) humic acid sodium salt, HANA, at different NaHCO_3 concentrations.

lowest rate constant while the rate constant was maximum when flocculation was negligible. While it cannot be excluded that TiO_2 photocatalyst flocculation is disadvantageous with respect to PCO efficiency, it is beneficial for photocatalyst recovery by sedimentation and also by sand filtration as recently shown [6].

3.2. Precoat Filtration. The filtrates received by vacuum filtration over the spunbond polypropylene fabrics were turbid in all cases. Without addition of PAC, the filtrates were white opaque suspensions similar to the suspensions before filtration. When PAC was added to TiO_2 suspensions

prior to filtration, the filtrates appeared as grey suspensions. However, opacity of the filtrates decreased with increasing PAC dosage prior to filtration. Increasing PAC concentrations led to longer periods of time required for filtering one batch of 50 mL. In Figure 4, total solids (TS) concentrations in mixed TiO_2 /PAC suspensions filtered over spunbond polypropylene fabrics are displayed which were corrected by subtraction of total solids of the liquid phases. Figures 4(a) and 4(b) show that TiO_2 “P25” was not retained from 1 g/L suspensions in deionized water when no PAC was added. So, the investigated fabric does not remove the nanoparticles without precoat. However, the addition of increasing amounts of Merck

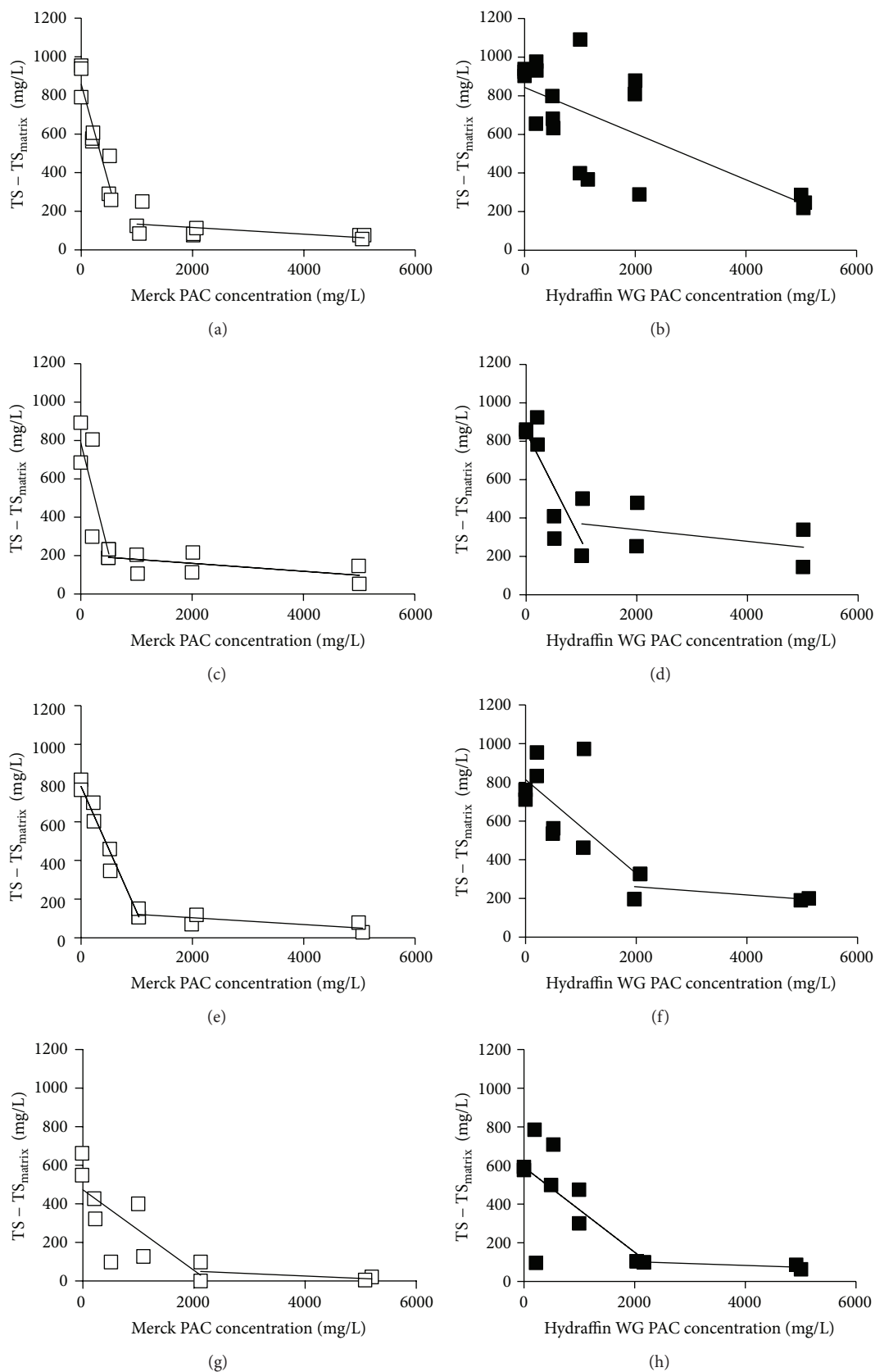


FIGURE 4: Total solids concentrations (corrected for TS concentrations of the matrices) in 1 g/L TiO_2 suspensions containing different amounts of Merck PAC or Hydriffin WG PAC in different matrices ((a), (b): deionized water; (c), (d): 0.1 g/L NaCl solution; (e), (f): 0.5 g/L NaCl solution; (g), (h): 1 g/L NaCl solution) subsequent to vacuum filtration over spunbond polypropylene fabrics.

PAC led to decreased concentrations of total solids in the filtrate indicating that this PAC type is a feasible precoat (Figure 4(a)). When the added Merck PAC concentration exceeded 1 g/L, further increase of PAC concentration did not result in pronounced reduction of TS concentration in the filtrate (Figure 4(a)). During the experiments with the Merck PAC in the deionized water matrix, the total solids obtained after drying the filtrates were subjected to glowing at 550°C (until weight constancy). While without addition of PAC the total nonvolatile solids concentration in the filtrate was about 800 mg/L, only around 70 mg/L nonvolatile solids were detected in the filtrates subsequent to addition of 2000 mg/L Merck PAC as a precoat (data not shown). This indicates that the particles in those filtrates obtained with sufficient Merck PAC addition consisted of TiO_2 particles for the most part. Nevertheless, precoat filtration with 2000 mg/L Merck PAC resulted in more than 90% TiO_2 removal.

The other investigated PAC type (Hydraffin WG) showed a completely different behaviour as precoat in the deionized water matrix (Figure 4(b)); although solid retention showed an increasing tendency with increasing PAC concentration in the original suspensions, it was less efficient and not as reproducible as with the Merck PAC. Nonvolatile solids determined in one of the filtrates were more than 800 mg/L when 2000 mg/L Hydraffin WG was used as a precoat (data not shown). A conclusion from these results is that the Hydraffin WG PAC is a less efficient precoat than the Merck PAC when the aqueous solutions contain NaCl.

It was not expected from particle size data of the two PAC types (Table 1), that precoat filtration with Hydraffin WG PAC would have resulted in a lower TiO_2 retention than with the Merck PAC; Hydraffin WG consisted of slightly smaller particles than the Merck PAC. So, it was assumed that TiO_2 particles should be retained to a larger extent in the filter cake formed by Hydraffin WG, because it will exhibit smaller pores than the Merck PAC filter cake. Probably, some more Hydraffin PAC particles escaped through the pores of the fabric filter. However, as mentioned above more than 800 mg/L of the solids in the filtrate were nonvolatile, that is, TiO_2 . So, the least part of the particles in the filtrate was represented by Hydraffin WG PAC.

Lower precoat efficiency of Hydraffin WG might be caused by a lower extent of interaction of the TiO_2 surface with functional groups on the surface of Hydraffin WG PAC in comparison to the Merck PAC. Coordinative interactions of Ti centers on the TiO_2 photocatalyst surface with particular oxygen-containing carbon-functional surface groups such as carboxylic acids or cyclic ethers were claimed by Matos et al. [14]. Interactions between TiO_2 "P25" and the Merck PAC which was also utilized in this study were indicated by the disappearance of FTIR peaks of the Merck PAC at 3400 cm^{-1} (phenolic PAC surface groups) and at 1000–1200 cm^{-1} (attributed to cyclic ether groups) when it was mixed with TiO_2 [20]. On one hand, this coordination might enable injection of charge carriers from illuminated TiO_2 particles into activated carbon grains. On the other hand, such interactions can also be hypothesized to lead to enhanced adhesion between TiO_2 photocatalyst particles and particular PAC types.

This hypothesis was also supported by results of the precoat filtration experiments with the NaCl solution matrices (Figures 4(c)–4(h)); in all cases, addition of Merck PAC above 2000 mg/L resulted in lower TS concentrations in the filtrates than addition of the Hydraffin WG PAC. Obviously, increase of NaCl concentration in the aqueous phase was beneficial for precoat filtration with both PAC types; especially at PAC concentrations ≥ 2000 mg/L, total solids concentrations in the filtrate were decreasing. This might be a consequence of intensified flocculation of TiO_2 nanoparticles caused by compression of the electric double layer. Agglomerated TiO_2 particles are probably more readily retained in the PAC filter cakes.

Replacement of NaCl by NaHCO_3 led to similar results of TiO_2 precoat filtration (Figure 5). Both PAC types at concentrations of ≥ 2000 mg/L clearly reduced particle concentrations in the filtrates. However, precoat filtration with Merck PAC in the NaHCO_3 matrix showed slightly worse results than in the NaCl matrix, while precoat filtration with Hydraffin WG at concentrations ≥ 2000 mg/L was a bit more efficient in the NaHCO_3 matrix. When NaHCO_3 concentration was 0.5 g/L, the Hydraffin WG PAC was an even better precoat than Merck PAC. At NaHCO_3 concentrations of 0.1 and 1 g/L, precoat filtration with both PAC types at concentrations above 2000 mg/L was nearly equally efficient.

In a matrix of biologically treated greywater, more particles escaped through the spunbond polypropylene fabric (Figures 6(a) and 6(b)) than in experiments with aqueous NaCl and NaHCO_3 solutions (Figures 4 and 5). Biologically treated greywater contains more salts additional to NaCl [5]. Substances contained in biologically treated greywater might have affected interactions between photocatalyst and PAC particles. Obviously, they deteriorate the precoat filtration. These findings are in contrast with results obtained with TiO_2 /PAC suspensions in secondary municipal effluent (Figures 6(c) and 6(d)); in the secondary municipal effluent, precoat filtration with both PAC types was more efficient than in the greywater matrix. Similar to findings in the greywater, the Merck PAC was more suitable than the Hydraffin WG PAC.

Overall, the impact of the wastewater matrix on precoat filtration seems to be quite complex. As mentioned above, it can be hypothesized that there are interactions between TiO_2 nanoparticles and PAC grains such as coordinative complexation of Ti centers on TiO_2 surface by carboxylic acid or cyclic ether functional groups on surfaces of the activated carbon [14, 20]. These interactions are probably influenced by the surrounding aqueous solution similar to interactions between activated carbon surface functional groups and organic adsorptive molecules which have been recently reviewed [21]. The two key factors found in the surrounding aqueous solution which influence activated carbon/adsorbed organic molecule interactions were identified to be pH and ionic strength. While NaCl only affects ionic strength, NaHCO_3 influences both pH and ionic strength. The pH has a strong impact on surface chemistry of activated carbon [21]. Except by NaHCO_3 , the pH of the TiO_2 /PAC suspensions is affected by the acidic nature of the TiO_2 itself and the acidity or basicity of the activated carbon (see Table 2). Hydraffin

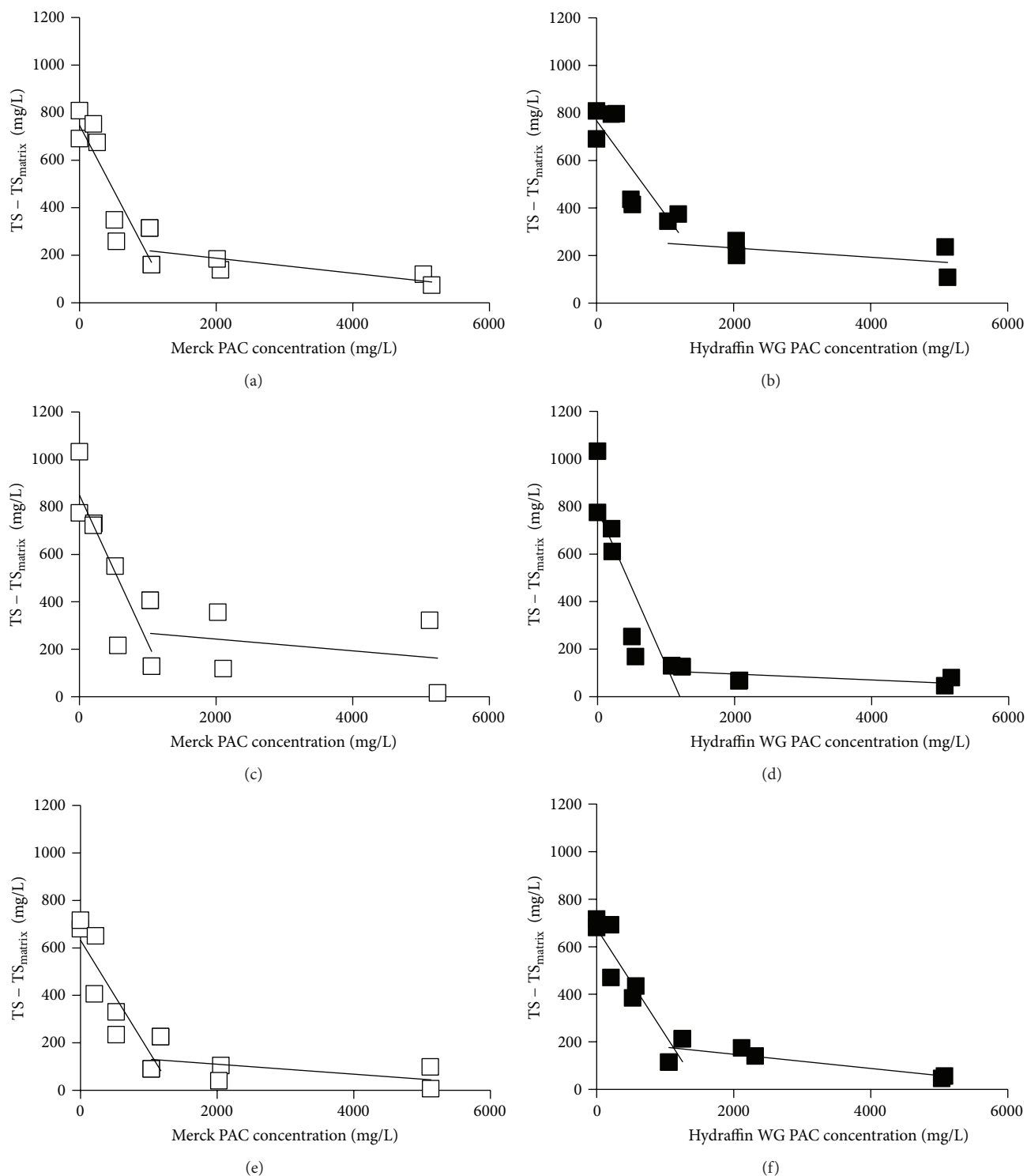


FIGURE 5: Total solids concentrations (corrected for TS concentrations of the matrices) in 1 g/L TiO_2 suspensions containing different amounts of Merck PAC or Hydraffin WG PAC in different matrices ((a), (b): 0.1 g/L NaHCO_3 solution; (c), (d): 0.5 g/L NaHCO_3 solution; (e), (f): 1 g/L NaHCO_3 solution) subsequent to vacuum filtration over spunbond polypropylene fabrics.

WG PAC is more acidic than the Merck PAC (Table 1). When no hydrogen carbonate was added to suspensions containing 1 g/L TiO_2 and 2 g/L PAC, the TiO_2 /Hydraffin WG PAC suspensions exhibited a pH of about 3.5, while the pH of

the TiO_2 /Merck PAC suspensions was in the range of 6.5 to 7 ("Deionized water" and "0.5 g/L NaCl" in Table 2). Replacing the NaCl with 0.5 g/L NaHCO_3 increased the pH in the suspensions to 8.0 and 8.4 for Hydraffin WG and Merck

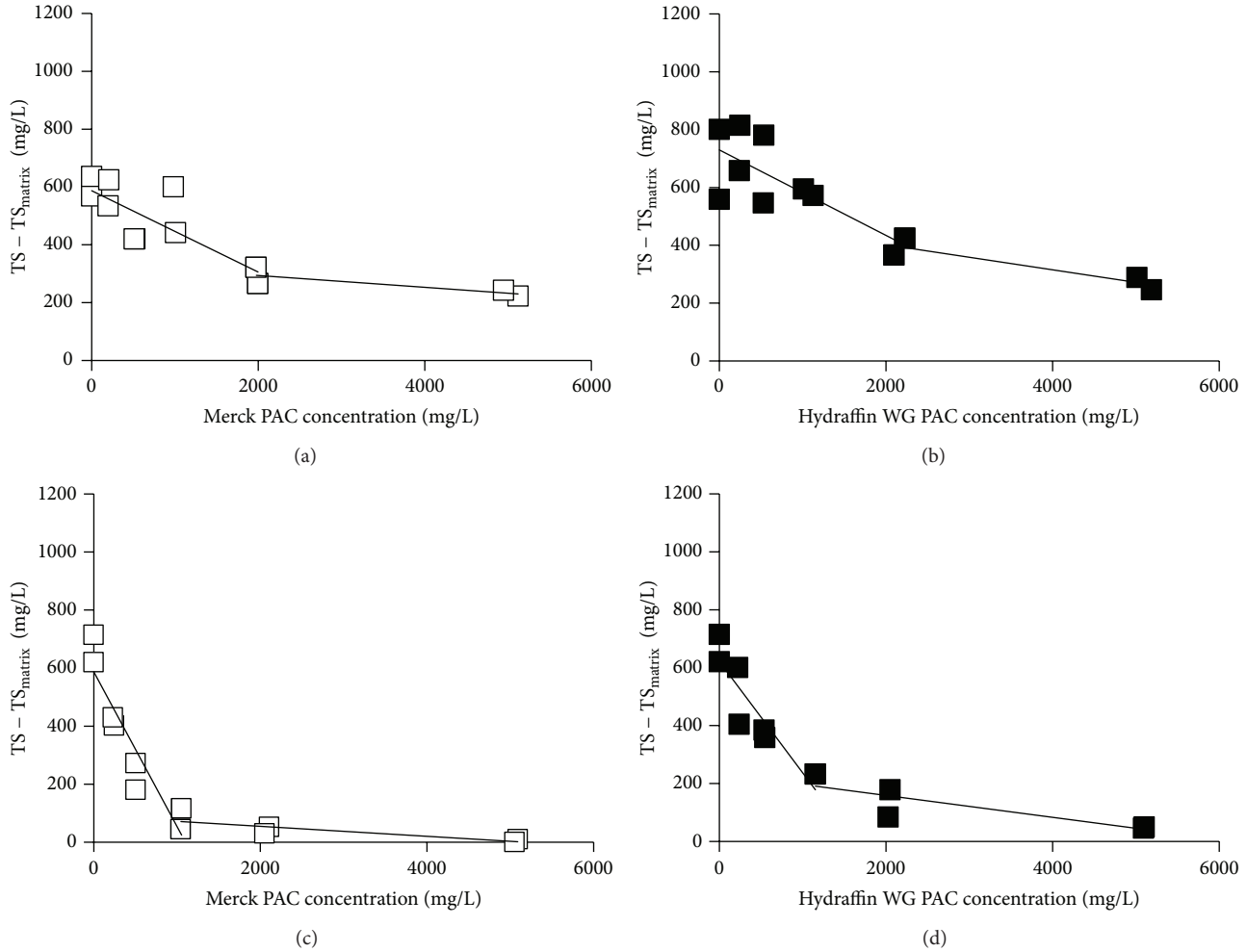


FIGURE 6: Total solids concentrations (corrected for TS concentrations of the matrices) in 1 g/L TiO_2 suspensions containing different amounts of Merck PAC or Hydriffin WG PAC in a matrix of biologically pretreated greywater ((a), (b)) and secondary municipal effluent ((c), (d)) subsequent to vacuum filtration over spunbond polypropylene fabrics.

TABLE 2: Impact of aqueous matrix and PAC type on pH of suspensions containing 1 g/L TiO_2 and 2 g/L PAC.

Matrix	pH	
	Merck PAC	Hydriffin WG PAC
Deionized water	6.5	3.5
0.5 g/L NaCl	6.9	3.6
0.5 g/L $NaHCO_3$	8.4	8.0
Biologically treated greywater	8.1	7.4
Secondary municipal effluent	7.7	7.1

PAC, respectively (Table 2). Also in the secondary municipal effluent and in the biologically treated greywater, the pH was above neutral (7.1 to 7.4 for Hydriffin WG and 7.7 to 8.1 for Merck PAC). This is due to some alkalinity in the biologically treated wastewaters predominantly represented by hydrogen carbonate in the pH range of 7 to 8.

Flocculation of the TiO_2 nanoparticles might also have an impact of the wastewater matrix on precoat filtration

of nanoparticles. The extent of flocculation is affected by different wastewater constituents as investigated in the first part of this study and also in other studies (e.g., [5]). TiO_2 nanoparticles agglomerated to larger aggregates are retained more efficiently in the PAC filter cake than single nanoparticles. Efficient flocculation of TiO_2 nanoparticles was observed in this study with NaCl concentrations of 1 g/L (Figure 2(a)) and $NaHCO_3$ concentrations between 0 and 1 g/L (Figure 3(a)) when no humic acid was present. Addition of humic acid sodium salt was deteriorating flocculation caused by NaCl or $NaHCO_3$ (Figures 2 and 3) except when pH was between 5.5 and 6.0 (Figure 2(b)). Flocculation impaired by the presence of humic substances might be an explanation for low precoat filtration efficiency in biologically pretreated greywater. However, also secondary municipal effluent contains humic substances formed during biological treatment. As secondary municipal effluent was an excellent matrix for precoat filtration of TiO_2 nanoparticles with Merck PAC in concentrations above 1 g/L (Figure 6(c)), the presence of humic substances cannot be the explanation for deterioration

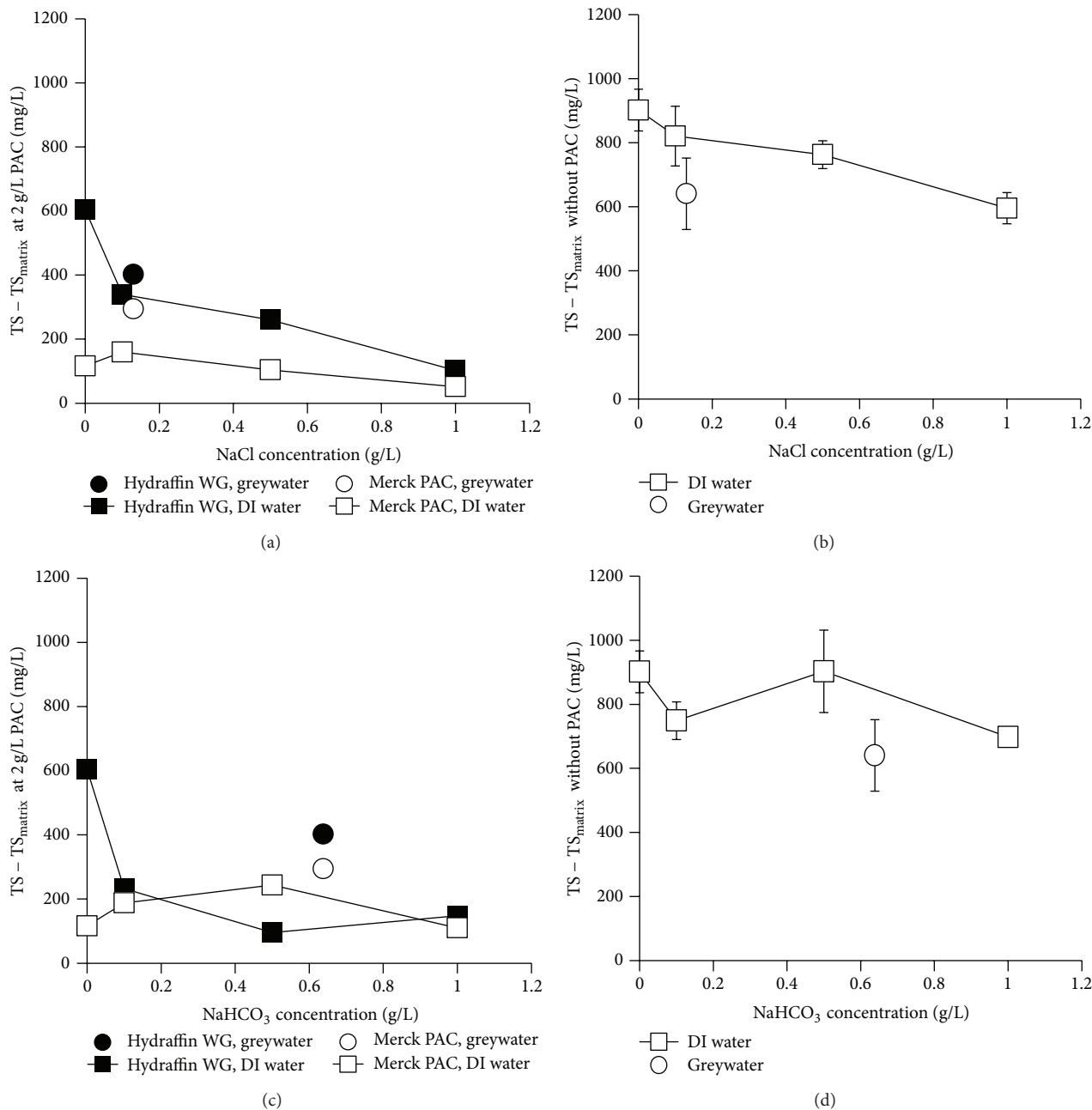


FIGURE 7: Total solids concentrations (corrected for TS concentrations of the matrices) in 1 g/L TiO₂ suspensions containing 2 g/L PAC ((a), (c)) and in 1 g/L TiO₂ suspensions without any PAC ((b), (d)) at different NaCl ((a), (b)) and NaHCO₃ concentrations ((c), (d)) subsequent to vacuum filtration over spunbond polypropylene fabrics.

of precoat filtration. Moreover, TiO₂ flocculation in biologically pretreated greywater was shown to be considerable [5].

Figure 7 summarizes the results displayed in Figures 4, 5, and 6. In Figures 7(a) and 7(c), only the TS concentrations in the filtrates of suspensions containing 1 g/L TiO₂ and 2 g/L PAC are shown depending on the NaCl (Figure 7(a)) and on the NaHCO₃ concentrations (Figure 7(c)). As the biologically treated greywater used in this study was not analyzed for chloride or hydrogen carbonate, chloride and alkalinity analyses (2.23 mmol Cl⁻/L, 7.6 mmol H⁺/L acid-neutralizing

capacity) of another biologically treated greywater sample from the same source [5] were used for calculating approximate NaCl and NaHCO₃ concentrations. The circles in Figures 7(a) and 7(c) which were based on these approximations indicate that precoat filtration of TiO₂ in a biologically treated greywater matrix is less efficient than in the respective NaCl or NaHCO₃ matrices prepared with deionized water. On the other hand, lack of TiO₂ flocculation cannot be looked at as a reason for inefficient precoat filtration with PAC, because in biologically pretreated greywater, TiO₂ flocculation was very

pronounced as shown by the pipet method in another study [5]. Overall, replacement of NaCl with NaHCO₃ impaired TiO₂ precoat filtration with the Merck PAC but enhanced precoat filtration with Hydrafine WG PAC. Therefore, in the NaHCO₃ matrix, TS concentrations in the filtrates obtained with both PAC types did not differ largely.

When TiO₂ suspensions in different matrices were filtered over the polypropylene fabric without addition of PAC (Figures 7(b) and 7(d)), increasing flocculation due to increased salt concentrations obviously increased particle retention. It has to be noted that in these experiments there was no sufficient time for complete flocculation, because the TiO₂ suspensions in different matrices were filtered over the fabric filters immediately after preparation of the suspensions after a very short stirring period. Nevertheless, with increasing NaCl (Figure 7(b)) and NaHCO₃ concentrations (Figure 7(d)) increasing amounts of TiO₂ were retained on the filter. The TiO₂ suspensions in biologically treated greywater showed a better particle retention than expected from the assumed respective NaCl and NaHCO₃ concentrations of the greywater when they were not precoated with PAC. This comparably good TiO₂ retention can also be explained by good flocculation of TiO₂ particles in the biologically pretreated greywater.

In a previous study [22] about the hybrid process comprising PCO and PAC adsorption (1 g/L PAC combined with 1 g/L and 5 g/L TiO₂, resp.) with separation and recovery of the photocatalyst/PAC mixture by centrifugation, it was shown that the efficiency for DOC removal from biologically pretreated greywater with a UV dose of 11 Wh/L was only slightly decreasing for both TiO₂ concentrations from 84% (with fresh TiO₂/PAC mixtures) to about 71% when the TiO₂/PAC mixtures were reused for the 13th time. It has to be stated that the centrifugation supernatants in that study, although not analyzed for total solids, were similarly turbid by visible inspection as the filtrates in this study when 1 g/L TiO₂ was precoated with 2 g/L PAC. Therefore, the loss of efficiency of the PCO/PAC hybrid process during consecutive solids reuse cycles can be attributed to a slight loss of photocatalyst due to incomplete recovery of photocatalyst by centrifugation.

4. Conclusions

- (1) Flocculation of TiO₂ nanoparticles is influenced by ionic strength and pH. In the neutral and slightly basic pH range, humic acid prevents the nanoparticles from agglomeration. Due to complexity of wastewater matrices, the flocculation of TiO₂ particles in real wastewaters is hardly predictable.
- (2) Addition of 2 to 5 g/L PAC as a precoat to 1 g/L TiO₂ nanoparticle suspensions substantially increases nanoparticle retention by filter fabrics which are usually not able to retain the nanoparticles.
- (3) Efficiency of TiO₂ nanoparticle precoat filtration is also influenced to some extent by selection of the PAC type and by the concentrations and types of constituents of the solution matrix.
- (4) Precoat filtration of TiO₂ with PAC is feasible for technical application in the photocatalytic oxidation process, because in the PAC/PCO hybrid process PAC removes organic wastewater constituents by adsorption additional to photocatalytic oxidation.
- (5) Precoat filtration with PAC can retain > 90% of TiO₂ nanoparticles. It is thus a suitable pretreatment for further nanoparticle removal, for example, by membrane filtration.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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