

# Consequences of pH change on wastewater depth filtration using a multimedia filter

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## Abstract

Different media materials in a multimedia filter have the potential to trap particles of different characteristics dependent on the media-suspension particle interactions. However, the removal of particles from wastewater secondary effluent using granular media filtration is relatively poorly understood because of the complexity of the wastewater matrix. Often the wastewater treatment process is liable to undergo pH changes due to removal or addition of chemicals in the treatment chain or from biological instability which in turn may alter the wastewater characteristics. Wastewater contains a mixture of organic and inorganic components, dissolved or particulate which may influence the aggregation and deposition of suspension solids during depth filtration. Changes in wastewater pH has the potential to change the wastewater matrix and media surface properties hence affecting aggregation and deposition in wastewater filtration. This study investigated how pH change affects wastewater filtration by monitoring zeta potential, aggregation and deposition of solids. The wastewater and filter media were also characterised over a range of pH from 1-13. Aggregation and deposition of wastewater solids was found to be most efficient near neutral pH. This was not concurrent with the conditions of lowest net charge in the system.

## 23 **Keywords**

24 Multimedia; depth filtration; surface charge; zeta potential; aggregation; deposition

### **Nomenclature**

|          |                                  |              |   |
|----------|----------------------------------|--------------|---|
| $F_{DL}$ | Double layer force               | $d_p$        | Suspension particle diameter            |
| EDL      | Electric double layer            | $\zeta$      | Zeta potential                          |
| DLVO     | Derjaguin-Landau-Verwey-Overbeek | $\zeta_g$    | Media zeta potential                    |
| ZP       | Zeta potential                   | $\zeta_p$    | Particle zeta potential                 |
| M        | Molar                            | $\epsilon_0$ | Permittivity of free space              |
| TSS      | Total suspension solids          | $\epsilon_r$ | Relative permittivity                   |
| PSD      | Particle size distribution       | $\kappa$     | Debye reciprocal double layer thickness |
| IEP      | Isoelectric point                | $\delta$     | Separation distance                     |
| ES       | Effective size                   | $\psi$       | Filter media sphericity                 |
| UC       | Uniformity coefficient           | $\epsilon$   | Media bed porosity                      |
| V        | Potential energy                 | $R^*$        | $d_p d_m / (d_p + d_m)$                 |

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## 26 **1. Introduction**

27 Filtration of wastewater is becoming ever more important as regulations such as the Water  
 28 Framework Directive requires wastewater discharged to the environment to reach higher

water quality standards. Suspended solids present in discharged wastewater may pollute the natural environment through the presence of nutrients, such as phosphorus, that may cause eutrophication in surface waters. Suspended solids also act as a support for survival and transport of viruses and bacteria, which can attach onto particle surfaces (Walshe et al., 2010) and can subsequently pose a risk to human health. Granular media filtration is one of the important tertiary treatments used to remove particulate materials from treated wastewater effluents. Filtration efficiency depends on physicochemical properties of the particulates and the porous medium (size, shape, chemical composition, surface properties), the suspension chemistry (pH, ionic strength, ionic composition), the biotic activity, the hydrodynamic conditions, and the ambient temperature (Bradford and Torkzaban, 2008; Petosa et al., 2010; Yuan et al., 2012). Wastewater treatment is often accomplished by removal or addition of chemicals that may result in a pH change (Shanahan and Semmens, 2015). For example, through the use of ferric sulphate for coagulation, phosphorous or odour removal (Alias and Assari, 2007; Zhu et al., 2012). A pH change may alter the wastewater matrix as well as the characteristics of wastewater solids and subsequently compromise solids aggregation and deposition on porous media in depth filtration.

Understanding the conditions for optimum removal of suspension solids passing through porous media and the effect of pH change is of practical importance in wastewater secondary effluent polishing. It has been shown before that one of the most important controlling parameters for deposition of solids in depth filters are the electric double layer (EDL) forces and the London-van der Waals forces (Stumm and Morgan, 1996; Tien and Ramarao, 2007). The force balance between repulsive and attractive forces is summarised in the Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction model which has been successfully applied for filtration of drinking water (Bradford and Torkzaban, 2008; Yuan et al., 2012). Because of the nature of wastewater, other forces such as hydrogen bonding, hydrophobic interaction,

capillary forces, steric interactions (Bradford and Torkzaban, 2008; Tien and Ramarao, 2007; Yuan et al., 2012), polymer bridging (Elimelech et al., 1995; Lee et al., 2014) and biotic colloidal behaviour (Yuan et al., 2012) may also play a significant role in aggregation and deposition. This uncertainty in the nature of interactions constitutes a key knowledge gap that exists between drinking water filtration processes and the growing practice of wastewater filtration.

The purpose of this study was to therefore investigate the effect of changing the pH of wastewater and porous media on the aggregation and deposition of solids in a multimedia filter treating real wastewater secondary effluent. The filter was used as it combines media of different density and grain size, with the grain size decreasing in the direction of flow. This enabled the impact of media properties on filtration over a range pH to be determined. Different media materials also have the potential to trap particles of different characteristics dependent on the media-suspension particle interactions. In addition to altering the wastewater solids characteristics, pH adjustment causes a number of other interactions with the wastewater, such as with the alkalinity (Shanahan and Semmens, 2015), heavy metals (Corbitt, 1998; Freeman, 1989; Fu and Wang, 2011) and the microbes (Shanahan and Semmens, 2015). Extremes of pH from very low to high was investigated as a means of altering the particle surface charge, which was hypothesised to be the driving force for aggregation and deposition.

## **2. Materials and Methods**

A filtration pilot plant located at the Cranfield Sewage Treatment Works (United Kingdom) filtering real secondary treated wastewater effluent was used for this research. Upstream wastewater treatment comprised preliminary grit removal, primary sedimentation, alum dosing, trickling filters, and secondary sedimentation.



## 2.1 Filter Equipment Setup

The wastewater secondary effluent from the discharge well was pumped to a mixed holding tank for pH adjustment prior to transfer to the filter rig. The surface charge on the wastewater particles was measured using zeta potential (ZP) following pH adjustment of the wastewater under constant ionic strength, following a similar approach to that used by Kim and Lawler (2005). Sodium hydroxide and hydrochloric acid of 2 molar (2M) strength was used to adjust the wastewater pH. In this research, a quadruple granular media filter adapted from a FilterClear pressure filtration system (BluewaterBio, UK) was used to investigate removal performance of each media at different pH. The pilot filter consisted of four columns (clear acrylic Perspex, 74 mm internal diameter and 700 mm height) connected in series, each containing 100 mm media depth of either anthracite, flint, alumina and magnetite respectively; the detailed description of the filter equipment is found in Ncube et al. (2016).

The media properties were as follows; anthracite (Effective Size (ES)=1.12 mm, Uniformity Coefficient (UC) =1.49, loose bed porosity ( $\epsilon_0$ ) = 0.51, filter grain sphericity ( $\psi$ ) = 0.54), flint (ES=0.55 mm, UC =1.42,  $\epsilon_0$  = 0.52,  $\psi$  = 0.64), alumina (ES=0.58 mm, UC =1.13,  $\epsilon_0$  = 0.55,  $\psi$  = 0.63) and magnetite (ES =0.26 mm, UC =1.54,  $\epsilon_0$  = 0.47,  $\psi$  = 0.84) respectively. The wastewater in the holding tank was continually mixed by a submersible centrifugal pump to keep the solids in suspension and maintain a uniform influent to the filter. The wastewater was pumped from the holding tank to the filter columns by a variable rate peristaltic pump (620 Industrial LoadSure, Watson Marlow, UK) through a flowmeter (SM6000, IMF Electronic Ltd, Germany) to monitor the flow rate.

Online instruments (flowmeter, pressure sensors and turbidity monitors) were connected to the pilot rig and the output analogue signals were logged into a laptop by an analogue-digital data logger. The columns were fitted with pressure transducers (PN2026, IMF Electronic Ltd,

Germany) at the inlet and outlet of filter to measure the pressure drop across the filter bed. The sampling points were positioned at the influent and effluent of the filter as well as between the columns. The influent and effluent turbidity was monitored by probes placed in the holding tank and the effluent pipe (Turbi-Tech 2000LS and WaterWatch 2310, Partech, UK, respectively). The filter was run at a constant filtration rate of  $25 \text{ m h}^{-1}$ , as used for the full-scale quadruple media filter. Grab samples were collected on an hourly basis for total suspended solids (TSS), pH and ZP. After a five hour filter run, the columns were backwashed individually by an air scour for two minutes followed by high rate water wash for 10 minutes at  $60 \text{ m h}^{-1}$  using filtered wastewater which enabled at least one third bed expansion.

## **2.2 Solid deposition measurements**

Filtration experiments were designed to investigate the particle deposition on media materials at different pH by measuring the solids load retention of the filter treating wastewater secondary effluent. The TSS was determined using gravimetric analysis (Method 290D, (APHA et al., 2005) and turbidity was measured using a turbidity meter (2100 Lab Turb, Hach, US).

## **2.3 Wastewater Particle Aggregation**

Wastewater was flocculated at different pH to understand the effect of different particle surface charge on particle aggregation. The sample used for flocculation studies was collected from the pilot filter influent and partitioned into thirteen 800 mL samples for flocculation in a jar tester. The wastewater pH was adjusted using either sodium hydroxide or hydrochloric acid just prior to flocculation and particle size analysis. The wastewater pH was measured before and after flocculation; ZP was measured using a zetasizer (Zetasizer Nano ZS, Malvern, UK) from samples extracted before and after flocculation. Wastewater was flocculated on a jar tester at 30 RPM using a rectangular paddle. Online particle size analysis

was carried out using a laser diffraction instrument (Mastersizer 2000, Malvern, UK) measuring floc growth each minute for up to 100 minutes of flocculation following a similar protocol used before in Jarvis et al (2005b). The particle sizes were analysed in the classification of National Science Foundation/American National Standards Institute (NSF/ANSI) Standard categories for particles in water: 0-5, 5-15, 15-30, 30-50 and 50-100  $\mu\text{m}$  (NSF/ANSI Standard 42 and 53).

#### **2.4 Media and wastewater zeta potential measurement**

The surface charge of wastewater solids and media materials was characterised at different pH to assess optimum conditions for aggregation and deposition using ZP as a surrogate for surface charge. A wastewater sample was collected from the pilot filter effluent and partitioned into subsamples of equal volume. The pH of the subsamples was adjusted incrementally between 1 and 13. Each sample was mixed in a closed bottle by shaking vigorously for one minute before being left overnight to stabilise. The following day the pH, ZP and particle size distribution (PSD) were measured on the stabilised samples. The pH was measured using a pH meter (Jenway 3540, Bibby Scientific, UK), ZP by a zetasizer and the PSD by a Spectrex (PC-2200, Spectrex Corporation, California).

The media surface charge characteristics (ZP) were measured for the four-different media. The media were milled to a uniform size range between 0 – 20  $\mu\text{m}$  prior to analysis to enable processing through the zetasizer using a method adapted from Fuerstenau et al (1983). The ZP measured on milled samples was also identical to that seen for the media fines. The media was then suspended in either ultrapure water or wastewater secondary effluent to understand how the wastewater influenced the surface charge on the media compared to a pure system. Here, wastewater was first filtered through a 0.45  $\mu\text{m}$  filter paper to remove the particulate component prior to addition of the media (Schrader et al., 2005; Yun et al., 2011). A single large sample of each media was initially prepared by adding 50 g of powdered media to 2 L

suspension liquid and shaking the mix in a closed bottle, then the supernatant was partitioned into equal subsamples. The supernatant contained particles that were <3 µm which ensured that the particles were of an appropriately small size for ZP measurement.

## 2.5 DLVO Forces

The DLVO interactions are the combined effect of repulsive electric double layer (EDL) forces ( $F_{DL}$ ) and attractive London-van der Waals forces ( $F_v$ ) and were used here to describe aggregation of particles and attachment or deposition on to filter media. The expressions used here assumed a suspension particle to be very small compared to media grains such that the particle is modelled as a small sphere near a very large collector, approaching a flat surface. The force balance used as given by Janssen et al. (1995) was:

$$V(\delta) = 2\pi\epsilon\epsilon_0\xi_p^2R^*\ln[1 + \exp(-\kappa\delta)] - \frac{HR^*}{12\delta} \quad (1)$$

In this work the particle and media diameters ( $d_p$  and  $d_m$ ) and particle ZP ( $\zeta_p$ ) were measured directly.  $R^*$  is defined by  $R^* = d_p d_m / (d_p + d_m)$ . The constant parameters were evaluated as: Debye reciprocal double layer thickness  $\kappa = 1.0 \times 10^8 \text{ m}^{-1}$ ; relative permittivity of water  $\epsilon_r = 80$ ; permittivity of free space  $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ ; (Stumm and Morgan, 1996); Hamaker constant  $H = 1.4 \times 10^{-20} \text{ kgm}^2\text{s}^{-2}$  (Bai and Tien, 1997); and the surface-to-surface separation ( $\delta$ , m) was varied. Attractive forces are conventionally represented as negative hence the minus sign on the second half of the term in equation (1). Apart from the adhesive forces, there are other forces acting on particles as the water flows through the porous media, such as the hydrodynamic forces associated with a scouring effect on deposited solids (Bai and Tien, 1997; Ncube et al., 2016). However, such forces were assumed not to vary at any pH investigated since the filter hydraulic loading rate was maintained constant.

### 3. Results and Discussions

#### 3.1 Filter performance at different pH

The highest level of filter performance occurred at the wastewater pH range 6-8, peaking at neutral pH as shown by the highest solids load retention (Figure 1a). There was reduced solid load removal at pH less than 6 and above 8 (Figure 1a). The solid load retention was also found to vary significantly in the ZP range from -11 to -13 mV, however retention remained stable, but low, for ZP from -11 to +0.2 mV (Figure 1b). Therefore, the filter removal effectiveness seemed more dependent on pH and less so on ZP since in the pH range 3.5 to 10 the ZP was stable around -13 mV while solid load retention varied significantly. The solids deposition was highest close to the neutral pH where ZP was -13 mV.

The solids retention of each of the media layers closely matched that of the overall filter, with high solids retention realised around neutral pH (at ZP of -13 mV), and lower retention for pH <6 and >8 (Figure 2). The solids retention in the four media materials varied in the same way with pH irrespective of the media material. Therefore, the surface properties of the four different media (anthracite, flint, alumina, and magnetite) seemed to have little influence on the selectivity of particle removal from the wastewater. Alumina and magnetite had relatively better solids retention at the pH extremes compared to anthracite and flint (Figure 2). Alumina and magnetite were comparably smaller media and hence were able to retain more small particles, which had their largest concentration at the pH extremes. However, the different media materials have an obvious practical benefit because of the different media sizes and densities that enable the filter bed to stratify such that the filter has a tapered void after backwash. Small media of high density forms the bottom filter layer while progressively larger media of lower density overlays one another producing a filter of ideal media structure.

The filter headloss increased with filtered water volume, with the rate of increase changing with wastewater pH (Figure 3a). The filter runs fed with high pH wastewater developed more headloss than those at low pH (Figure 3a and b). This corresponded to low solid load retention (2.4g) at low pH (pH 2-4), with increasing retention (11.4g) around neutral pH (Figure 3Error! Reference source not found.c). At higher pH, the headloss development was less related to the solids retention (as shown in Figure 3c). Fewer solids were retained at pH 10.3, 11.5 and 12.5 than at neutral pH yet the headloss developed was much greater than for the lower pH ranges (Figure 1a and 3). Therefore, pH change influenced solids retention and headloss development, with changes in pH likely causing changes in the wastewater solids characteristics, as discussed in the next section.

### **3.2 The characteristics of wastewater secondary effluent at different pH**

Retention of solids in the filter is a function of both the interactions of the particle with the filter media and the solids loading onto the filter. Therefore, to understand more about the filter performance, the characteristics of wastewater were investigated at the different pH tested. At the environmental wastewater pH ( $7.6 \pm 0.1$ ), the influent TSS was  $46 \pm 3 \text{ mgL}^{-1}$  while the turbidity was  $24.8 \pm 0.3 \text{ NTU}$ . The secondary treated wastewater was also measured to have a biological oxygen demand ( $\text{BOD}_5$ ) of  $13 \pm 3 \text{ mgL}^{-1}$  and a chemical oxygen demand (COD) of  $83 \pm 8 \text{ mgL}^{-1}$ . Typical treated wastewater also contains heavy metals such as chromium, copper, cyanide, cobalt, manganese, zinc and lead (Burton et al., 2003). There were small changes in both TSS and turbidity for samples adjusted to low pH but a more significant increase was observed as the pH was increased above 9 (Figure 4a). Both the TSS and turbidity rose steeply between pH 9 and 11.5; these then dropped with further pH increase beyond 11.5. The rise in TSS and turbidity was attributed to hydroxide or carbonate precipitation; the various metals in wastewater have different minimum solubility pH, hence

precipitation was observed over a range of pH (Freeman, 1989; Fu and Wang, 2011; Stumm and Morgan, 1996).

At pH >9, the solids retention was lower than at neutral pH (Figure 1a) although the solids concentration onto the filters was high (Figure 4a). The low solids retention was most likely due to hydroxide precipitates not being easily filterable as they are weak and fragment under high shear forces (Freeman, 1989). Beyond pH 11.5, the TSS and turbidity dropped as the hydroxides became more soluble again due to their amphoteric nature (Fu and Wang, 2011). The amphoteric character of hydroxides means that they can go back into solution at high pH. This presents problems in metal removal from mixed metal suspensions since the ideal precipitation pH of one metal may put another back into solution (Baltpurvins et al., 1996; Fu and Wang, 2011).

The surface charge of wastewater solids was measured using zeta potential to determine its influence on solids retention in the filter. At the different pH investigated, the wastewater was predominantly negatively charged. The zeta potential moved from close to 0 mV at pH 2 to -17 mV at pH 13, with a ZP of  $-13.9 \pm 0.2$  mV at the normal wastewater pH ( $7.6 \pm 0.1$ ) and an isoelectric point (IEP) at  $\text{pH } 1.80 \pm 0.02$  (Figure 4b). This result was consistent with results reported previously for treated wastewater with ZP of -14 mV at pH  $7.2 \pm 0.2$  (Yun et al., 2011) and an IEP at pH 2-3 for bacterial flocs (Montgomery and Consulting Engineers Inc, 1985), and a ZP of -12.5 to -15 mV for a secondary wastewater sample between the pH range 4-8 (Schrader et al., 2005).

The effect of the different ZPs on particle size and concentration was then examined by measuring the wastewater floc size. The pH change resulted in alteration of the PSD in the wastewater due to a change in the balance of particle aggregation, breakage and concentration in the wastewater as well as other bio-chemical factors (Figure 4c). For small particles

between 5-15  $\mu\text{m}$ , the lowest count was 5,800 particles/mL at the normal wastewater pH, increasing to up 9000 particles/mL at both extremes of pH (Figure 4c). Conversely at the normal wastewater pH, larger particle size classes registered their highest counts at neutral pH while the lowest particle counts were seen at the extremes of pH (Figure 4c). It was apparent that particles were aggregating or fragmenting from one size class to another as the total particle count in the system remained consistent across all pH (minimum =  $9.6 \times 10^3$ , average =  $10.4 \times 10^3$  and maximum =  $11.4 \times 10^3$  particles per mL). It would therefore seem that the hydroxide precipitates enmeshed and aggregated with existing particles at pH >9 hence this caused no significant change in particle count but caused a significant increase in particle volume and TSS.

The relatively low number of small particles and the higher number of large particles at the natural wastewater pH when compared to the extremes of pH indicated optimum aggregation at that pH. Optimal filter deposition was also found around the pH range 6-8 or neutral pH region (Figure 4a), consistent with aggregating/larger particles being easier to remove by filtration than stable, smaller ones (Burton et al., 2003). Therefore, better particle aggregation and deposition (Figure 4c and Figure 1a) was observed under conditions when the ZP was  $-13.9 \pm 0.2$  mV rather than under conditions of near zero surface charge (the IEP was at pH  $1.8 \pm 0.2$ ). These results were contrary to what would be predicted from DLVO theory, where optimum particle aggregation would be expected near the IEP and where the wastewater particles would have minimum repulsion. The non-congruency between the ZP and PSD measurement suggested that there was some other mechanism responsible for the aggregation of particles in wastewater other than DLVO interactions. Based on similar findings, Zita and Hermansson (1994) found DLVO theory alone could not explain aggregation in wastewater flocs in municipal wastewater. Their observations suggested that biological mechanisms and interactions were more important. The present research has extended this further to show that



the mechanisms in wastewater filtration were also strongly influenced by non-charge driven processes.

The complex nature of wastewater, with considerable amounts of dissolved organic matter and a varied consortium of particles and organisms promote other interactions. In addition, as wastewater biosolids are usually characterised as being highly porous, loosely connected aggregates with an irregular structure (Jarvis et al., 2005a), the primary constituent particles in wastewater flocs can be at separation distances where the DLVO interactions may be less significant and long range structural forces dominate. Such forces were dominant in promoting aggregation at natural pH, where the wastewater is unaltered in its environmental state. These forces are hydration, hydrophobic and steric interactions which act over longer ranges (Elimelech et al., 1995). Studies have shown microbes forming bacteria-floc interfaces or secretions that sterically aggregate wastewater flocs (Sheng et al., 2010; Zita and Hermansson, 1994) or bio-polymer bridging and floc forming bacteria (such as filamentous or saprophytes) bridge particles together (Lee et al., 2014). Additionally, low or high pH may inactivate microbes and alter the organic compounds due to reactions with  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions, hence altering the structure of the wastewater, therefore inhibiting the formation of biological flocs in comparison to the neutral pH condition. Aggregation of particles is a desirable feature in depth filtration, it upgrades small particles (which are difficult to remove) to larger particles, which are easier to remove in a filter (Bradford and Torkzaban, 2008). Furthermore, particles attached onto filter grains can aggregate with particles in the flow if conditions are conducive. The resultant charge interactions between the filter media and the particles being filtered were then investigated to determine further whether DLVO forces were of importance in the subsequent capture of particles.

### 3.3 Filter media zeta potential

To understand further the interaction between the wastewater suspended solids and the media materials during filtration, the surface charge of the media was also analysed at different pH. The results were broadly in line with previous analysis of similar systems. The anthracite suspensions in deionised water had an IEP at pH 5.7 (Figure 5a). Anthracite has previously measured with an IEP of pH 3-6 for material derived from pulverised coal sourced from various locations (Siffert and Hamieh, 1989). Flint is a mineral silicon oxide and its IEP was determined to be at pH 1.4 (Figure 5b) which is in close agreement with values measured previously at pH 1.8-2.5 (Kosmulski, 2014) and less than pH 2 (Kim and Lawler, 2005). Alumina was measured with two IEP's at pH 3.3 and 8 (Figure 5c). Other studies have measured IEPs at pH 8 or 9 (Sprycha, 1989), at pH 8.6 and 5.4 (Gulicovski et al., 2008) and in the range pH 2-5 (Chera et al., 2007). It was thought that the presence of impurities or surfactants in the alumina used in this study were the reasons why the mineral had multiple IEPs (Chera et al., 2007; Gulicovski et al., 2008). The magnetite suspensions had an IEP at pH 2 (Figure 5d). This was different to previous studies that have determined the IEP at pH 6 (Sun et al., 1998) and at pH 5 (Erdemoğlu and Sarikaya, 2006). This was likely to have been due to the differences in the mineral purity of the magnetite through inclusion of surfactants or heavy metals (Erdemoğlu and Sarikaya, 2006).

When the media were suspended in filtered wastewater, the IEP moved to a similar value to that observed for the wastewater alone (IEP at pH 2, 1.7, 2 and 2.3 for anthracite, flint, alumina and magnetite respectively) (Figure 5). In other words, the ZP of the media in wastewater closely matched that of wastewater (Figure 4b). This concurs with previous research which has shown how organic compounds present in the system may influence the characteristics of suspension particles (Yun et al., 2011). This occurs because organic matter adsorbs onto particles altering the surface properties, thus changing the ZP of the particle to

match that of the organic matter (Petosa et al., 2010; Chera et al., 2007; Erdemoğlu and Sarikaya, 2006; Yun et al., 2011). This finding has implications for the consideration of aggregation and deposition processes in wastewater as the organic matter alters media surface charge. In the filtration experiments (Figure 2), there were no differences in solids deposition in different media materials. From these results, it can be concluded that for wastewater granular media filtration, the media surface charge itself is not important for deposition due to its immediate transformation to match that of wastewater.

### **3.4 Particle Attachment**

Using the ZP measurements, the EDL force and the van der Waals force (Equation (1)) between particles and media was used to further assess the contribution of DLVO forces to particle deposition. Using the media and wastewater ZP, the EDL force was calculated to be 29-170 mV for median sized particles in the wastewater being filtered ( $d_{50}$  size = 32  $\mu\text{m}$ ) across the pH range 2.8-12 for all of the filter media (Figure a), assuming a separation distance of  $3 \times 10^{-10}$  m (from Bai and Tien, 1997). The van der Waals force between particles of the median size (32  $\mu\text{m}$ ) and all of the filter media was calculated as -746 mV (Figure b). Similar trends were observed in the EDL force and van der Waals force for the d10e (16  $\mu\text{m}$ ) and d90 (70  $\mu\text{m}$ ) particle sizes (Figure 6a and b). The magnitude of the attractive van der Waals force was therefore much greater than the repulsive EDL force, implying that all particles were strongly attracted to the media surface at all pH investigated with the implication that solid removal would be uniform at all pH. However, although the DLVO interactions were stable at different pH, the solid load retention varied greatly in the filtration test at different pH (Figure 1a and Figure 2).

The net force between EDL force and van der Waals force was therefore calculated at different separation distances for various particle sizes across the pH range investigated in this work (Figure 7). The potential energy was modelled for the d10 particle size (16  $\mu\text{m}$ )

(Figure 7a), for the d50 particle size (32  $\mu\text{m}$ ) (Figure 7b) and the d90 particle size (70  $\mu\text{m}$ ) (Figure 7c). The DLVO interaction potential energy profiles were similar, differing mainly in the depth of the energy barrier for different suspension particle sizes. There was no energy barrier to deposition at pH 2 at any separation distance such that all interaction would have been favourable. However, all other pH showed an energy barrier to deposition (Figure 7). The separation distance between particles and collector at which the energy barrier was encountered fell between 2-40 nm across the pH range, reaching a maximum energy barrier of 37, 73 and 155 mV at pH 12 for the d10, d50 and d90 particle sizes respectively. Despite these DLVO predictions, particle deposition was observed to occur at all pH investigated and the more favourable deposition observed around neutral pH (Figure 1 and 2), which did not coincide with the most favourable conditions for deposition based on the DLVO force balance.

The differences in the particle capture at different pH must therefore have been predominantly explained by other phenomena. Wastewater characteristically has a high concentration of organic matter components that may have biological activity (Yu et al., 2011) as well as producing irregular shaped flocs (Jarvis et al., 2008). These factors may give rise to the dominance of other forces that hold particles together in aggregates or cause attachment following deposition of solids on filter media (Petosa et al., 2010). The long-range forces and biotic activity that were thought to account for differences in particle aggregation would similarly account for differences in deposition of the solids on the porous media and particles already deposited at different pH. Based on this study, such forces appear more effective near the neutral pH based on the PSD (Figure 4c) and solid load retention (Figure 1a) at different pH. The wastewater biotic conditions were unaltered around the neutral pH whereas low or high pH may have been biocidal.

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369 Many previous studies have used model suspensions to investigate the removal efficiency of  
370 particles under different chemical conditions in depth filtration where interactions can be  
371 explicitly explained by DVLO interactions. Tufenkji et al (2004) explained the removal of  
372 *Cryptosporidium parvum* oocysts in quartz sand filter at different ZP using the DLVO forces.  
373 Likewise, other researchers (Bai and Tien, 1997; Elimelech et al., 1995; Kim and Lawler,  
374 2006) found similar results, with high removal observed at low pH values when the ZP was  
375 close to zero. In this body of work, the DLVO interaction explained the observed changes in  
376 removal efficiencies; such studies were carried out in conditions where the concentration of  
377 organic matter and biological activity were low, typical of filtration in drinking water  
378 treatment.

379 However, in this study, little removal was observed at low pH when the product of the ZP for  
380 the media and suspension particles was small, high removal was seen around neutral pH, and  
381 low removal was also seen at pH greater than the neutral pH. Therefore, in wastewater  
382 filtration, DLVO interactions did not adequately explain differences in aggregation and  
383 deposition of wastewater solids alone, rather other mechanisms such as longer range  
384 interactions, bio-polymer bridging and biotic activity were the important mechanisms. The  
385 dependence of removal efficiency on wastewater pH implies that caution has to be taken  
386 when the treatment processes alters the wastewater pH such as when dosing acids, bases or  
387 coagulant to avoid impacting wastewater filtration performance (Schrader et al., 2005).  
388 Therefore, in wastewater granular media filtration, high solid removal would be achieved  
389 when the wastewater pH is in the range 6 to 8, which is close to the neutral pH. Processes  
390 such as chemical dosing with ferric sulphate for phosphorous removal lowers the pH to acidic  
391 conditions and hydroxide precipitation to remove heavy metals using lime ( $\text{Ca(OH)}_2$ ) raises  
392 pH to alkaline conditions (Freeman, 1989). Consequently, due to the sensitivity of filtration

to pH, conditioning to neutral prior to filtration would be necessary to achieve optimal solids removal.

#### **4. Conclusions**

This study investigated the removal of solids at different pH from wastewater secondary effluent using a pilot scale quadruple media filter. The wastewater solids were found to be negatively charged (negative ZP) over a wide range of pH with an isoelectric point at pH 2.

The different media materials were also found to match the wastewater ZP when suspended in wastewater which means that the media surface characteristics were not of significance in solids removal from wastewater. The implication is that the media material in a clean bed may have their individual surface charge/properties but this change immediately on contact with wastewater during filtration.

The wastewater solids aggregation and deposition was not solely dependent on DLVO interactions being favourable, but other forces associated with the organic material were significant in particle-particle or particle-media interactions. Long-range interactions such as hydration, hydrophobic and repulsive steric interactions, bio-polymer bridging and biotic activity were also thought to be responsible for controlling wastewater aggregation and deposition in granular media filters. These forces were more effective around the neutral pH where the wastewater matrix was unaltered.

Each of the four media materials were found to remove wastewater solids, and effective retention by all media layers enabled solids to be distributed such that the entire depth of filter was used for solid retention. Consequently, the filter will have a high solid holding capacity and slow headloss development since solids were distributed throughout the depth of

filter. The quadruple media filter hence has a capacity to operate efficiently in depth filtration of wastewater secondary effluent.

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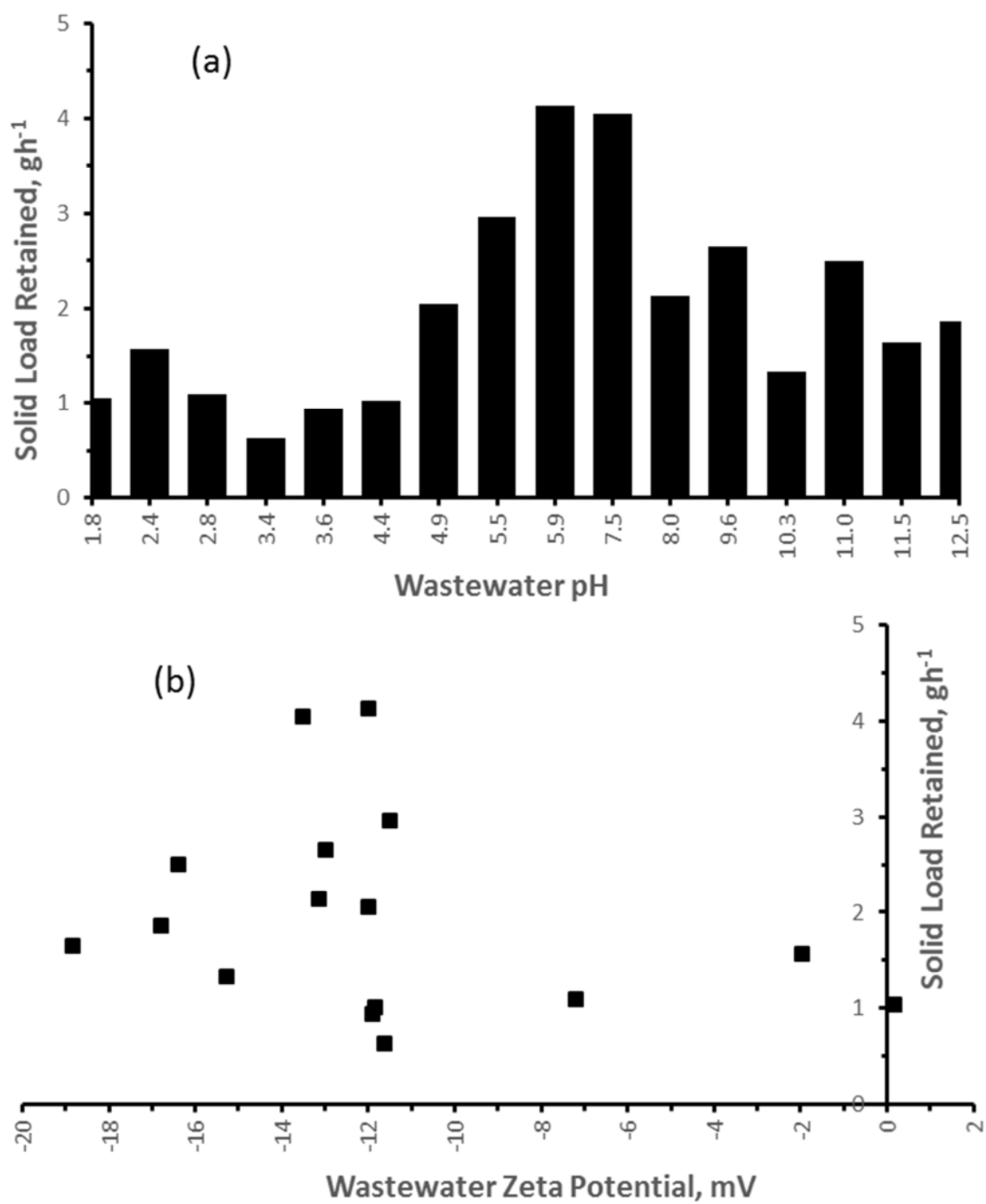


Figure 1: Solid load retention at different (a) wastewater pH, (b) wastewater ZP.

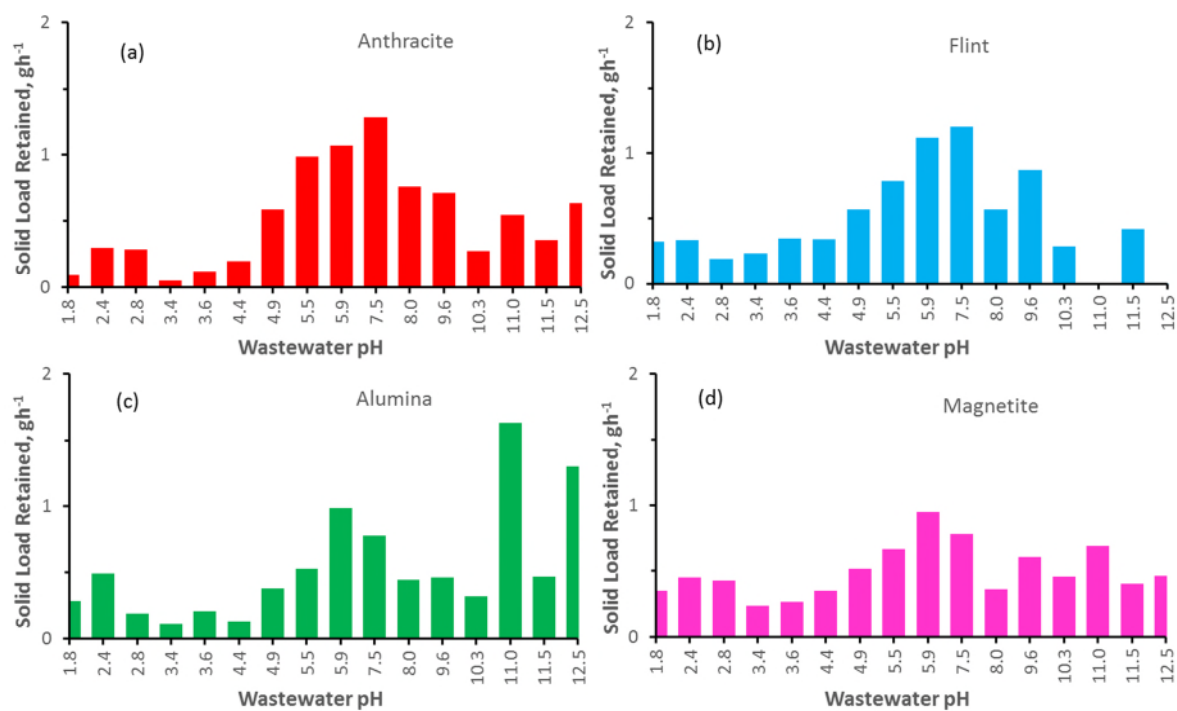
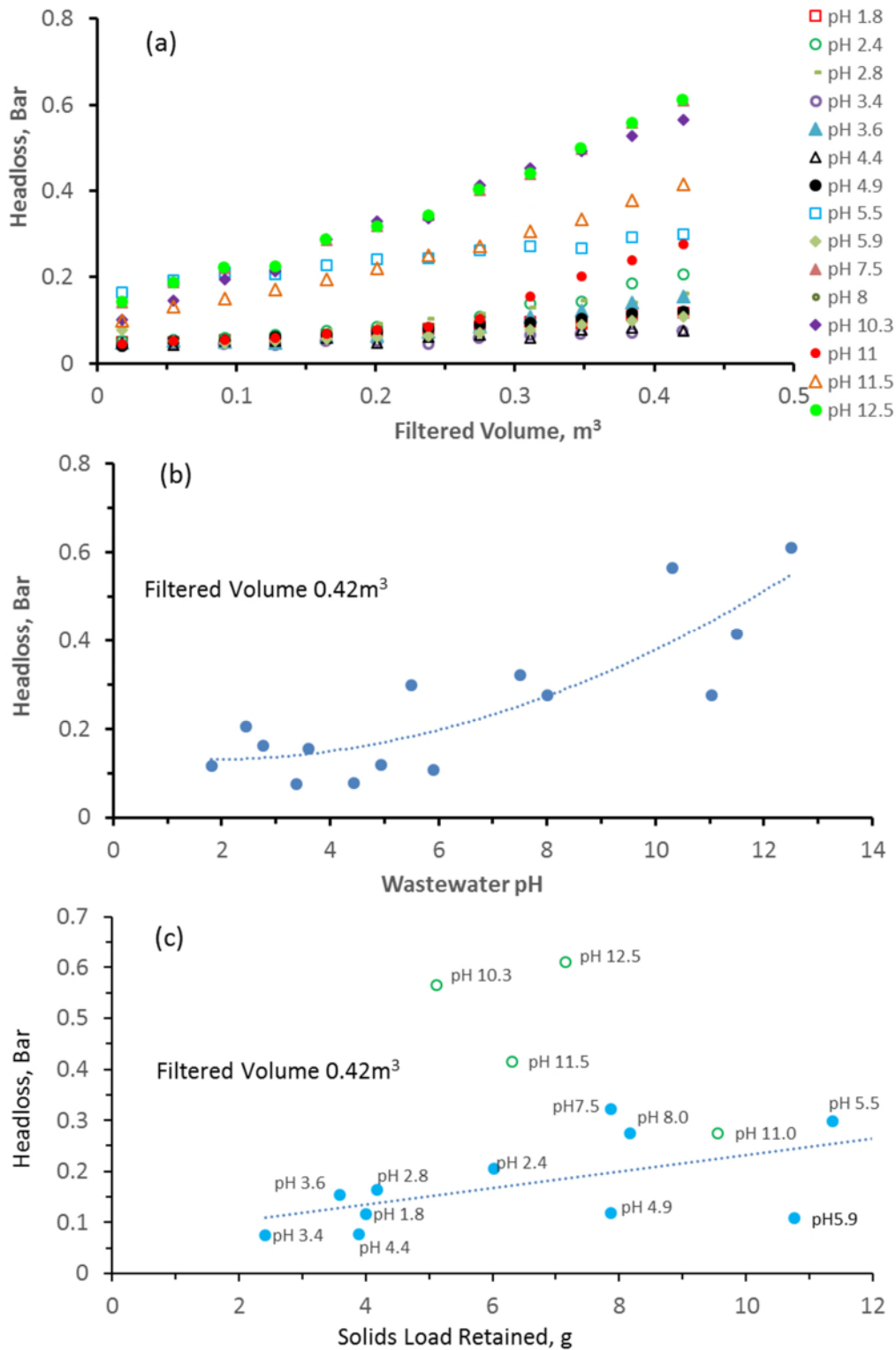


Figure 2: Solids load retention as a function of wastewater pH for the media (a) anthracite, (b) flint, (c) alumina and (d) magnetite.



547

548 Figure 3: (a) Headloss development with filtered wastewater volume at different pH for the  
 549 whole filter. (b) The filter headloss when filtered wastewater reached 0.42  $m^3$  at different  
 550 wastewater pH. (c) Headloss development with solids load retained, the full blue dots are for  
 551 pH < 9 while the empty green dots are for pH > 9 where there is precipitation.

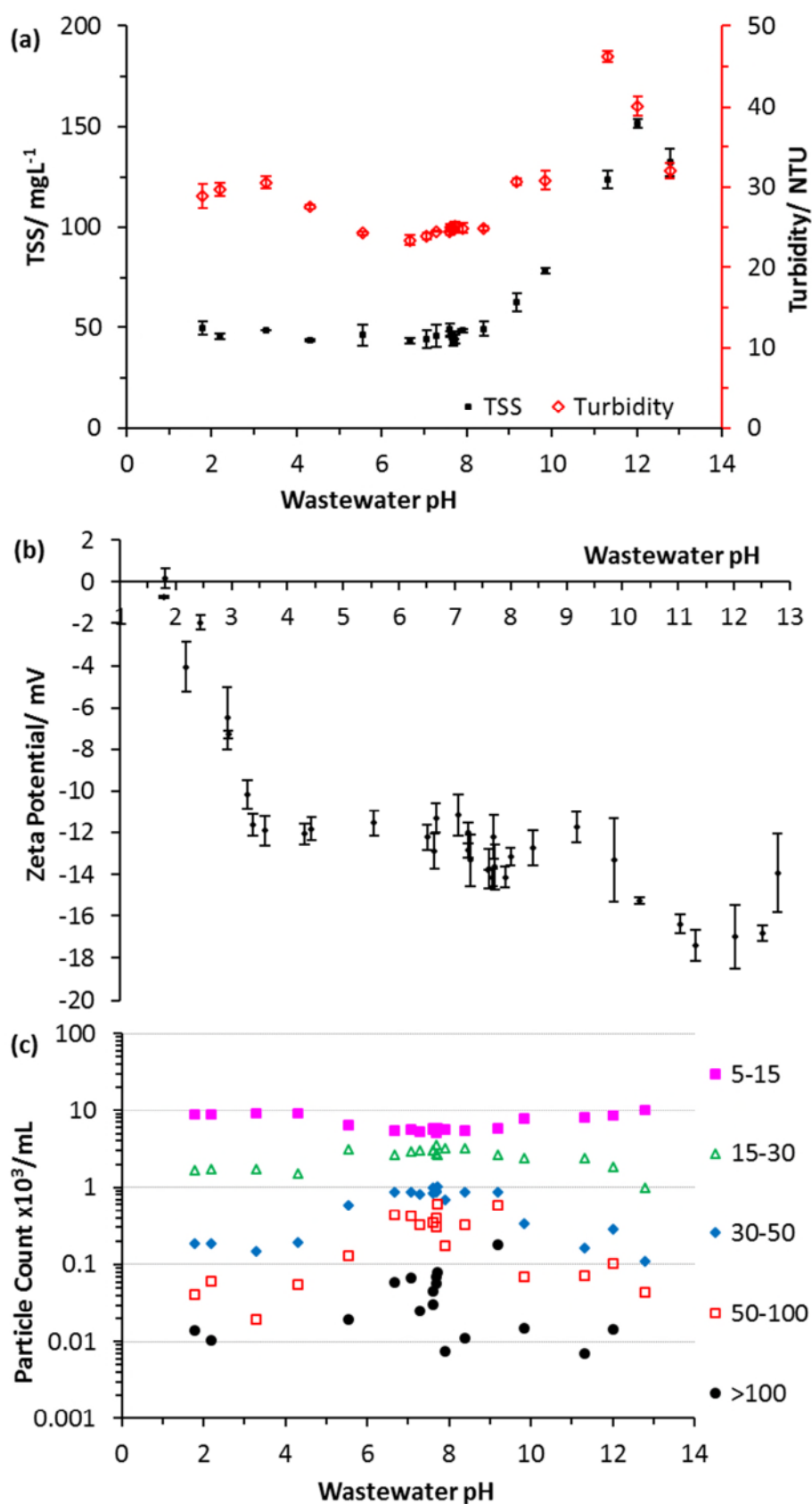
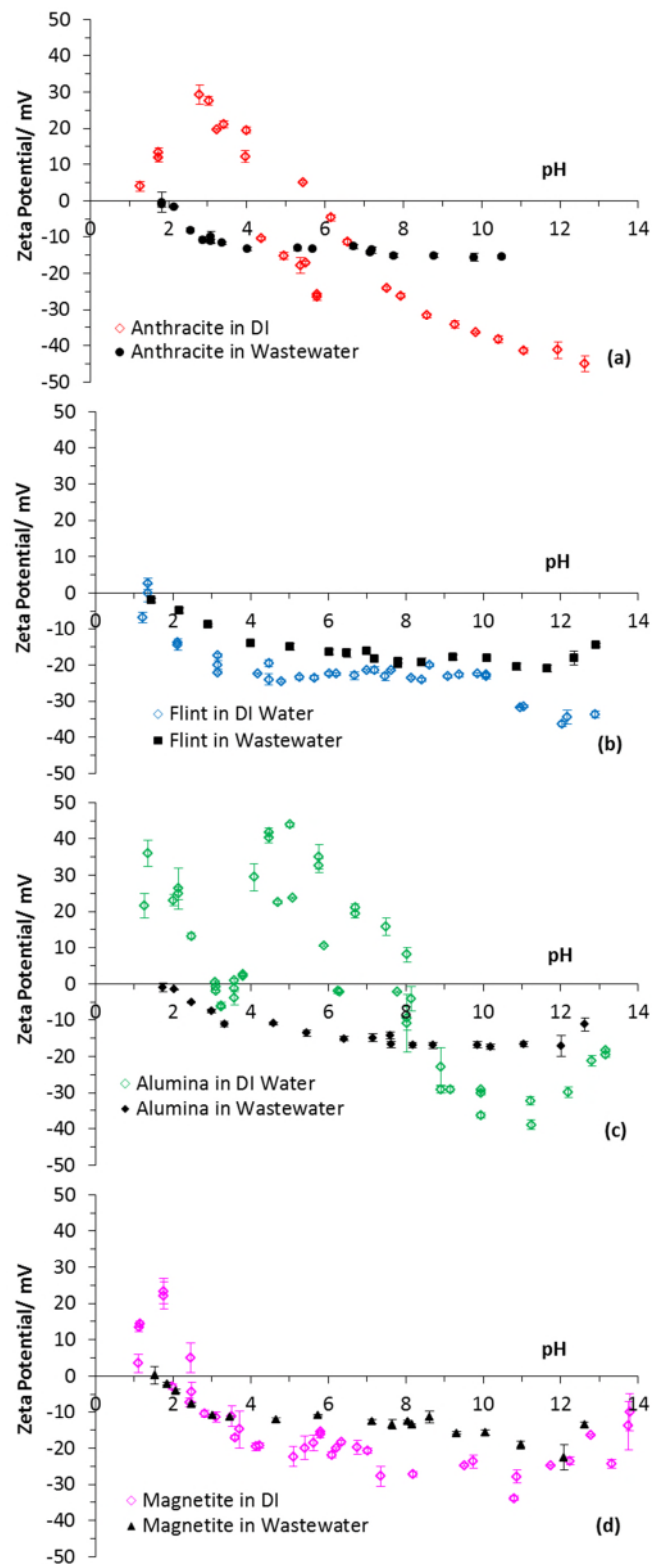


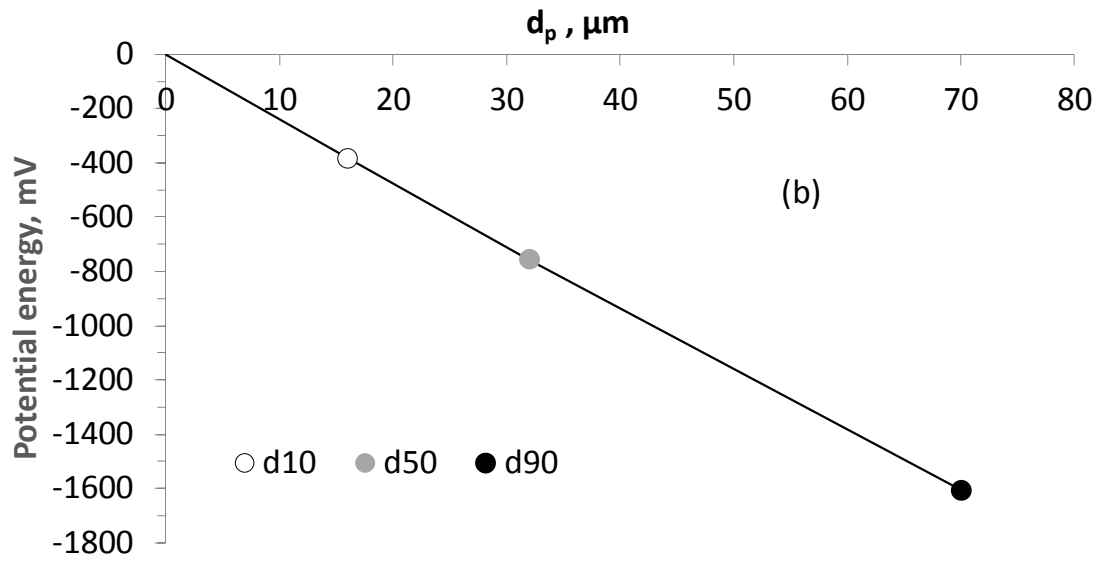
Figure 4: The characteristics of wastewater secondary effluent at different pH. (a) TSS and turbidity, (b) ZP, (c) PSD measured using a laser diffraction instrument.



555

556 Figure 5: The zeta potential of (a) anthracite, (b) flint, (c) alumina and (d) magnetite with  
 557 changing pH, in a suspension of either de-ionised water or filtered wastewater secondary  
 558 effluent.





559

560 Figure 6: DLVO forces between media and suspension particles calculated assuming a  
 561 separation distance of  $3 \times 10^{-10}$  m used by Bai and Tien (1997): (a) electric double layer force;  
 562 (b) van der Waals force.

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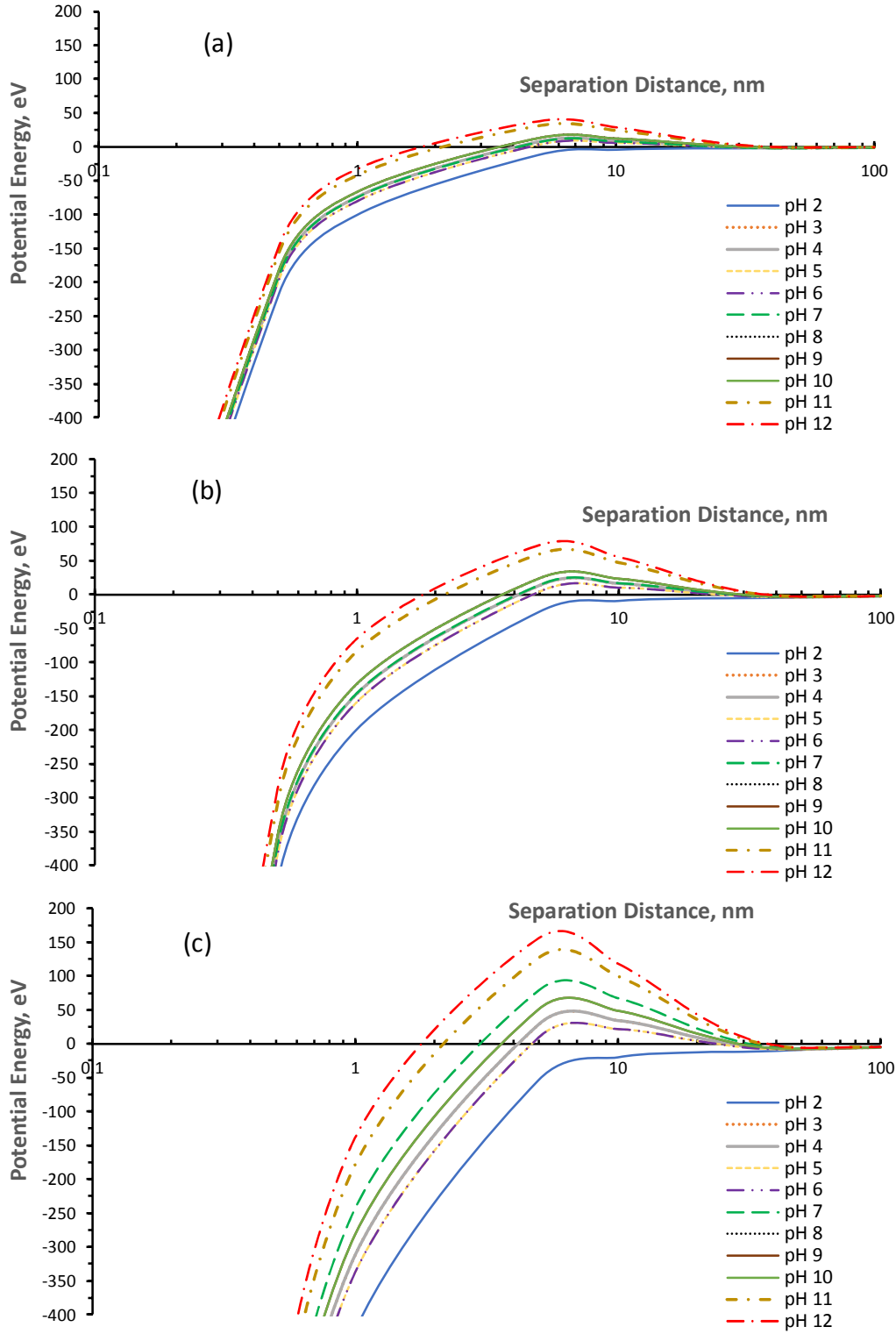


Figure 7: The modelled net DLVO potential energy on particles near a collector at different pH and separation distance using equation (Bai and Tien, 1997): (a) d10 (16 μm) suspension particle size; (b) d50 (32 μm) suspension particle size and; (c) d90 (70 μm) suspension particle size.

# Consequences of pH change on wastewater depth filtration using a multimedia filter

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