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Functionalised pseudo-boehmite nanoparticles as an excellent adsorbent material for anionic dyes†

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Pseudo-boehmite has been functionalised with l-lysine by refluxing an aqueous solution containing these two reactants overnight. The resulting nanosized (<10 nm) product is insoluble in water and has been characterised by solid-state NMR spectroscopy, powder X-ray diffraction analysis, N2 adsorption–desorption analysis and zeta potential measurements. The affinity of this new nanostructured organic–inorganic hybrid material for anionic dyes has been quantified using UV-vis spectrophotometry and by constructing the adsorption isotherms for Acid Blue 9 (AB9), Acid Yellow 23 (AY23), and Acid Red 37 (AR37). Elemental/micro analyses indicate that one lysine molecule is covalently bonded to every 8 nm2 of the functionalised material giving a composition [(AlOOH)230(C6N2O2H15)] for AB9, 1.5 mmol g−1 for AY23 and 8.4 mmol g−1 for AR37. AR37 gave a higher monolayer coverage (Cm) value of 0.13 mmol g−1 than AB9 (0.085 mmol g−1) and AY23 (0.081 mmol g−1). Dye adsorption is correlated with surface coverage of l-lysine and, in the case of AR37, two dye molecules are concluded to be adsorbed per l-lysine while for AY23 a multi-point interaction is proposed to result in a lower dye capacity and a relatively higher affinity of this dye for FPB when compared with AR37.

Introduction

The development of functionalised inorganic nanoparticles to tailor surface properties continues to be an active area of research. A considerable amount of work has been undertaken to modify the surface of inorganic nanoparticles through non-covalent or electrostatic interactions.1–5 However, many potential applications6 require the functional material to be stable enough at moderate temperatures and to retain the potentially useful functionality when processed (chemical/physical), alone or with other materials, to produce products of commercial value. This has prompted us to investigate a surface modification route that will bind (coordinate) the functional moiety strongly to the nanoparticles. When coated on a paper substrate, this new nanomaterial is envisaged to encapsulate anionic dyes during ink-jet printing.

A good starting point would be a well known, relatively low cost material which exhibits a high surface area. Pseudo-boehmite is one well-studied aluminium hydroxide having the general formula of AlO(OH)·nH2O. In contrast to boehmite, pseudo-boehmite has a smaller particle size and has more crystal defects, leading to broader lines in its X-ray diffraction pattern.6–10 The aluminium ions are situated in an octahedral position.11 Wefers and Misra,10 and Tsukada et al.,12 have reported that water binds more strongly to pseudo-boehmite than the more crystalline boehmite, although this may not affect the lattice parameters.13 Both of these materials are amphoteric and are more soluble in acidic and alkaline solutions.14 Pseudo-boehmite has found useful applications as catalyst supports,15,16 in anti-corrosion,17,18 deodorants19,20 and UV-protection agents.21 Particularly interesting is its wide usage as an adsorbent material in areas ranging from chemical instrumentation22 to biochemical systems23,24 and from environmental pollution control25,26 to paper coatings.27

Previously, we reported the adsorption and intercalation of Acid Blue 9 on Mg/Al layered double hydroxides, focusing on the effect of varying the metal composition (Mg/Al) on its adsorptive properties.28 We have now investigated the surface modification of pseudo-boehmite with l-lysine in an effort to produce a water insoluble material that has higher affinity for anionic dyes commonly used in the printing industry. This work can be contrasted to that of Callender29 who reported the
A typical reaction leading to functionalised pseudo-boehmite nanoparticles involved refluxing overnight 30.5 g of l-lysine monohydrochloride (Sigma-Aldrich) and 10.0 g of pseudo-boehmite (Sasol) in 200 mL of de-ionised (Milli-Q) water. All chemicals were used without further purification. The pH of the mixture was measured prior to and after refluxing and found to be the same, i.e., ca. 7.0 (± 0.2). At this pH, lysine will carry a total positive charge. The resulting slurry was filtered and the filtrate containing any unreacted lysine was discarded. The white precipitate was washed once with distilled water by stirring slowly for about 2 min. Care was taken not to over-expose the product to water as the product converts to gibbsite forming a gel which is difficult to separate from the liquid phase. The white product was air dried at room temperature for at least 36 h. It was then ground with an agate mortar and pestle prior to characterisation and used in dye adsorption experiments. C,H,N and Al analyses of the functionalised pseudo-boehmite (FPB) material are shown in Table 1.

### Dye affinity/adsorption experiments

Dye solutions consisting of 1 mM of Acid Blue 9 (Saujanya Dyechem), 5 mM of Acid Yellow 23 (Sigma-Aldrich) and 5 mM of Acid Red 37 (Sigma-Aldrich) were prepared in water (Milli-Q) from the as-received dyes taking into account the dye content (Table 2). Table 2 also lists the experimental wavelength of maximum absorbance ($\lambda_{\text{max}}$) and molar absorptivity ($\varepsilon$). The dye concentrations were based on commercial ink-jet ink concentrations (note higher $\varepsilon$ value of AB9). In the absence of crystal structures, the gas phase molecular structure and size of the dyes were estimated using HyperChem software to find the lowest energy conformation (MM+) prior to geometry optimization (AM1-UHF).

Commercial pseudo-boehmite (PB) and the functionalised pseudo-boehmite (FPB) were subjected to dye affinity tests (triplicates) according to a modification of a published method, using Acid Blue 9 (AB9), Acid Yellow 23 (AY23) and Acid Red 37 (AR37) solutions. The dye solution (5 mL) was added to the pigment (PB or FPB; 0.05 g) in a centrifuge tube. The tube was agitated using a vortex mixer (2500 rpm) for 1 min followed by centrifugation (3000 rpm, 10 min), as described in previous work. The supernatant liquid was carefully removed and an aliquot of 25 mL was diluted with distilled water (5 mL) giving a ratio of 1 : 200 and was analyzed using a VARIAN CARY 300 Bio UV-vis spectrophotometer. For the FPB system, a different dilution factor was used so that the absorbance reading was in the measurable range. Absorbances were recorded at the $\lambda_{\text{max}}$ of visible absorption (see Fig. 2). The amount of dye adsorbed per unit area (molecules nm$^{-2}$) was calculated according to:

$$\text{Amount of dye adsorbed} = \frac{A}{\varepsilon \times \text{mass of pigment}}$$

where $A$ is the absorbance, $\varepsilon$ is the molar absorptivity, and mass of pigment is the mass of dye adsorbed per unit area.

### Materials and methods

#### Synthesis

A typical reaction leading to functionalised pseudo-boehmite nanoparticles involved refluxing overnight 30.5 g of l-lysine monohydrochloride (Sigma-Aldrich) and 10.0 g of pseudo-boehmite (Sasol) in 200 mL of de-ionised (Milli-Q) water. All chemicals were used without further purification. The pH of the mixture was measured prior to and after refluxing and found to be the same, i.e., ca. 7.0 (± 0.2). At this pH, lysine will carry a total positive charge. The resulting slurry was filtered and the filtrate containing any unreacted lysine was discarded. The white precipitate was washed once with distilled water by stirring slowly for about 2 min. Care was taken not to over-expose the product to water as the product converts to gibbsite forming a gel which is difficult to separate from the liquid phase. The white product was air dried at room temperature for at least 36 h. It was then ground with an agate mortar and pestle prior to characterisation and used in dye adsorption experiments. C,H,N and Al analyses of the functionalised pseudo-boehmite (FPB) material are shown in Table 1.

#### Table 1 Elemental analyses of functionalised pseudo-boehmite (FPB)

<table>
<thead>
<tr>
<th></th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>Al%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>0.62</td>
<td>2.46</td>
<td>0.18</td>
<td>39.60</td>
</tr>
<tr>
<td>Calculated$^a$</td>
<td>0.46</td>
<td>2.69</td>
<td>0.18</td>
<td>40.08</td>
</tr>
</tbody>
</table>

$^a$ Calculated for [(AlOOH)$_{230}$·(H$_2$O)$_{35}$·(C$_6$N$_2$O$_2$H$_{13}$)].

<table>
<thead>
<tr>
<th>Name</th>
<th>Dye content (%)</th>
<th>Molecular mass/g mol$^{-1}$</th>
<th>$\varepsilon_{\text{exp}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB9</td>
<td>85</td>
<td>792.85</td>
<td>1.37 × 10$^4$</td>
<td>629</td>
</tr>
<tr>
<td>AY23</td>
<td>70</td>
<td>534.36</td>
<td>2.57 × 10$^4$</td>
<td>426</td>
</tr>
<tr>
<td>AR37</td>
<td>90</td>
<td>514.53</td>
<td>1.88 × 10$^4$</td>
<td>513</td>
</tr>
</tbody>
</table>

$^a$ UV-vis analysis in our study.

### Table 2 Some properties of commercial dyes used in this work

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**Fig. 1** Salts of (a) Acid Blue 9; (b) Acid Yellow 23 and (c) Acid Red 37.
Zeta potential measurements (triplicate) were carried out using a ZetaPALS instrument manufactured by Brookhaven Instruments Corporation fitted with an autotitrator (BI-ZTU) at room temperature. An aliquot of 300 ppm ultrasonically dispersed particles containing 1 mM KNO₃ electrolyte was placed in a flow cell. Acidity and basicity were adjusted using 0.1 M or 1 M HNO₃ or KOH as required.

Surface area, pore volume, pore size, and pore size distribution measurements were made using a Micromeritics ASAP 2010 instrument. The samples were degassed at 378 K prior to analysis using nitrogen adsorption–desorption at 77 K.

The density was determined by the helium pycnometry technique using an AccuPyc 1330 gas displacement pycnometer manufactured by Micromeritics. Samples were dried at 333 K overnight in static air and placed in a desiccator prior to analysis.

Microanalysis was performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand and Dairy Technical Services Ltd, Victoria, Australia. Aluminium content was determined via Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) by ALS Environmental, Victoria, Australia.

Results and discussion

Surface modification of pseudo-boehmite

Recent work in our laboratory has focussed on producing an insoluble inorganic-based material suitable as an inorganic pigment in the formulation of an ink-receptive layer for paper coatings. To this end, we have investigated the reaction of pseudo-boehmite (PB) with l-lysine in water. Modification of PB involved refluxing PB with l-lysine overnight at pH ca. 7.0. Such materials do have some solubility over a broad range of pH, but the rate of dissolution is considerably pH-dependent, with a minimum near neutral pH. Surface modification could therefore be achieved via either direct reaction of the deproto- nated carboxylate on l-lysine with the PB surface or by a dissolution–chemical reaction (also involving carboxylate binding)–reprecipitation mechanism.

Unequivocal evidence of the carboxylate group of lysine being coordinated to aluminium atoms of pseudo-boehmite is provided by ¹³C CP MAS NMR spectroscopy. The chemical shifts for the carboxylate and aliphatic carbons are expected to be at 160–190 ppm and 0–62 ppm respectively. Fig. 3 shows the ¹³C CP MAS NMR spectra of PB, FPB and pure l-lysine monohydrochloride. The ¹³C NMR spectrum of pure lysine (Fig. 3a) shows the carboxylate carbon signal peak at 178 ppm. However, for the lysine functionalised pseudo-boehmite (Fig. 3b) two resonances can be observed at 167 and 184 ppm. The latter can be assigned to the carboxylate carbon of lysine coordinated to aluminium(III). According to Barron et al.,¹¹,¹⁸ carboxylate groups can have either bridging (Fig. 4a) or terminal monodentate ligation (Fig. 4b) to aluminium and not chelation (Fig. 4c), which is unfavoured due to ring strain. In our study, the significant downfield shift of ca. 6 ppm for the carboxylate carbon supports a bridging interaction since an increase in polarization of the carboxyl bond is expected for bridging compared with the terminal monodentate ligation. The second resonance at 167 ppm could be carboxylate or carbonate ion chelating to the
aluminium ions. Narayanan and Laine$^{39}$ reported that the carboxylate carbon of gibbsite formate $[\text{Al(O}_2\text{C})_3]$ gave a solution $^{13}$C NMR resonance at 165 ppm, which is similar to the commercial aluminium formate (166 ppm) and indicated that this corresponds to a chelating formate ligand. This signal could also be due to some $\text{HCO}_3^-$ or $\text{CO}_3^{2-}$ groups that adsorbed on the aluminium surface. In the $^{13}$C NMR spectrum of a uranyl(V) carbonate complex, a signal at 169 ppm was assigned to free $\text{CO}_3^{2-}$. Thus, in this study the signal at 167 ppm could be due to some $\text{HCO}_3^-$ or $\text{CO}_3^{2-}$ adsorbed on the aluminium surface as evident in the $^{13}$C spectrum of the PB material measured before functionalisation (Fig. 3c).

27$^{Al}$ MAS NMR spectra of PB and FPB (ESI)$^\dagger$ showed strong signals at ca. 4 ppm, which can be assigned to six-coordinate Al(III) centres. In 27$^{Al}$ NMR spectra, signals in the ranges of 300–200 ppm, 200–70 ppm, ca. 50 ppm and ca. 0 ppm are normally assigned to three, four, five and six-coordinate aluminium centres, respectively.$^{41-43}$ In this study, surface functionalisation had no effect on the Al(O/OH) coordination environment.

Fig. 5a and b show that the PXRD patterns of the pseudo-boehmite material before and after functionalisation are essentially identical. Peaks characteristic of the mineral boehmite (JCPDS-ICDD: 83-2384) confirm that the pseudo-boehmite core structure does not undergo transformation during the reaction with the lysine molecule. The broadened peaks can be attributed to the colloidal nature of the pseudo-boehmite particles and thus smaller particle size. Application of Scherrer’s equation,$^{35}$

$$t = \frac{0.9\lambda\cos\theta_p}{b},$$

where $t$ is the crystallite size, $\lambda$ is the wavelength of the radiation used, $\beta$ is the pure diffraction breadth and $\theta_p$ is the Bragg diffraction angle, enabled us to estimate that the crystallite sizes of both PB and FPB were between 5–10 nm. This value is within the values reported by previous studies.$^{11,13,44,47-49}$ It has been noted$^{11}$ that the composition of the hybrid material is difficult to obtain owing to the variation of the physical characteristics of the individual PB particles, such as particle size, surface morphology and the identity of surface groups, such as Al–O–Al or Al–O(H)–Al. Nevertheless, the number of lysine molecules on the PB surface can be obtained even though the loading is very low. Microanalyses (see Table 1) were consistent with the composition of $[\text{AlOOH}]_{230}(\text{H}_2\text{O})_{86}(\text{C}_6\text{N}_2\text{O}_2\text{H}_15)$ and indicate that one lysine molecule is covalently bound per 8 nm$^2$ of FPB surface. This composition is consistent with thermogravimetric analysis (ESI)$^\dagger$ giving about 9% of surface bound water. The observed %C value is slightly higher than the calculated value probably due to the presence of small amounts of $\text{HCO}_3^-$ or $\text{CO}_3^{2-}$ (<0.8% by mass) which is consistent with our solid state NMR results. The amount of lysine, <1% (by weight) of the hybrid material, could not be observed in the thermogravimetric profile (ESI)$^\dagger$ Given that there are 65 $\mu$mol of lysine per gram of FPB and assuming a particle diameter of 5–10 nm...
(PXRD analysis) there would be in the order of 2–10 lysine molecules bound per isolated FPB nanoparticle.

The isoelectric points (IEP) of the PB and FPB particles were determined to further confirm the presence of the positively charged amino groups on the surface of pseudo-boehmite. The electrophoretic mobility (μ) of the particles was measured at varying pH and the electrokinetic/zea (ζ) potential calculated by the Smoluchowski equation, ζ = μη/ε, where η and ε are the viscosity and permittivity of the solution, respectively. A plot of ζ potential versus pH can be used to determine IEP (pH of zero ζ potential), the pH at which the average surface charge is zero. If the IEP is < 7 the surface is acidic, if it is > 7 the surface is basic.50,51 A plot of the zeta potential as a function of pH for PB and FPB (Fig. 6) shows that both materials have a similar zeta potential of ca. +43 mV below pH 7. At the pH of the adsorption experiments of 7.8, however, the ζ potential of FPB is 6 mV higher than that of PB. This should result in greater adsorption of the dye to FPB. In addition, strong H-bonding interactions between the dyes and the positively charged groups on L-lysine would be expected to lead to a higher affinity.

As previously noted, the dissolution of aluminium oxides is at its minimum in the neutral pH range. In fact, the amount of aluminium in the supernatant liquid after the dye affinity tests was negligible (3–5 ppm). The presence of an additional positively charged group on the PB surface is indicated by an increase in IEP from ca. 9.3 for PB to 9.7 for FPB. According to Bruce,52 the pKᵢ of the amino groups in lysine (8.95 and 10.79) would give rise to an isoelectric point of 9.87. Since this value is very close to the IEP of FPB, the increase in shift in IEP reflects the presence of lysine amine groups.

**Fig. 6** Zeta potential (ζ) of PB and FPB as a function of pH. The isoelectric point (IEP) of PB is at pH = 9.26 (±0.02) whilst that of FPB is at pH = 9.69 (±0.04). Curves were fitted using a polynomial equation.

**Dye affinity/adsorption studies**

The attachment of the L-lysine to the pseudo-boehmite surface introduces positively charged amino groups that leads to substantially enhanced dye affinity. Initial experiments carried out at pH = 7.8 indicated that, in addition to having a high affinity for FPB, AB9 forms adducts with FPB leading to colloidal stabilization (as described by the Debye–Hückel equation).51,53 Since the dye adsorption measurements relied on the separation of the supernatant dye from the solid FPB, the experimental conditions were designed to avoid colloidal stabilization (i.e., low masses of FPB to volume of dye solutions were used). Such problems were not encountered for AY23 and AR37.

Preliminary tests on both PB and FPB indicated that the affinity of the dyes for the adsorbent follows the order AR37 > AY23 > AB9 (see ESI†). A higher amount of AR37 was adsorbed which may be due to the lower number of negative charges on this dye (2 vs. 3 for the others, see Fig. 1). This means that more dye is needed to balance the positive surface charge. All three dyes show substantially greater adsorption on FPB than PB (by ca. two-fold), as would be expected if the oxide surface had been decorated with positively charged functional groups. Quantification of the adsorptive properties of both (PB and FPB) materials is discussed below. Analysis of the data taking account of the textural properties of PB and FPB (see Table 5, later) allowed the determination of dye coverage on the surface, as summarised below in Table 3.

Fig. 7 shows the adsorption isotherms for AB9, AY23 and AR37 binding to the FPB surface. Fitting of the data was approximated using the Langmuir model developed for monolayer adsorption on a homogeneous surface. Whilst not ideal, this enabled us to estimate the maximum adsorption capacity (Cᵢ) and binding constants (Kᵢ). According to the classification of Giles et al.54 the isotherms for AY23 and AR37 binding to FPB can be classified as L-2 type curves that indicate a very strong intermolecular attraction between the adsorbate and the adsorbent. This is particularly evident for AR37 and AY23, for which the initial part of the isotherm is nearly vertical. For a Langmuirian system, the plateau would represent complete monolayer coverage from which maximum adsorption capacity can be taken.59 Although our system is not strictly Langmuirian, the data provide useful information about dye adsorption. Fig. 8 shows the adsorption isotherms for AB9, AY23 and AR37 binding to the untreated PB surface. This sub-type of L curve does not have a plateau or an inflection indicating that surface saturation has not been reached. An attempt to reach the saturation point by increasing the proportion of dye (smaller amount of PB) gave the same result but with a larger standard deviation. None of the well known adsorption–sorption models such as Langmuir, Freundlich and Temkin could satisfactorily fit the data. The linear increase in dye adsorption with dye concentration indicates that the dye has little or no affinity for the unfunctionalised pseudo-boehmite surface. As the surface

<table>
<thead>
<tr>
<th>Dye</th>
<th>Adsorbed dye number of dye molecules per 8 nm² FPB</th>
<th>Molecular box dimension/ nm (see ESI†)</th>
<th>x-axis</th>
<th>y-axis</th>
<th>z-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB9</td>
<td>1.5</td>
<td>1.03</td>
<td>1.00</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>AY23</td>
<td>1.4</td>
<td>0.74</td>
<td>0.24</td>
<td>1.69</td>
<td></td>
</tr>
<tr>
<td>AR37</td>
<td>2.2</td>
<td>0.94</td>
<td>0.33</td>
<td>1.54</td>
<td></td>
</tr>
</tbody>
</table>

a) Microanalysis, adsorption isotherm (Cᵢ) and BET surface area.

b) Hyperchem simulation (shown for easy correlation).
concentration of dye increases, the hydrophobicity of the surface may increase leading to an increase in adsorption.

The Langmuir model parameters ($C_m$ and $K_a$) for FPB are listed in Table 4 and reveal interesting trends. The FPB material has the highest affinity for AY23 ($K_a = 1.5 \times 10^6$ M$^{-1}$) followed by AR37 ($8.4 \times 10^4$ M$^{-1}$) and AB9 ($2.6 \times 10^3$ M$^{-1}$). These differences may be correlated with the charge on the dyes (three for AY23 and two for AR37 and AB9). In addition, positive charge on AB9 appears to reduce its affinity for FPB. The $K_a$ value for AY23 is only slightly higher than that for AR37, despite the fact that in AY23 one of the three charged groups is a carboxylate which is more basic than the sulfonates and would be expected to have higher affinity for the boehmite surface. A likely explanation, which is in keeping with the lower binding capacity of AY23 (vide infra), is that multipoint interaction is possible for this dye.

Although we have been unable to determine the parameters ($C_m$ and $K_a$) for dye binding to untreated PB surfaces, inspection of the data in Fig. 7 and 8 indicates that the dye binding capacity of the modified FPB is over two-fold higher than the untreated PB. For FPB, AR37 gave a higher dye coverage ($C_m = 0.13$ mmol g$^{-1}$) than AB9 and AY23 ($C_m = 0.08$ mmol g$^{-1}$). This finding is discussed further below.

Computational chemistry was employed to provide some insight into the three-dimensional shape and size of these dyes in the gas phase (Table 3; ESI).† The conclusion reached was that the l-lysine coverage is such that the steric bulk/size of the dye will not affect dye binding. Table 3 shows the number of dye molecules adsorbed per 8 nm$^2$ of FPB. If it were assumed that the binding of the dye results in charge neutralization then every

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**Fig. 7** Adsorption isotherms for: (a) Acid Red 37; (b) Acid Yellow 23; and (c) Acid Blue 9 binding to functionalized pseudo-boehmite (FPB) system at pH = 7.8 and room temperature. The full lines represent fitting of the data to the Langmuir equation.

**Fig. 8** Adsorption isotherms for: (a) Acid Red 37; (b) Acid Yellow 23; and (c) Acid Blue 9 binding to pseudo-boehmite (PB) system at pH ~ 8.4 and room temperature. Data could not be fitted with the Langmuir, Freundlich or Temkin models.

**Table 4** Langmuir model parameters for the adsorption of Acid Blue 9 (AB9), Acid Yellow 23 (AY23) and Acid Red 37 (AR37) binding to functionalised pseudo-boehmite (FPB) at pH = 7.8

<table>
<thead>
<tr>
<th>Dye</th>
<th>$C_m$/mmol g$^{-1}$ ($\times 10^{-2}$)</th>
<th>$K_a$/M$^{-1}$ ($\times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB9</td>
<td>0.85 ($\pm$0.03)</td>
<td>2.65 ($\pm$0.35)</td>
</tr>
<tr>
<td>AY23</td>
<td>0.81 ($\pm$0.03)</td>
<td>151 ($\pm$44)</td>
</tr>
<tr>
<td>AR37</td>
<td>1.28 ($\pm$0.05)</td>
<td>84 ($\pm$17)</td>
</tr>
</tbody>
</table>
lysine molecule (8 nm of FPB) requires 1.0 AR37 and 1.0 AB9 (2− charge), and 0.67 AY23 (3− charge). The amount of dye adsorbed is well above these values (Table 3). One possible origin of this difference is the adsorption of the dye directly onto the ‘lysine free’ pseudo-boehmite surface (see Fig. 9). Further explanations for the observed behaviour can be based on the idea that complete charge neutralization (dye−⋯l-lysine+) does not occur, either because the interaction does not involve all anionic groups on the dye or because of dye aggregation occurs on the FPB surface. For AR37, the fact that approximately two molecules of dye are adsorbed per molecule of l-lysine indicates that two dye molecules can access and interact with each ammonium group on the diprotonated l-lysine (SO3−⋯H2N+).

Table 5 summarizes the textural properties of the PB and FPB particles. The surface area of pseudo-boehmite was found to be 284 m² g⁻¹, which is in agreement with literature value.55,56 There is no significant difference between PB and FPB in terms of their textural properties. This means that the excellent dye adsorptive behaviour exhibited by the FPB system could only be due to the presence of the positively charged amine group pendant to the surface. Technically, these materials are considered to be mesoporous, i.e., having pore openings between 20 Å and 500 Å.58 Fig. 10 shows the N₂ adsorption–desorption isotherms of PB and FPB nanoparticles. Clearly, both systems are considered to be mesoporous because they exhibit a type IV isotherm. Since the actual material is amorphous in nature, it is likely to have a wide range of pore sizes.57,58 Regardless of their pore structure, both the external and internal surfaces will be available for adsorption as long as they are accessible to the dye adsorbate. The PB and

Table 5 Textural properties of pseudo-boehmite (PB) and functionalised pseudo-boehmite (FPB)

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area/m² g⁻¹</th>
<th>Ave. pore diameter/Å</th>
<th>Corrected pore vol./cm³ g⁻¹</th>
<th>Ave. density/g cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB</td>
<td>284</td>
<td>49</td>
<td>0.35</td>
<td>2.70 (±0.00)</td>
</tr>
<tr>
<td>FPB</td>
<td>287</td>
<td>44</td>
<td>0.33</td>
<td>2.73 (±0.01)</td>
</tr>
</tbody>
</table>

a BET method. b BJH method. c BJH method. d Helium density.

Fig. 9 Schematic representation of anionic dyes binding to the functionalised pseudo-boehmite (FPB) surface.

Fig. 10 N₂ Adsorption–desorption isotherms of (a) pseudo-boehmite and (b) functionalized pseudo-boehmite. Adsorption is represented by the solid line and desorption by the dashed line.

Fig. 11 Scanning electron micrographs of (a) pseudo-boehmite (PB) and (b) functionalized pseudo-boehmite (FPB).
The presence of the positively charged organic moiety on the surface of pseudo-boehmite nanoparticles resulted in a substantial increase in the ability of the pseudo-boehmite material to adsorb species of opposite charge. This excellent adsorption behaviour can be correlated to an increase in electrostatic attraction and/or hydrogen bonding interactions between the positively charged pseudo-boehmite nanoparticles and the negatively charged anionic dyes. For AR37, dye adsorption correlated with surface coverage of 1-lysine. That is, two dye molecules were adsorbed per 1-lysine. For AY23, a multi-point interaction is proposed to account for the lower dye capacity and the high affinity of this dye for FPB when compared with AR37.

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