CHAPTER 7

Synthesis of Bentonite ZnO nanocomposites and applications.

7.1. Introduction

Bentonite is a natural clay powder, comprising of finely grained particles. Bentonite word was proposed by Knight (1989) and in 1926 by Ross & Shannon. Bentonite has smectite and montmorillinite minerals, and it is a deposit of clay elements. It has applications in various fields of environmental application, like protection of land erosion, soil pollution protection, purification of drinking and wastewater. Major types of bentonite powder are Na- Bentonite (swelling bentonite) and Ca – Bentonite (Non- swelling type).

Bentonite and zeolites are aluminosilicates. The essential component of bentonite is montmorillonate, it is the finest crystals of clay, zeolites have three-dimensional crystalline structure with the channels of molecular dimensions, both bentonite and zeolites have adsorption capacity, bentonite powder consists of ash made of volcanoes. Bentonites can be used as such or after the activation of bentonites by several physico-chemical treatments like acid activation, ion exchange process and heating techniques. Acid-activated bentonite has diverse applications as an adsorbent, catalyst, bleaching earth and nanocomposites. (Kodi 1997: 633-643). Acid activation process brings some physicochemical changes in bentonite powder, like the change in crystallinity, swelling, pore structure, surface area, catalytic activity, strength, surface acidity and also the chemical and mineral composition (Banat 2000: 391-398, Onal 2002: 409-416, Park S.J. 2002: 160-165).

In this work, clintonite bentonite powder has been activated with hydrochloric acid. Clintonite is a South African natural zeolite, and it is a good choice material because it has high cation exchange capacity, mechanical and chemical stability, low cost and easy availability. ZnO is the most effective nano metal oxide with a band gap of 3.37 eV, and high surface area. ZnO nanocatalyst has materialized as more efficient photocatalyst for the detoxification of water, because it generates hydrogen peroxide more efficiently, and it has more active sites (Nazar Elamin 2013: 32-35).

BP-3 and caffeine are the emerging contaminants and being recognised as emerging pollutants to aquatic organisms in water. Humans and domestic animals
release large quantities of PPCPS into the environment through excretion, disposal of unused pharmaceutical products and agricultural wastes (Polynton and Vulpe, 2009: 83-95) a wide range of pharmaceutical products have been detected in surface and groundwater. Caffeine, nicotine and nicotine metabolite like cotinine, are widely detected in groundwater, personal care products are transmitted into aquatic system. Sewage treatment plants do not have PPCPs removal equipment, the majority of compounds used as sunscreens are lipophilic, conjugated aromatic compounds, but these are found in the aqueous environment (Jeon 2006: 192-202). PPCP’s act as endocrine disruptors interfering with hormone production and aquatic life is at risk.

Yusan S. 2016: 2158–2163, synthesized ZnO, and diatomite-supported ZnO nanostructures, and it was prepared using a direct precipitation and co-precipitation method, respectively. The surface charge of the samples was assessed by zeta potential measurements. Characterization exhibited that the ZnO particles were efficaciously distributed in the diatomite support. Synthesised nanoparticles have the potential for different applications.

Bel Hadjltaief H. 2016, ZnO–TiO$_2$/ clay photocatalyst was prepared using a natural Tunisian clay as support. Its efficiency was assayed in the photocatalytic degradation of methyl green in aqueous solutions, in the presence of UVA irradiation. The photocatalyst was synthesised using a metal organic chemical vapour deposition (MOCVD) with Ti (OPr)$_4$ deposed on the natural Na$^+$ clay, followed by a modified sol-gel synthesis method. The activity tests showed that the photodegradation efficiency for ZnO–TiO$_2$/ clay is higher than for the TiO$_2$/ clay catalyst. Almost complete mineralisation was obtained upon 30 min of light irradiation in the presence of the ZnO–TiO$_2$/ clay catalyst.

The experimental results indicate that this ZnO–TiO$_2$/ clay catalyst shows high photocatalytic activity, higher than the Na$^+$ exchanged clay and TiO$_2$/ clay, pointing to a positive effect of the presence of ZnO in the catalytic composition, due to the suitable arrangement of their respective valence and conduction bands, favoring both electron and hole transfer and delaying their recombination.

Samira Bendou 2014: 404-413, studied the effect of acid treatment (HCl) for the activation of bentonite using diluted hydrochloric acid at room temperature, it was found that bentonite sample activated at lower acid concentration 0.4 M HCl showed
maximum efficiency, having more surface area and active sites, and bentonite activation with higher acid concentration (0.6 M) caused the decrease in the surface area.

The above-referred literature survey provides the clear evidence for the preparation of bentonite supported ZnO nanoparticles. Acid-activated bentonite powder shows more efficiency as compared to commercial plane bentonite powder.

The aim of the study is the activation of bentonite powder, and synthesis of bentonite supported ZnO nanoparticles, characterisation of synthesised nanoparticles by XRD, SEM-EDS, ATR-IR and ICP-OES. It's application as photocatalyst for the elimination of caffeine in water and elimination of BP-3 in water. Meanwhile, bentonite ZnO Cellulose acetate composite membranes were prepared and used for BP-3 removal in water.

7.1.1. Experimental details

7.1.1.2. Materials

Cellulose acetate (CAc, molecular weight =25,000 Da) was purchased from Aldrich, Dimethylformamide (DMF) and acetone were purchased from Merck (India) Ltd. ZnO nanoparticle (product code: 677450) was purchased from Sigma, 2-hydroxy4-methoxybenzophenone (C_{14}H_{12}O_{3}), caffeine (C_{8}H_{10}N_{4}O_{2}), APS ((NH_{4})_{2}S_{2}O_{8}), HCl (36 %) were purchased from Arva synthesis, Merck and Fischer scientific respectively and were used without further purification. Bentonite (clintoptile) was purchased from local vendor and ground to a fine powder sieved and used for the studies. Double distilled water, generated from the double distilled water plant in the lab was used for preparation feed, membrane preparation.

7.1.1.3. Activation of Bentonite/ clintoptile powder.

Bentonite powder finely grounded and sieved was activated explained below, experiments were conducted in a 500 mL clean beaker, 3 g of clay was added to 100 mL of 0.4 M HCl solution, and the solution was heated up to 80 °C. Solution was stirring continuously for 10 h at a speed of 400 rpm. After the stirring solution was centrifuged for 15 min at 4000 rpm, the supernatant acid solution was drained, and the bentonite paste was washed with distilled water to remove the traces of chloride and finally dried in a hot air oven at 105 °C for 5 h, to get a constant
weight. The activated sample was stored in closed plastic bottles and then used for further studies.

7.1.1.4. Synthesis of Bentonite supported ZnO composite material

The solid-state dispersion technique was used for the preparation of composite material. The ZnO nanoparticles were purchased from Sigma. The bentonite supported ZnO (10 %), ZnO (20 %) catalyst was prepared. ZnO (1 g) and clintoptile/ bentonite natural and activated (9 g) weighed in a clean beaker of 10 mL, and ethanol was added. A slurry of the mixture was prepared, agitated by the use of pestle and mortar and stirred for 40 min at ambient condition. After the evaporation of the solvent in a hot air oven at 90 °C, the dried solid powder was crushed by grinding in mortar and pestle for the formation of homogeneous solid-state mixture. The powdered mixture was then calcined at 480 °C for 4 h, to get the bentonite supported ZnO catalyst (Durga Kumari 2002: 155-165). The bentonite supported ZnO was characterised by XRD, ICP-OES, ATR-IR, EDS, SEM, and then used for the photocatalytic degradation studies.

7.1.1.5. Preparation of Cellulose Acetate, Bentonite supported ZnO composite membranes:

Bentonite/ clintoptile supported ZnO nanoparticle was prepared by solid state dispersion technique, composite membrane was prepared by DIPS method (Mulder M. 2000: 331-334). The different concentration of bentonite supported 10 % ZnO was used for the preparation of composite membranes. Table 7.1 displays the concentration of nanoparticles and cellulose acetate in the membranes. The composite membrane with different concentration of zeolite supported ZnO nanoparticle was labeled as CAM, CABe-1, CABe-2 and CABe-3.
### Table 7.1. Membrane code and their composition

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>CA (g)</th>
<th>10% ZnO Bentonite (g)</th>
<th>Acetone (ml)</th>
<th>DMF (ml)</th>
<th>Membrane descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAM</td>
<td>15.00</td>
<td>0</td>
<td>60</td>
<td>25</td>
<td>Neat CA</td>
</tr>
<tr>
<td>CABe – 1</td>
<td>14.75</td>
<td>0.25</td>
<td>60</td>
<td>25</td>
<td>CA+ 0.25, wt% bentonite- ZnO (10%)</td>
</tr>
<tr>
<td>CABe – 2</td>
<td>14.50</td>
<td>0.5</td>
<td>60</td>
<td>25</td>
<td>CA+ 0.50, wt% bentonite- ZnO (10%)</td>
</tr>
<tr>
<td>CABe -3</td>
<td>14.25</td>
<td>0.75</td>
<td>60</td>
<td>25</td>
<td>CA+ 0.75, wt% bentonite- ZnO (10%)</td>
</tr>
</tbody>
</table>

### 7.2. Results and discussions

Bentonites are aluminosilicates, the pore size distribution is very uniform and sharp due to the fact that the pores form the part of the crystal structure itself. Na-bentonite clay particles tend to swell during operation, the ion exchange capacity is inversely proportional to the Si/Al ratio. Based on the previous studies, the specific ion exchange capacity depends on the structure of the zeolite. However the impregnation of ZnO in bentonite matrix increases the hydrophilicity as well as charge due to the metal oxide and bentonite composites.

#### 7.2.1. X-ray diffraction analysis

The XRD studies of ZnO nanoparticle, bentonite supported 10% ZnO nanoparticles and pure bentonite powders were conducted. XRD pattern of the same are shown in figure 7.1 XRD pattern of ZnO nanoparticles exhibited the peaks at 2θ equal to 31.67°, 34.31°, 36.14°, 47.40°, 56.52°, 62.73°, 66.28°, 67.91° and 69.03° which corresponded to a typical diffraction of zincite with hexagonal symmetry. These peaks perfectly matched with the reference to JCPDS card no 36-1451 and the lattice parameters are a = 3.24982 Å, c = 5.20661 Å.

Hosseinfeld M.2013: 396-399. Synthesized pure ZnO nanoparticles, as no impurity peaks were detected. From the XRD analysis of bentonite powder, it was found that the peaks are at 7°, 12°, 19°, 21°, 23°, 29.05° and 40.9° are equal to, characteristic peaks of bentonite (Leite 2008: 303, Leite 2010: 596). Peaks at 12°, 29.05° and 40.9° are conforms kaolinite form of bentonite and peaks at 21°, 23°, 42.08° are due to the presence of montmorillonite in bentonite powder. XRD
Intensity of characteristic peaks of bentonite material is not high because of non-crystallinity form (Kumar 1995: 1440-1448). From the XRD pattern of bentonite supported 10 % ZnO, it is found that there is an increase in intensity of peaks at 20 equals to 7°, 16°, 19°, 21°, 23°, 29°, 31.67°, 34.31°, 36.14°, 47.40°, 56.52°, 62.73°, 66.28°, 67.91° and 69.03° confirms the impregnation of ZnO on the bentonite powder (10 % ZnO benonite powder).

Figure 7.1. XRD Images of bentonite powder, ZnO pure and 10 % ZnO bentonite powder.

7.2.2. SEM and EDS analysis of ZnO, bentonite supported ZnO NPs

Figure 7.2. SEM Images of a) ZnO pure b) Bentonite pure (10 KX), c) Bentonite supported 5 % ZnO d) Bentonite supported 10% ZnO powder.
Figure 7.2 presents the SEM micrographs of ZnO, bentonite, and bentonite supported 10 % ZnO samples. SEM analysis examines the distribution of ZnO species over the bentonite. It is seen that the clean surface of bentonite powder is covered by the ZnO particles, and there is no noticeable change in the typical morphology of the support after the loading of ZnO. As can be seen from the SEM images, ZnO nanoparticles are like clusters attaching to the bentonite surface. The EDS spectra of ZnO nanoparticles confirms the presence of pure oxygen and zinc without impurities. It is evidenced from the EDS spectra and elemental compositions in tables the presence of Si, Al constituent of bentonite and also the presence of Zn conforms the impregnation of ZnO on bentonite composite powder.

7.2.3. ICP studies of bentonite supported ZnO nanoparticles

ICP –OES elemental analysis of bentonite supported ZnO powder was carried out after sample digestion in order to determine the concentration of aluminum, silica and zinc. It is found that the silica and aluminum content in zeolite powder is 24.14 % and 12.15 % respectively and the zinc content was found to be 9.8 % W/V basis. This summarizes the ZnO loading state dispersion technique. Activated bentonite was also tested for silica and aluminium content and it was found to be 28.12 and 13.41 % respectively. Si/ Al ratio is 1.98 and after activation of bentonite the Si/ Al ratio is found to be 2.09.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Elements</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO pure</td>
<td>Zinc</td>
<td>86.47</td>
<td>38.99</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>13.53</td>
<td>61.01</td>
</tr>
<tr>
<td>Bentonite powder</td>
<td>Aluminium</td>
<td>15.47</td>
<td>11.57</td>
</tr>
<tr>
<td></td>
<td>Silica</td>
<td>32.58</td>
<td>23.41</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>51.25</td>
<td>64.65</td>
</tr>
<tr>
<td></td>
<td>Potassium</td>
<td>0.70</td>
<td>0.36</td>
</tr>
<tr>
<td>Bentonite supported 10% ZnO powder</td>
<td>Aluminium</td>
<td>13.88</td>
<td>11.27</td>
</tr>
<tr>
<td></td>
<td>Silica</td>
<td>21.01</td>
<td>16.38</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>51.12</td>
<td>63.87</td>
</tr>
<tr>
<td></td>
<td>Potassium</td>
<td>3.52</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>Zinc</td>
<td>10.47</td>
<td>6.51</td>
</tr>
</tbody>
</table>

Table 7.2 Elemental composition of the samples obtained by EDS.
7.2.4. Morphology studies of CAc and CAc/ZnO/ bentonite composite membrane:

The surface morphology of the membrane as illustrated in figure 7.3 (a), (c) and (e). The cross section images are depicted in figure 7.3 (b), (d) and (f). Clearly, it is noted that the dispersion of ZnO/ bentonite NPs on the membrane surfaces was varied according to the concentration of NPs. The membranes prepared with less amount of NPs exhibited more dispersion of NPs in figure 7.3 (a), as compared to membranes of higher amount of NPs (i.e. figures 7.3 (c) and (e). The higher amount of NPs agglomerates and forms clusters in figure 7.3 c and e. The cross-sectional images give fine information on the incorporation of NPs embedded in the polymer matrix layers as well as productivity of the membranes. {figure 7.3 (b), (d) and figure 7.3 (f)}. Also, the structure of membrane layers has been changed accordingly with ZnO/ bentonite content increases, the viscosity of the casting solution will also increase which will disturb or troubles the penetration of NPs deeper into the polymer matrix during phase inversion.

Figure 7.3. SEM images of the membrane surface (a) CABe-1 (c) CABe-2 and (e) CABe-3 Cross sectional images (b) CABe-1 (d) CABe-2 and (f) CABe-3 of CA/ZnO bentonite composite membranes

It is found that increasing the NPs could intensify the formation of crosslinking structure between NPs and polymeric chains, inhibiting the growth of finger-like projections, as can be seen in figure 7.3 (a), (b), (c), (d), (e) and (f). The main factor
contributing to the formation of macro voids is the liquid-liquid demixing behaviour during phase inversion process. Since ZnO/bentonite has more affinity towards water than the polymer chains, the penetration velocity of NPs into the polymer matrix and the increase of solvent-diffusion velocity of the membrane to water are higher during phase inversion.

7.2.5. Effect of bentonite activation rejection of BP-3, 3 ppm solution.

![Figure 7.4. BP-3 rejection studies with and without activation of bentonite.](image)

Bentonites can be activated by acid or hot mineral solutions treatment; hydrogen ions attack the aluminosilicate layers through the interlayer regions as a result of this attack, there is a change in the structure, chemical composition and physical properties of clay. The structure of raw clay is opened and becomes porous, acid activated clay exhibit significantly different physical, chemical properties than non-activated bentonite. The surface area and porosity structure of bentonite can be changed to the desired extent by acid treatment. (Jacobs 1984 and Persquera 1992) The mechanism of acid activation involves ion exchange process or replacement of metallic ions by H⁺ ions, giving clay a highly active structure, which is acidic in nature. As depicted in the figure 7.4 the rejection of BP-3 with the non-activated bentonite membrane was 73 % and with the use of activated bentonite powder rejection was found to be 86 %, there is an increase in the rejection of 3 ppm BP-3 solution with the use of activated bentonite powder for the preparation of CAc, ZnO bentonite mixed matrix membrane.
7.2.6 Rejection with different concentration

The membrane flux was influenced by the composition of the membrane material. Figure 7.5 shows the BP-3 and caffeine permeation results. It is evident from the figure 7.5 that there is an increase in flux with an increase in the pressure and the composition of membrane material. Flux increased with an increase in the composition of bentonite supported ZnO nanoparticles. CABe-3 membrane showed highest water flux because bentonite powder is hydrophilic in nature.

7.2.7. Rejection of BP-3 with activated and natural Bentonite.

![Figure 7.5. Permeate flux studies with different pressure 3 ppm BP-3 solution with and without the activation of Bentonite powder.](image)

![Figure 7.6. Rejection studies of 3 ppm BP-3 solution versus pressure.](image)
Figure 7.7. Rejection studies of caffeine 1 ppm solution versus pressure.

The rejection of BP-3 and caffeine experiments were conducted. The experiments were repeated three times and mean results were reported. The effect of pressure and feed concentration on performance were studied. The figure 7.6 shows permeate flux and figure 7.7 show rejection of feed sample. The rejection rate of CAZe-3 membrane is higher when compared with all membranes, it showed 82% of rejection of BP-3 and almost negligible rejection of caffeine at 200 kpa pressure.

7.2.8. Photocatalytic Experiment

Photocatalytic activity of bentonite supported 10 % ZnO nanoparticles were evaluated on the degradation of caffeine in UV light illumination. A known weight of the catalyst was dispersed in a known volume of the caffeine along with an electron scavenger ammonium persulphate, and the resultant mixture was stirred throughout the experiment for uniform exposure of the catalyst to light. 5 mL aliquots were withdrawn every 20 min, filtered through Millipore syringe filter (0.45 µm pore size). The degradation of the caffeine was monitored after removal of photocatalyst by centrifugation at 4000 rpm and measured the decrease in the absorption maxima at 270 nm caffeine.

7.2.9. Photocatalytic degradation of caffeine

Synthesised bentonite supported 10 % ZnO nanomaterial is tested as a photocatalyst for degradation of caffeine under UV light. The effect of different parameters such as photodegradation efficiency of ZnO, and 10 % ZnO bentonite
powder with and without APS was evaluated. Effect of catalyst load of 10 % ZnO bentonite powder on photodegradation was also evaluated. ZnO only showed only 39 % degradation whereas 10 % ZnO bentonite powder showed 79 % degradation of caffeine. Bentonite supported 10% ZnO with 0.015 M APS showed almost complete degradation (91 %) whereas ZnO with APS showed 63 % rejection. Degradation efficiency of ZnO is increased by 1.5 times with the support of Bentonite on 10 % ZnO, as depicted in figure 7.8. The synthesised catalyst is very reactive in UV light.

Figure 7.8. Caffeine photodegradation with ZnO and 10% ZnO bentonite powder

7.2.10. Effect of catalyst load on degradation of caffeine.

Figure 7.9. Effect of catalyst load on the photodegradation of caffeine.
Figure 7.9 shows the effect of catalyst load on the photo degradation efficiency of caffeine. The results showed that photodegradation efficiency is increased with an increase in catalyst loading and an optimum loading, and after which it is decreased. The set of experiments were conducted by changing the catalytic load from 0.50 to 1.0 g/L, using 1 ppm caffeine solution by maintaining the constant concentration of pollutant constant. The degradation of caffeine was increased, when the catalytic load was increased of 0.50, 0.75 g to 1.0 g (52 %, 83 % and 73 % degradation were observed respectively, this is because of the increase of active sites on ZnO surface. Maximum degradation of caffeine was found to be at 0.75 g/L, and beyond this catalyst load, the photo catalytic activity is decreased, because of the formation of turbidity which reduces the light penetration into the solution and increased light scattering (Chakrabarti 2004). This observation can be explained regarding the availability of active sites on the surface of the catalyst and the penetration of solar radiation into the suspension. An increase in catalyst dosage results in an increase in the total active surface area of a catalyst which in turn increases the photo degradation efficiency (Jang 2006). However, this effect is counteracted at high catalyst dosages due to increased turbidity of the suspension. This is also due to aggregation of catalyst particles, which reduced the interfacial area between the reaction solution & the photocatalyst. The increased turbidity reduces penetration of the much-needed light due to scattering, hence a decrease in photodegradation efficiency at high catalyst dosage. With the help of above results, it was concluded that 0.75 g/L ZnO catalyst could be used as an optimum catalytic amount for the degradation reactions.
7.3. Conclusion

10 % ZnO supported bentonite nanoparticles were synthesied by solid state dispersion technique, and characteried by XRD, SEM and EDS. From the above observation, it can be concluded synthesied 10 % ZnO supported bentonite is a very good photocatalyst, and experimental results deplete that photodegradation of caffeine was enhanced when bentonite supported 10 % ZnO was used as a catalyst, which suggests that it has a great potential in the removal of emerging contaminants from wastewater. The mixed matrix membrane cellulose acetate with bentonite supported ZnO composite membrane were prepared by DIPS method. The membrane was also characterized by XRD, SEM, and ICP studies. The membrane with 0.75 g ZnO: Bentonite content (CABe-3) shows the maximum BP-3 rejection of 81 % which was in good agreement with log Kow of feed and hydrophilicity of the membrane. Increasing in the concentration of Benzophenone-3 increases the rejection efficiency. However the rejection decrease with applying higher pressure.