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The speed of light in a vacuum is always constant – a fundamental concept made famous by Albert Einstein. But light propagates more slowly when it enters a different medium, such as glass. The degree to which the speed is reduced is given by a material’s dielectric constant; a higher dielectric constant indicates slower propagation. Rather than rely on a limited source of natural substances, scientists have started to design optical materials with a broader range of beneficial properties including ‘slow’ light. A method for designing materials capable of slowing the propagation of light over a broad range of wavelengths has been developed by researchers at the A*STAR Institute of High Performance Computing, Singapore.

One approach is to combine two materials with different dielectric constants into a periodic structure. This can result in properties that dramatically differ from those of the constituent materials, particular when the length scale of the periodicity is similar to the wavelength of light.

These so-called photonic crystals, when appropriately designed and in ideal conditions, can almost stop the propagation of light altogether. The requirement that the periodicity of the structure be similar to the wavelength of interest, however, is a limitation for practical applications. It means that most of these materials only work with light of a single colour. The researchers have now developed a scheme for designing photonic crystals that operate over a broader range of wavelengths.

The researchers considered a structure in which two different materials are layered on top of each other. To obtain two different periodicities, however, a third material with a dielectric constant midway between the two other materials would typically be needed. This makes physically creating the structure difficult. The researchers instead focused on developing a mathematical technique to combine two materials in such a way that the dielectric profile in the stacking direction is almost the same as in the more complicated three-material structure.

They simulated the optical properties of their combined photonic crystal. They identified a broad range of wavelengths known as the strong coupling region that has a high density of slow modes. The invented linear optical multi-scale architecture will facilitates the creation of broadband slow light and could potentially revolutionize current optical buffering technologies.

Heartfelt congratulations to the Scientists of A*STAR Research Institute, Singapore, for the revolutionary research.

Biranchinarayan Tosh
Editor
Synthesis of Polymer-Protected Nanoparticles of Copper on Oxide-Carbon Carrier

Kydyrmolla Akatan¹, Yesbol Shaimardan¹, Kunaigul Kabdisalim¹, Ainur Kabdrakhmanova², Malik Maulet Khan¹, Zhandos Ukibaev³, Alibek Khabyev⁴ & Sana Kabdrakhmanova¹

¹National Science Laboratory, S. Amanzholov East Kazakhstan State University, Ust-Kamenogorsk, Kazakhstan
²I.Zhansugurov Zhetysu State University, Taldykorgan, Kazakhstan
³Kazakh National Agrarian University, Almaty, Kazakhstan
⁴Karaganda State Industrial University

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Abstract
This article deals with a method for the synthesis of nanoparticles of copper in combination with functional polymer polyvinylpyrrolidone with introduction to inorganic and organic carrier. The composition, morphology, structure and size of copper nanoparticles protected by polyvinylpyrrolidone, were established based on studies using dynamic light scattering, REM and SEM.

Keywords
Polymer, Nanoparticles of copper, Polyvinylpyrrolidone, Organic carrier, Zinc oxide

One of the priority directions in the chemistry of polymer materials is to obtain composite materials based on polymers and inorganic particles, wherein the polymer acts as a stabilizing agent of metal nanoparticles, preventing agglomeration and predetermining their catalytic, optical, electrical, etc. properties. For the application of polymer stabilized metal nanoparticles in the field of catalysis, they are needed to be passivated maintaining high reactivity¹. Therefore, one of the most important directions of research in this area is to find effective ways of controlled chemical stabilization of metal nanoparticles. At present, various types of polymer-immobilized nanocatalysts with activity and stability of the action were obtained on the basis of metals and functional polymers. Advances in this area are largely dependent on the capabilities of methods for obtaining nanoparticles. Various studies to create nanocomposites of transition metals have been carried out¹⁻¹². Strong reducing agents are generally used for the synthesis of mono- and bimetallic nanoparticles of metals, including disperse ether or hydrocarbon solutions of the alkali metals, usually sodium tetrahydroborate. Homo- and heterometallic metal nanoparticles were obtained¹³⁻¹⁷.

The use of various water-soluble polymers for stabilization of colloidal platinum nanoparticles was studied in detail¹⁹. Nanoparticles of different morphology and catalytic activity were obtained depending on the type and length of the block-copolymer, precursor type and the method of recovery¹⁸. Also the dependence on the metal type was established. It was found that polymer-protected coating affects particle size, morphology, colloid stability, catalytic activity²⁰. Protecting polymer type and its properties have a dominant influence on the properties of catalytic systems formed by creating a favorable environment for nanometals exhibiting catalytic activity.

Colloidal Pd-catalyst immobilized in the matrix of polyvinylpyrrolidone (PVPD) showed high selectivity to cyclic olefins in the hydrogenation of mixture of cyclic and linear alkenes²¹. The main advantage of colloidal particles stabilized by polymers is that they exhibit a high catalytic activity in hydrogenation processes and are stable during repeated use in catalytic processes. Polymer-protected metal nanoparticles have a number of disadvantages along with the numerous
advantages: partial or complete leaching of metal nanoparticles from the polymer matrix, the influence of the diffusion factor, which is due to difficulty in transferring substrates to the active centers located within the polymer matrix. Therefore, in order to stabilize nanoparticles, inorganic polymers or inorganic carriers of different structures are used along with organic polymers.

This paper deals with a method for the synthesis of nanoparticles of copper in combination with functional polymer PVPD with introduction to inorganic and organic carrier. The main physico-chemical and structural characteristics of the resulting composite were studied.

**Experimental**

Copper nanoparticles stabilized by PVPD were prepared as follows: 0.001 M solution of copper nitrate and 10 M solution of PVPD with molecular weight of 40,000 were prepared. The solution was aged for a day. Preparation of the colloid solution based on PVPD-protected copper ions was performed by simple stirring for 2 hours with volumes ratio of \( V_{PVPD40} : V_{Cu} = 1:1 \) to form metal-ligand coordination bond. To recover coordinated copper ions to the zero-valent state, resulting mixture was titrated with 0.01 M sodium borohydride solution with constant stirring using a magnetic stirrer until the color changes (Fig. 1). Nanosized copper particles were formed uniformly in the volume, the formation of which was fixed visually.

![Fig. 1 Preparation of polymer-protected copper nanoparticles](image)

Optical properties of the resulting copper nanoparticles were investigated by spectroscopic method (Specord 210 plus BU) in the UV-visible region of the spectrum. Catalytic system of PVPD\(_{40}\)-Cu synthesized by the liquid phase chemical recovery was deposited on the zinc oxide for further stabilization of the nanoparticles. For this, 5 mL of colloidal solution of PVPD\(_{40}\)-Cu catalytic system were mixed with 0.1 g of zinc oxide with intensive stirring for 5 h to obtain a uniform distribution of the nanoparticles on ZnO carrier. Resulting suspension was separated by filtration on Buchner funnel, washed repeatedly with water and then dried at the temperature of 100°C for 2-3 h.

Coating of catalyst systems on the superfine carbon carrier allows to maximize the catalytically active surface of transition metal, so the resulting catalyst system after immobilization of copper nanoparticles on zinc oxide was mixed with suspension of BUA-A marked activated carbon coal. To do this, 0.05 g of charcoal and 10 mL of distilled water were used to prepare coal slurry, which was added by 0.1 g of Cu-PVPD\(_{40}/\)ZnO catalyst with intensive stirring for 2 hours. The resulting mixture was centrifuged and dried at 100°C for 2 h.

Polymer-protected Cu-PVPD\(_{40}/\)ZnO/C catalyst systems were studied by various physico-chemical methods. Hydrodynamic diameter of the particle of PDCA-protected copper nanoparticles was determined by dynamic laser light scattering method using Malvern Zetasizer Nano ZS90 (UK). Spectrophotometric measurements were performed using UV-spectrophotometer (Specord 210 plus BU). Structure and morphology of copper nanoparticles deposited on solid carrier were studied by scanning (SEM), raster (REM) electron microscopy and optical (Leica DM 6000M) microscopy. The catalytic activity was determined by pre-reaction of hydrogen peroxide decomposition in the volumetric unit.

**Results and discussion**

Formation of copper nanoparticles was seen by the sharp color change after titration with reducing agent. Solution is a homogeneous colorless liquid (Fig. 2).

![Fig. 2 Colloidal solution of copper nanoparticles stabilized by PVPD 1 day after synthesis](image)

Estimated overall reaction scheme was:

\[
2Cu^{2+} + 2H_2O + BH_4^- \rightarrow 2Cu + BO_2^- + 4H^+ + 2H_2↑
\]

Methods based on the effect of the absorption or scattering of light by nanoparticles are applied to study the disperse systems of different nature, since the aggregation of small colloidal particles is
accompanied by the change in the optical properties of disperse systems, which is due to the electrodynamic interaction of particles due to multiple intracluster scattering. The size distribution of copper nanoparticles synthesized with borohydride is shown in Fig 3.

![Fig. 3 Dimensions of copper nanoparticles (a) not polymer-protected; (b) protected by PVPD_{40}](image)

It is known that stabilization of the nanoparticles in polymers is carried out by interaction of functional groups of a macromolecule with the surface of the nanoparticles. Addition of PVPD_{40} as a stabilizer with optimal concentration of 10 M makes a colloidal solution of copper nanoparticles more stable (Fig 3 (a), (b)). The stabilizing effect is due to the appearance of fine particles of reactive zero-valent metal in the system. Chemisorption between the polymer and the colloidal metal particles occurs at the time of their formation on the metal surface that leads to the formation of nanocomposite of the metal particles and the polymer molecules. Narrow particle size distribution is a major feature of pseudomatrix mechanism of formation of new phase in the polymer solution\(^\text{23}\). It indicates that during the process of formation of new phase, macromolecules form the protective screens on the surface of the growing particles after their size reaches a certain minimum value required to form a stable polymer-particle complex. The stronger the interaction of macromolecules with the nanoparticles, the smaller the average size of the nanoparticles formed in such processes.

Comparative dimensional characteristics of copper nanoparticles obtained without protecting and with protecting by PVPD_{40} polymer showed that functional polymer provides a reduction in size of copper nanoparticles. The obtained data on the synthesis of copper nanoparticles without protecting by polymer is in the range of 342.0 nm (Fig. 3). The use of the polymer as a stabilizer leads to a significant reduction in the size of the particles (Fig. 3). The experimental data are in good agreement with literature data\(^\text{23}\).

It is known that increasing the molecular weight of PVPD reduces the size of metal particles\(^\text{23}\). Therefore, PVPD with molecular weight of 40,000 was used in this study. In the presence of PVPD_{40}, size of copper nanoparticles is equal to 4.187 nm and do not change over time (Fig. 3). Nitrogen and oxygen atoms in the PVPD structure form a complex with metal ions, whereby PVPD is adsorbed on metal surfaces and helps to stabilize the nanoparticles.

![Fig. 4 Absorption spectrum of copper nanoparticles stabilized by PVPD](image)

Absorption spectrum of copper nanoparticles stabilized by PVPD has a maximum at 525 ± 5 nm, which is characteristic for zero-valent copper particles (Fig. 4).

Photomicrographs of the catalyst system of Cu-PVPD(PEI)/ZnO/C obtained using Leica DM 6000M optical microscope show the formation of porous catalysts, pore sizes of which fluctuate in the range from 0.38 microns to 1.38 microns (Fig. 5). This distinctive characteristic of catalytic systems fits well with many of the requirements of catalysis. Large agglomerates of copper nanoparticles are irregular in size. Cu nanoparticles stabilized by PVPD distributed uniformly on the carrier, which is consistent with the above results.

![Fig. 5 Optical microscope photograph of copper nanoparticles protected by PVPD and immobilized on zinc oxide and carbon](image)

Morphological structure of the catalyst system of Cu-PVPD(PEI)/ZnO/C and Me-Me-PVPD(PEI)/ZnO/C was investigated using raster and scanning electron microscope.

It was found that the obtained catalyst has a heterogeneous structure, the inorganic substrate (zinc oxide) is not evenly distributed throughout the volume of activated carbon (Figure 6). Coal is
presented by clearly faceted crystallites, where zinc oxide is distributed as a crumpled agglomerates with the size of the individual grains of 446.6 nm (Fig. 7-8). Particles containing copper of 7.58% (wt.) are concentrated mainly on zinc oxide. The copper content in the coal carrier is 1.03%

The obtained catalytic system was investigated for the decomposition of hydrogen peroxide at the volumetric unit. Fig. 9 shows the curve of the kinetics of hydrogen peroxide decomposition by polymer-protected copper nanoparticles (PVPD) of PVPD-Cu/ZnO/C at the temperature of 40-50 °C. Conditions of catalysis: $C_{Cu} = 0.001 \text{ mol/L}; C_{NaBH4} = 0.002 \text{ mol/L}; C_{PVPD40}: C_{Me} = 10,000:1; V_{PVPD40}: V_{Me} = 1:1.$

Increasing temperature promotes a slight increase in catalyst activity. The yield of the reaction product across the temperature range is approximately the same and was about 85%.
Fig. 9 Kinetics of hydrogen peroxide decomposition by PVPD-Cu/ZnO/C catalyst (m_{Cu} = 0.03 g, V (H_{2}O_{2} 30%) = 1 mL, temperature 40-50°C)

**Conclusions**

The method for the synthesis of copper nanoparticles stabilized by polymers on organic-inorganic carrier was developed. The composition, morphology, structure and size of copper nanoparticles protected by PVPD were established based on studies using dynamic light scattering, REM and SEM. It was found that in the presence of PVPD_{60} sizes of monometallic nanoparticles lie within 4.187 nm.

Obtained nanosystem showed catalytic activity in the reaction of hydrogen peroxide decomposition. It was found that the increase in temperature promotes a slight increase in activity of the catalyst.

**References**

Capacitor with PEO/Activated Carbon based Electrode and Nanocomposite Polymer as Electrolyte

Nirbhay K Singh, Mohan L Verma & Ajay Taide

1Department of Applied Physics, Shri Shankrachayra Institute of Engineering and Technology Khapri, Durg (Chhattisgarh),
2Condensed Matter Physics Research Laboratory, Department of Applied Physics Shri Shankaracharya College of Engineering and Technology – Junwani, Bhilai (Chhattisgarh), 490020
3Government V. Y. T. Art and Science College, Durg (Chhattisgarh), India

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Abstract Poly (ethylene oxide) (PEO) based Nano-Composite Polymer Electrolyte (NPE) membranes (PEO_{70}Ag_{30}(100-x)(TiO_{2})_{x}, where x = 0≤x≤15 wt%) have been casted by hot-press/solution free technique. Solid Polymer Electrolyte (SPE) composition PEO_{70}Ag_{30} (wt. %), reported earlier as highest conducting film with room temperature conductivity σ_{rt}~ 3.3 × 10^{-7} S cm^{-1}, has been used as the first phase host matrix and TiO_{2} filler particles of nanodimension (< 100 nm) as second phase dispersoid. The fractional dispersal of TiO_{2} filler (viz. x = 3 wt. %) in SPE host resulted into nearly threefold increase in room temperature conductivity. This NPE film (PEO_{70}Ag_{30})_{97}(TiO_{2})_{3} referred to as Optimum Conducting Composition NPE(OCC) film. Scanning Electron Microscopy (SEM), Energy Dissipative Spectroscopy (EDS), and thermogревemitr analysis (TGA) techniques have been used to study the morphological, compositional, and thermal behaviour of NPE(OCC) film. The ion transport behaviour has been characterized in terms of basic ionic parameters viz. conductivity (σ), mobility(µ), mobile ion concentration (n) and ionic transport number (t_{ion}). A thin symmetric capacitor has prepared using PEO based electrode (PEO_{70}Ag_{30})_{70}(AC)_{30} and NPE(OCC) membrane as electrolyte. The symmetric capacitor, studied by galvanostatic (charge–discharge) cycling in the range of 0–1.6 V at 0.5 A g^{-1} exhibited a specific discharge capacitance of 5 F g^{-1}.

Keywords Impedance spectroscopy (IS), Ionic conductivity, SEM, Activation energy, ionic transport number, SEM, EDS.

Polymer electrolytes are solutions of salts dissociable in the polymer host. It must function both as a separator and an electrolyte in a solid-state configuration and possess a number of essential electrochemical characteristics i.e. ionic conductivity, electrochemical stability, compatibility, thermal stability and mechanical stability. Fenton et al.¹ and Wright² has generated research activities leading to significant advances in the characteristics and structure of these polymer-salt complexes. In thin flexible forms they shows great technological potentials to fabricate all-solid-state electrochemical power sources viz batteries, fuel cells, super capacitors etc.³⁻²². The first ion conducting solid polymer electrolyte was reported in 1973³ and SPE based battery in 1979⁶. Since then, wide variety of SPE materials, involving different mobile ionic species have been investigated⁵⁻²². Poly (ethylene oxide) PEO possesses relatively higher electrochemical stability, exceptional ability to dissolve wide variety of salts compare to other polymers⁴⁻²². The polar and flexible main chain dissociates the salt and hence, carrier ions are generated. These ions can migrate through the amorphous region of the polymer via inter/intra chain segmental motion. The degree of amorphpousity of the polymer predominantly controls the ion conduction phenomenon in the polymer salt complexes. PEO based SPEs exhibit low ionic conductivity at room temperature but it can be significantly increased by fractional dispersal of nano size inert filler particles such as Al_{2}O_{3}, SiO_{2}, TiO_{2} etc.¹¹⁻²².
In the current work, a fine powder of TiO$_2$ filler has been dispersed on the host matrix having a composition (PEO$_{70}$AgI$_{30}$) which is termed “solid polymer electrolyte having optimal composition of AgI” (SPE (OCC))$^{15, 20}$ when it incorporated with TiO$_2$ filler particles are termed “nanocomposite polymer electrolytes” (NPE). The NPE electrolytes are synthesized via a hot press technique. The TiO$_2$ filler at the optimum amount was found to be very effective in reducing the crystallinity of PEO-based polymer matrix. The effect of TiO$_2$ filler and its influence on structural (physical), electrochemical, and capacitive properties have been investigated. The presence of the optimum amount of filler (3wt %) showed the maximum ionic conductivity of $\sigma$$\sim$2.35 x $10^{-5}$ S/cm. The electrochemical double-layer capacitor (EDLC) involving an electrostatic phenomenon (non-faradaic) is reported. A new class of solid state capacitors consisting of (PEO$_{70}$-AgI$_{30}$)(AC)$_{30}$ as the electrodes sandwiched with a synthesized NPE(OCC) electrolyte is presented, and the results are discussed.

Materials and Methods

NPE films (PEO$_{70}$AgI$_{30}$)$_x$ (TiO$_2$)$_y$ where $x = 0 \leq x \leq 10$ wt. (%) prepared by AR grade chemicals: poly (ethylene oxide) (PEO) (Mw $\sim$ 6x10$^5$, Aldrich, USA), AgI (purity $\sim$ 99.9%, Reidel, India), TiO$_2$ (size 100nm, Aldrich, USA) using hot press technique$[13-19]$. In this technique materials were mixed homogeneously in appropriate wt% and melted up to melting point of polymer host (for PEO $\sim$70 °C) then it pressed between block of stainless steel by applying pressure about two ton. The membrane so obtained subject for conductivity measurement using LCR meter [HIOKI 3522-50, Japan in the frequency range 50 Hz to 5 MHz. The activation energy $E_a$ calculated by Arrhenheous plot at different temperature and composition. Ionic mobility ($\mu$), ionic transference number ($t_\sigma$) and carrier ion concentration ($n$) of NPE (OCC) measured by a dc polarization Transient Ionic Current (TIC) technique$^23$ using x-y-t recorder (Graphtec WX 2300). In this method, a sample pallet is sandwiched between a blocking (graphite) and non-blocking (silver metal) electrodes. A fixed dc potential is applied across the sample, current in the external circuit is monitored simultaneously with time using x-y-t recorder. The current decreases rapidly with time; as a result of accumulation and dissolution of Ag$^+$ ion into Ag electrode. In order to separate out the cationic (Ag$^+$) transport number, a combined ac/dc technique is used$^26$. For this NPE film was placed between two Ag-metal electrodes and an external fixed dc potential ($\Delta V$) = 0.5 V for 5 h. Surface morphology and EDS analysis performed with the help of SEM (JEOL-JSI microscope) fitted with EDS and their thermal stability analyzed by (TGA). The capacitance of prepared capacitor was analysed by Cyclic Voltammetry.

Results and Discussion

The experimental Impedance plot for NPE found to be semi-circular arc which intercept on real axis, corresponds to blocking impedance $R_0$. Thickness $t$ of each sample found to be decreases with the filler in polymer host, which is clear indication of increase in amorphosity. The conductivity of composition calculated by equation

$$\sigma = \frac{t}{R_0A}$$

where area A = 1.85 cm$^2$ is cross section area of membrane. It is found that the room temperature conductivity increases initially with increase in nano size filler in SPE host, it reached at maximum value $\sigma_{\text{max}}$ ($\sigma$$\sim$2.35 x $10^{-5}$ S/cm) at $x$ = 3 wt. (%) of TiO$_2$ it referred as optimum conducting composition (OCC) and then decreases. Conductivity enhancement is due to the dissociation of ion aggregates and/or undissociated salt which resulted into the generation of free ion carriers as a consequence of addition of nano-sized TiO$_2$. Arrhenius plot indicate that initially conductivity increases linearly with temperature followed by a slight upward change in the slope $\sim$ 65-70°C then increased linearly again. It shows lowest activation energy (0.22eV) corresponds to OCC. The Ionic mobility ($\mu$), mobile ion concentration ($n$) and total ionic transference number ($t_\sigma$) of OCC films have also been determined, $\mu$ has been measured at different temperatures below $T_m$ subsequently, $n$ has been evaluated with the help of basic equation $n = \sigma/\mu$.q. From the log $\mu$ – 1/T” and, log n – 1/T” plots for OCC film it is found that $\mu$ remained almost unaltered while $n$ increased with increasing temperature because of more carrier ions generation.

The Complex impedance plots for the cell before and after polarization are shown in Fig. 1. The cell resistance of the film sample was measured before and after polarization using IS (impedance spectroscopy) technique. From the two semi-circles the cell resistances $R_0$$\equiv$ $R_0$ and $R_0$$\equiv$ $R_0 + R_s$ before and after polarization respectively, have been obtained. The initial ($I_0$) and final ($I_1$) currents of the cell during polarization, is show in Fig. 2. The cationic (Ag$^+$) transference number ($t_\sigma$) has been evaluated with the help of equation:

$$t_\sigma = \frac{I_0(\Delta V - R_0I_0)}{I_0(\Delta V - R_sI_s)}$$
Fig. 1 Complex impedance plots for the cell before and after polarization

Fig. 2 Variation of the cell current during polarization

Table 1 lists the room temperature values of ionic parameters calculated experimentally. It is found that with the addition of TiO$_2$ activation energy decreases and conductivity increases. The ionic transference number for all composition is found nearly unity, which is clear indication of ionic conductivity.

In Fig. 3 the surface morphology of the pure PEO is seen to be rough, with the addition of AgI electrolyte appears to be smoothen and the particle size tends to be smaller. The addition of TiO$_2$ further modified the surface morphology and amorphousity of NPE(OCC) increases. The EDS fingerprint alongwith SEM indicative element present in electrolyte. The TGA curve shown in Fig. 4 indicate of improve in thermal stability with the addition of salt and filler in polymer host.

![Fig. 3 SEM image of (a) PEO, (b) SPE, (c) NPE(OCC) (d) EDS Spectra of NPE(OCC)]

![Fig. 4 TGA curve of (a) PEO, (b) SPE, (c) NPE(OCC)]

![Fig. 5 CV curve of prepared capacitor]

With the use of NPE(OCC) as electrolyte and composition (PEO$_{70}$:AgI$_{30}$)$_{70}$(AC)$_{30}$ referred as PAC ($\sigma$~1.926x10$^{-3}$S/cm$^{-1}$) a thin capacitor is prepared. It is observed from Fig. 5 that the shape of CV curves is nearly rectangle and symmetry or mirror image about their zero current line, which is

| Table 1 Room temperature values of some basic ionic parameters viz. $\sigma$, $\mu$, $n$, and $t_{ion}$. |
|---|---|---|---|---|---|
| Film | $\sigma$ (S/cm$^{-1}$) | $E_a$ (eV) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | $n$ (cm$^{-3}$) | $t_{ion}$ |
| Pure PEO | 3.2x10$^{-9}$ | NA | NA | NA | NA |
| SPE (OCC) [PEO$_{70}$: AgI$_{30}$] | 3.3x10$^{-7}$ | 0.69 | NA | NA | 0.95 |
| NPE(OCC)(PEO$_{70}$:AgI$_{30}$)$_{97}$(TiO$_2$)$_3$ | 2.35 x 10$^{-5}$ | 0.22 | 2.93 x 10$^{-3}$ | 2.1x10$^{15}$ | 0.98 |
a clear proof of well developed capacitance properties. Using specific capacitance of capacitors calculated which shows capacitance value of $5 \text{ F/g}$ cycling in the range of $0$–$1.6 \text{ V}$ at $0.5 \text{ A g}^{-1}$.

**Conclusions**
The optimum conducting ($\sigma \ 2.35 \times 10^{-5} \text{S/cm}$) composition was found for $3\% \text{TiO}_2$ in SPE, confirm by lowest value of activation energy. Ionic nature is confirmed by ion transference ($t_{\text{ion}}$) calculation. The mobility ($\mu$) and carrier ion concentration ($n$) also calculated. All the physical characterization was studied on the best chosen material NPE (OCC). The thermogravimetric analysis suggests that all compositions are thermally stable up to $240 \degree \text{C}$ and suitable for device applications. SEM analysis shows that the addition if inorganic filler reduces the degree of crystalline while enhancing the ionic conductivity. The best chosen electrolytes was tested in the symmetric capacitor with PAC electrode. The result obtained experimentally shows comparatively good performance.

**Reference**
Studies on Biodegradability, Morphology and Mechanical Properties of Cotton-Polyester Composites

Sanjita Mohanty¹ & B. C. Singh²

¹Trident Academy of Technology, Bhubaneswar
²Department of Chemistry, Ravenshaw University, Cuttack 753 003

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Abstract In the present investigation composites have been prepared from natural cotton and synthetic polyester. Different properties of the composites like mechanical properties, morphology and extent of biodegradability were studied. Cotton, an important cellulosic fibre, can be incorporated in synthetic polymers like polyester in different ways for achieving desired properties and texture. Mechanical properties like tensile strength (TS), flexural strength (FS) and impact strength (IS) of the composites as a function of fibre loading have been evaluated. Composites containing 40 wt % of cotton fibre improved tensile and flexural strengths by 175% and 35% respectively in comparison with neat polyester. The impact strength of the composite with 40 wt% of fibre was found to be 141J/m. The elongation at break of the composites exhibits an increase with the introduction of fibre. The scanning electron micrographs (SEM) of various composites show uniform fibre surface. The results of biodegradability test indicate improved biodegradation in the composites compared to neat polyester.

Keywords Composites, Tensile strength, Flexural strength, Impact strength, Biodegradability.

A significant effort has been made recently to apply natural fibre reinforcement in synthetic polymer bonded composite materials. Natural fibres like jute, sisal, pineapple leaf fibre, coir and cotton have attracted attention as reinforcements in polymeric composites because of their easy availability as a renewable resource, easy processability, low density, light weight, low cost and above all “ecofriendly” characteristics. However, low and variable strength, poor resistance to weathering and lack of wettability with various polymeric matrices make natural fibres less desirable than synthetic fibres as reinforcements. Experimental and theoretical studies over the past decade have shown that control of the fibre matrix interfacial bond strength is a critical factor in obtaining the best mechanical properties of the resultant composite materials¹.

The natural fibre under investigation in this paper is cotton which is obtained from cotton plant. It is used for making wide varieties of materials viz. mattresses, clothes etc. Hence apart from the conventional uses, research and development efforts have been underway to find new uses of cotton including its utilization as reinforcements as polymer composites. Surface modifications of natural fibres like jute²,³ and pineapple leaf fibre (PALF)⁴ have improved mechanical properties of the resulting composites.

The use of natural fibres as reinforcing materials in both thermoplastic and thermoset matrix composites provides positive environmental benefits with respect to ultimate disposability and best utilization of raw materials⁵,⁶. Natural fibres are very attractive for composite materials because of their advantages compared to synthetic fibres as it causes lower levels of skin irritation and respiratory problems during handling, reducing tool wear during the processing, good recyclability, abundant supply, low cost, low density, high specific strength to weight ratio, non-toxicity and biodegradability⁷,⁹. Biocomposite from plant and wood based fibres are used in a different range of products including aerospace materials, automobile industry, building materials etc¹⁰. Using biomass fibres to reinforce plastics has several advantages over synthetic fibre. They are low cost, low density, have a high specific strength and modulus comparatively easy to process.

Corresponding Author:
Sanjita Mohanty
e-mail: mohantysanjita1@gmail.com
due to their nonabrasive, biodegradable and environment friendly nature.

However, research in this area of polymer science and technology is in its infancy and efforts are needed to achieve full commercial benefit. In the present communication, attempts have been made to study the mechanical performance, morphology and biodegradability of cotton-polyester composites.

Materials and Methods
The cotton fibre used here is of 95% pure cellulose and it was directly used for the experimental purpose and was purchased from Sigma Aldrich Chemicals, Bangalore. General purpose polyester resin (FB-333) with 34-36% volatile content, methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate were obtained from Rula chemicals Pvt. Ltd., Calcutta.

Composite Fabrication and Testing
Composite fabrication was carried out in a closed mold by hand layup method. First, the mold was polished, and then mold releasing agents were applied on the surface. General purpose polyester resin was mixed with 1 wt% cobalt naphthenate (accelerator) and 1 wt% methyl ethyl ketone peroxide (catalyst). The resin mixture was degassed in a vacuum desiccator and then poured on the cotton matrix placed in the mold. When the cotton was completely wet by the resin, the mold was closed, pressed at 0.2 Kg/cm² and cured at room temperature for 24 hours.

Tensile and flexural tests of the composite specimens were carried out at 23 °C and 56% RH using UTM (Universal Testing Machine) LR-100k, Lloyds instrument Ltd, as per ASTM-D 638, test speed 100 mm/min, gauge length 50 mm and ASTM-D 790, at test speed 2.8 mm/min, gauge length 100 mm respectively. The notched Izod impact energy per unit thickness of the sample (J/m) was determined by impactometer (CEAST, Italy) as per ASTM-D 256 with an average thickness of 3.2 mm and notch depth 2.54 mm and notch angle 45°. Each result reported is the average of five tests of a particular sample.

Scanning Electron Microscope (SEM)
Micrographs of fibre and composite samples were studied with JOEL JSM-5800 scanning electron microscope, made in JAPAN, operated at 20 kV. The specimens were coated with 50-µm thick gold film in an automatic sputter coater (Polaron, USA) to avoid surface charging under electron beam.

Biodegradability Study
The composite samples were tested for susceptibility to biodegradation. In the present study biodegradability test was carried out by soil burial test.

Soil Burial Test
The soil for the soil burial test was obtained from a fertile land. The soil was made free from large clumps, plant debris etc. and was kept in several earthen pots. Small composite samples of a particular weight were buried in the above pots at a depth of 10cms. The soil containing the samples was watered daily. The samples were removed after one month and washed well with water and dried at 50 – 60 °C in a vacuum oven for 24 h. Then weight of each sample was measured and the weight loss due to biodegradation was observed.

Results and Discussion

Mechanical Properties

| Table 1 Mechanical Properties viz. tensile strength, flexural strength and impact strength of cotton-polyester composites. |
| Sample No. | Fibre wt % | Tensile strength (MPa) | Flexural strength (MPa) | Impact strength (J/m) |
| 1 | 0 | 20 | 48 | 15 |
| 2 | 10 | 28.75 | 45.37 | 32.38 |
| 3 | 20 | 40.43 | 57.45 | 83.26 |
| 4 | 40 | 54.90 | 64.91 | 140.88 |
| 5 | 50 | 29.34 | 59.24 | 24.79 |

Table 1 shows the effect of cotton fibre content on tensile strength (TS), flexural strength (FS) and impact strength (IS) of the cotton-polyester composites. The fibre content was varied from 10 to 50 wt% to investigate the effect on the mechanical properties. From table-1 it is observed that with the increase of fibre content from 10 to 40 wt% tensile strength, flexural strength and impact strength increase. But with 50 wt% of fibre content all the values decrease. The addition of 40 wt% fibre increases the TS of the composite by 175 % over the neat polyester. Higher TS values at higher fibre content might be due to adequate fibre content and composites which lead to greater wetting. At still higher fibre content i.e. 50 wt%, more fibre ends create cracks at the fibre ends, which lead to composite failure. However the TS of the composite with 50 wt% fibre loading is found to be greater than that of neat polyester. This indicates that the fibre matrix interface in the 50 wt% loaded composite is quite strong. It has been reported earlier that incorporation of lower wt% of fibre decreases TS of the composite slightly. Some of the research workers have suggested poor wetting in such case which leads to weak interface. From Table – 1 it is seen that the values of flexural strength of cotton-polyester composite is found to
be less than that of neat polyester at 10 wt %. But with an increase in fibre content from 10 to 40 wt % increases FS by 44 %. Further increase of fibre content results in lowering in FS value. Decrease in FS at higher wt % fibre is due to increased fibre to fibre interaction and dispersion.

The percentage elongation at break is quite low in pure polyester resin. The elongation at break increases with increasing wt % of fibre loading (Fig. 1). The brittle nature of polyester resin decreases with addition of cotton fibre. This increase is quite comparable with coir-polyester composites unlike that in composites prepared from other natural fibre such as jute and sisal because the elongation at break of these fibres is low. The incorporation of cotton fibres therefore makes the polyester matrix acquire a higher elongation at break. The higher value of elongation is also possible due to good fibre matrix adhesion. But at 50% of fibre loading the elongation starts decreasing (Fig. 1). Similar results have been obtained in case of coir-polyester composites.

Impact strength (IS) values of composites increases as fibre is incorporated in the matrix (Table – 1), although large increase has been observed possibly due to toughness of the coir fibre. The increase of IS up to 40% fibre loading is basically due to good interfacial adhesion. There is a decrease in IS from 141 J/m to 25J/m when the fibre loading is increased from 40% to 50%. This decrease is similarly explained on the basis of poor wetting and adhesion. From the above observations it can be concluded that under the present experimental conditions, composites with 40% fibre content achieve optimum mechanical properties.

**Scanning Electron Microscopy**

Fig. 2 (a, b) depicts a comparative account of scanning electron micrographs of neat polyester and cotton-polyester composites. The scanning electron micrograph of cotton-polyester composite with 30 wt % fibre content shows a uniform fibre surface without much surface debris. This uniformity is most probably the cause of stronger adhesion and hence greater tensile strength of the composite. It has been also observed that at higher percentage of fibre loading, surface of the composites become highly non-uniform with a lot of surface debris. This non-uniformity results in poor mechanical anchorage between fibre and matrix for which tensile strength decreases.

**Biodegradability Test**

Table – 2 shows the extent of biodegradability with increase in cotton fibre wt % of the composites. It was seen that the percentage of biodegradation of neat polyester determined through soil burial test for one month shows no degradation. The increase of cotton fibre wt % from 10% to 50% shows increasing biodegradation. Such increase is very prominent up to 40 wt % fibre loading and thereafter the increase is slow.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fibre wt. %</th>
<th>Initial wt. (g)</th>
<th>Final wt. (g)</th>
<th>Diff. wt. (g)</th>
<th>% of BD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.5440</td>
<td>0.5440</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>2.3855</td>
<td>2.3749</td>
<td>0.0106</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1.9332</td>
<td>1.8941</td>
<td>0.0391</td>
<td>2.02</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>1.7876</td>
<td>1.6774</td>
<td>0.1102</td>
<td>6.16</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>2.2248</td>
<td>2.0826</td>
<td>0.1422</td>
<td>6.39</td>
</tr>
</tbody>
</table>
Conclusions
The results of the present study show that a useful composite with good strength could be successfully developed using cotton fibre as a reinforcing agent for polymer matrix. Best mechanical properties of cotton-polyester composites were reached for composites containing 40 wt% of fibre. There has been a fortunate coincidence of the fact that the maximum percentage of biodegradation is observed in the soil burial test for a month only with the same fibre content of the composite.

References
Leaching Behavior of Fly Ash from Talcher Thermal Power Station with Mineral acids

Niva Nayak
Orissa Engineering College, Bhubaneswar, Odisha

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Abstract Fly ash, the major industrial waste product generated from the coal fired power plants, has become an environmental concern due to its improper disposal. It is one of the most harmful pollutants that ravages the vast tracts of land and pollutes the air as well as the water. The low percentage utilisation of Fly ash in India is reflected in the low and medium value applications like brick, cement and noncement uses. For high value application fly ash can be considered as a waste of recoverable resources for metal extraction. Attempts have been made to study the leaching behaviour of TTTP fly ash using mineral acids such as HCl, HNO₃, H₂PO₄ and H₂SO₄. The aluminium and iron dissolution using HNO₃ are significantly lower than those obtained using HCl. However both the acids are found to be effective lechant for iron extraction as the extraction of Fe is more than Al compared to the other acids. In a similar way the study shows o-H₃PO₄ and H₂SO₄ as suitable leaching agent for Aluminium extraction.

Keywords Fly ash, Aluminum, Iron, Leaching, Mineral acids

The accumulation of solid wastes is a serious problem that threatens the environment of the entire planet and will continue its exponential growth due to the increasing population and industrial development. Fly ash, one of the major solid wastes can reduce agricultural productivity by settling on the leaves by which photosynthesis reduces. The heavy metals present in fly ash may leach into ground water resulting contamination. Soil pollution arises due to the use of high ash content coal and non utilization of fly ash by industries. Soil pollution due to fly ash accumulation in the nearby power plant causes land degradation, particularly soil erosion and loss of soil fertility. Application of fly ash in the manufacture of bricks, cement, concrete, ceramic products, building materials, composites, construction fill, road base, mineral filler in asphaltic mix, waste land reclamation and in agriculture has been proved to be beneficial. As fly ash is rich in minerals, another alternative use can be metal extraction. It is obvious that no single application is likely to consume all the generated fly ash but mineral extraction could provide additional markets and increased utilization of fly ash.

The physical and chemical properties along with its quality of fly ash depend upon various parameters such as coal quality, coal pulverization, combustion process, furnace type, ash collection technique and many other operational parameters. The mineralogy and chemistry of the parent coal control the mineralogy and chemistry of fly ash produced. Fly ash is a complex heterogeneous material consisting of silt-size particles ranging in color from grey to reddish brown. Both the crystalline and amorphous phases are seen in the morphological study. Generally, the fly ash matrix is composed of 15-35% crystalline and 65-85% amorphous glassy phase. According to Hulett et al. fly ash consists of three major matrices glass, mullite quartz and magnetic spinel. The major oxides present in coal ash are SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaO, MgO, Na₂O and K₂O. The mineral matters of coal are composed of rock forming minerals such as quartz, calcite, dolomite, clay minerals and iron sulphides. Besides quartz and pyrite, a clay fraction consisting of kaolinite, illite and any expandable irregular mixed-layer mineral has also been reported. A study on the composition of Indian fly ash agrees with the above as it shows the fly ash consisted of largely silica, alumina, iron oxides and carbon together with significant percentage of Ca, Mg, K, Ti and variable...
trace elements\(^6\). According to the report of Natusch et al.\(^7\) a number of potentially toxic elements are concentrated on the particle surface at varying depth. More refractory species like Al, Fe, Si and minor elements like Ca and Mg do not exhibit surface predominance rather they are strongly associated with the ash matrix. Most of the trace elements present in coal tend to be associated with the particle surface rather than core. The elemental concentration varies with particle size \(^8\).

As the fly ash is rich in mineral oxides, and most of them are in the glass matrix, it becomes essential to dissolve the glass matrix for the extraction of metal values. Thus, chemical process based on i) Sintering ii) Gas-solid reaction and iii) Leaching treatments alone or in combination are extensively studied. The leaching treatment is either acid or basic, in which inorganic acids (mineral acids) like HCl, HNO\(_3\), o-H\(_3\)PO\(_4\), H\(_2\)SO\(_4\) are used and for basic/alkali leaching solution of NaOH or alkaline salts such as Na\(_2\)CO\(_3\) is used. A large number of processes for the recovery of alumina from clays and other alumina bearing minerals (other than bauxite) have been proposed by several workers\(^9-11\). However, the recovery of Al, Fe, Ca, Mg, Si, Na, K and Ti from fly ash using classification, magnetic separation followed by leaching using HNO\(_3\), HCl and H\(_2\)SO\(_4\) were studied\(^12-14\).

For the purpose of high value application some fly ashes of different thermal power plants of Odisha, India have been studied for the extraction of aluminium\(^15-16\). The present investigation is based on the leaching of fly ash by using different mineral acids such as HCl, HNO\(_3\), o-H\(_3\)PO\(_4\) and H\(_2\)SO\(_4\). The effect of variation of acid concentration on the leaching behaviour of fly ash is investigated at a constant leaching time of 4h at a boiling temperature of the corresponding acids. A comparative study on the magnitude of aluminium and other metals extraction using these leachants has also been represented.

Materials and method

Sample collection and characterisation

The fly ash sample under study is collected from the electrostatic precipitator of Talcher thermal power station (TTPS), Odisha. These samples are characterized physicochemically for their mineralogy, morphology, particle size and chemistry using XRD (Philips PW 1400), Scanning Electron Microscope (Jeol JSM), Malvern particle size analyzer (UK, Model-3600), Atomic Absorption Spectrophotometer (Varian Spectra AA-20), Inductively Coupled Plasma Spectrophotometer (Perkin-Elmer,Plasma-400) and Flame photometer (Elico, Model CI-22D). The reagents used for the chemical analysis are of AnalR grade. The mineral acids used in the leaching experiments are generally of commercial grade.

Leaching with mineral acids (HCl, HNO\(_3\), o-H\(_3\)PO\(_4\), H\(_2\)SO\(_4\))

In each leaching experiment, 100g of fly ash were digested with different concentrations of mineral acids at its boiling point in a solid:liquid ratio 1:1. The mixture was taken in a 1 L flask, boiled at the boiling point on constant stirring. Boiling continued up to 4h with time-to-time addition of hot water to maintain the desired solid liquid ratio. Finally, the mixture was boiled to dryness. Then the mixture was further extracted with 500-ml hot distilled water followed by boiling and filtered through a G3 Buchner funnel using suction pump. The residue was washed twice with hot water and washings were collected with leach liquor. The leach liquor was evaporated and made up to a known volume (1 L) and analysed for various elements like Al, Fe, Ti, Ca and Mg. The residue was washed up to neutral and dried at 110°C.

Mineralogy (XRD) - Phase Assemblies

The X-ray diffractogram for fly ash was carried out on PHILIPS PW 1400, using CuK\(\lambda\) radiation. Similar parameters like kV = 40, mA = 20, Chart speed = 1 cm / min., Gonio meter speed = 2° / min. are maintained during the analysis to get the uniform information about the samples. The characteristic reflection peaks (dA\(^0\) values) were matched with JCPDS data files to identify different minerals.

Morphology (SEM)

The surface characterization i.e., morphology and crystal structure of fly ash was done by a Scanning Electron Microscope (JEOL JSM 840). The fly ash samples dried at 110°C were mounted on an aluminium stub with the help of adhesives to make the surface conducting and then sputtered in vacuum chamber at high voltage. These conducting samples were then observed under the microscope.

Particle Size

The particle size distribution pattern was determined with the help of a MALVERN Particle size analyzer (UK, Model 3600) where the measurement is based on the He-Ne laser. Apart from the above it gives different mean sizes of the particle size distribution and also specific surface area of the particles in terms of m\(^2\)/cm\(^3\).

Atomic Absorption Spectrometry (AAS)

The elements namely Ca, Mg, Fe, Mn and Ni are analysed by Atomic Absorption Spectrometer
Inductively Coupled Plasma Spectrometry (ICP-OES)
The quantitative evaluation of elements like Al, Ti, Si and B present in fly ash and leached liquor were done by ICP (PERKIN ELMER, PLASMA-400) Spectrophotometer. A high temperature (10,000K) Argon Plasma source is used for the excitation of the element and the concentrations are measured as a function of the emission intensity of the emission spectra generated by the particular element.  

Flame Photometry
The concentration of Na and K was determined by Flame Photometer (ELICO - MODEL CL 22D) using particular filter for the wavelength of particular element. Calibration curves were made with suitable standard solutions made from AR KCl and AR NaCl. Then the concentration of the text sample was calculated by using the methods as outlined by Vogel.

Results and Discussion
The chemical analysis of inorganic oxides found in TTPS fly ash are given as SiO₂: 59.490, Al₂O₃: 29.091, Fe₂O₃: 3.901, TiO₂: 1.902, K₂O: 0.722, CaO: 0.993, MgO: 0.332, Na₂O: 0.129 and P₂O₅: 0.619. The major metallic constituents in this fly ash are Si, Al, Fe, Ti, Ca, Mg, Na and K. Fly ash consists of both crystalline and amorphous phases. The crystalline phases identified are quartz, mullite, haematite, magnetite, sillimanite and spinel. Similarly, the amorphous phase consists of spherical micron sized particles composed of mullite enclosed in a glassy matrix. The external glass is enriched in Ca, Mg, Fe and Al. The interior glass matrix is composed primarily of Si and a major portion of the total Na and K. Thus, leaching is primarily controlled by dissolution of the external glass matrix after rapid dissolution of surface salts in amorphous phase along with the dissolution of crystalline phases.

Leaching with HCl
In the entire concentration range of HCl, the metal concentrations in the leached liquor are given in Table 1. It is observed from the data that leaching of iron is more than the other elements present in fly ash. The percentage extraction of aluminium increases slightly in the concentration range of 2N to 11.3N from 2.3 to 4.03% where as the iron extraction is 17.4 to 34.82%. This lower in concentration of aluminium may be due probably to the formation of relatively insoluble aluminium, silicon compounds. The iron in the ash is predominantly in the form of Fe₂O₃ and Fe₅O₇ produced by the oxidation of pyrite during the combustion process, whereas aluminium is present in the structure of crystalline phases and so is dissolved more slowly, in case of HCl as leaching agent. The dissolution of aluminium and iron in fly ash results AlCl₃ and FeCl₃ as suggested by Livingston et al. Although the concentration of the other metal values in leached liquor shows increasing trend but their concentrations are not appreciable. Hence, iron is the most preferred metal ion for a leachant like HCl.

<table>
<thead>
<tr>
<th>HCl Concentration</th>
<th>Al</th>
<th>Fe</th>
<th>Ti</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>% Extraction of Al</th>
<th>% Extraction of Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>2N</td>
<td>0.355</td>
<td>0.475</td>
<td>0.014</td>
<td>0.047</td>
<td>0.024</td>
<td>0.012</td>
<td>0.020</td>
<td>2.30</td>
<td>17.40</td>
</tr>
<tr>
<td>4N</td>
<td>0.555</td>
<td>0.581</td>
<td>0.015</td>
<td>0.068</td>
<td>0.024</td>
<td>0.013</td>
<td>0.029</td>
<td>3.60</td>
<td>21.29</td>
</tr>
<tr>
<td>6N</td>
<td>0.595</td>
<td>0.884</td>
<td>0.015</td>
<td>0.068</td>
<td>0.024</td>
<td>0.015</td>
<td>0.030</td>
<td>3.86</td>
<td>32.39</td>
</tr>
<tr>
<td>8N</td>
<td>0.593</td>
<td>0.906</td>
<td>0.016</td>
<td>0.070</td>
<td>0.028</td>
<td>0.017</td>
<td>0.030</td>
<td>3.85</td>
<td>33.20</td>
</tr>
<tr>
<td>10N</td>
<td>0.608</td>
<td>0.925</td>
<td>0.017</td>
<td>0.071</td>
<td>0.030</td>
<td>0.017</td>
<td>0.031</td>
<td>3.95</td>
<td>33.88</td>
</tr>
<tr>
<td>11.3N</td>
<td>0.620</td>
<td>0.950</td>
<td>0.020</td>
<td>0.072</td>
<td>0.031</td>
<td>0.024</td>
<td>0.034</td>
<td>4.03</td>
<td>34.82</td>
</tr>
</tbody>
</table>

Leaching with HNO₃
The dissolution of aluminium along with other elements in the leached liquor with HNO₃ is shown in the Table 2. It is observed that extraction of aluminium is 2.17 % for 2N HNO₃ and 3.80 % for 16N HNO₃. The dissolution of iron shows an increasing trend than that of aluminium. At an initial concentration of 2N HNO₃ extraction of iron is 2.62 % whereas at 16N extraction value is 19.4%.
The aluminium is taken into aqueous solution, as
$\text{Al}^{3+}$ and lies as $\text{Al(NO}_3\text{)}_3$ in the solution \(^{21}\). concentration of $\text{H}_2\text{PO}_4$ are chosen. Aluminum
along with other elements like Fe, Ca, Mg, Na and

\[
\begin{array}{cccccccccc}
\text{HNO}_3 \text{ Concentration} & \text{Al} & \text{Fe} & \text{Ti} & \text{Mg} & \text{Ca} & \text{Na} & \text{K} & \% \text{ Extraction of Al} & \% \text{ Extraction of Fe} \\
2N & 0.335 & 0.072 & 0.012 & 0.034 & 0.013 & 0.004 & 0.019 & 2.17 & 2.62 \\
4N & 0.410 & 0.204 & 0.015 & 0.043 & 0.016 & 0.005 & 0.026 & 2.66 & 7.45 \\
6N & 0.460 & 0.293 & 0.019 & 0.045 & 0.017 & 0.005 & 0.027 & 2.99 & 10.71 \\
8N & 0.475 & 0.335 & 0.020 & 0.049 & 0.020 & 0.005 & 0.027 & 3.08 & 12.27 \\
10N & 0.460 & 0.378 & 0.022 & 0.068 & 0.027 & 0.007 & 0.029 & 2.99 & 13.87 \\
12N & 0.475 & 0.454 & 0.026 & 0.077 & 0.028 & 0.016 & 0.030 & 3.08 & 16.63 \\
14N & 0.500 & 0.508 & 0.029 & 0.086 & 0.028 & 0.016 & 0.030 & 3.25 & 18.60 \\
16N & 0.585 & 0.530 & 0.030 & 0.105 & 0.029 & 0.018 & 0.031 & 3.80 & 19.40 \\
\end{array}
\]

Table 2 Metal extraction from fly ash with varied $\text{HNO}_3$ concentration
(Solid : Liquid =1: 1, metal concentration in g/L)

\[
\begin{array}{cccccccccc}
\text{H}_2\text{PO}_4 \text{ Concentration} & \text{Al} & \text{Fe} & \text{Ti} & \text{Mg} & \text{Ca} & \text{Na} & \text{K} & \% \text{ Extraction of Al} & \% \text{ Extraction of Fe} \\
4N & 0.259 & 0.123 & 0.001 & 0.064 & 0.046 & 0.006 & 0.006 & 1.68 & 4.51 \\
8N & 0.370 & 0.375 & 0.004 & 0.064 & 0.046 & 0.006 & 0.007 & 2.40 & 13.74 \\
12N & 0.529 & 0.791 & 0.012 & 0.048 & 0.034 & 0.007 & 0.008 & 3.43 & 28.99 \\
16N & 0.786 & 0.882 & 0.019 & 0.035 & 0.025 & 0.009 & 0.011 & 5.10 & 32.29 \\
20N & 0.830 & 0.905 & 0.034 & 0.035 & 0.025 & 0.010 & 0.011 & 5.38 & 33.16 \\
24N & 1.220 & 0.923 & 0.049 & 0.032 & 0.023 & 0.013 & 0.011 & 7.91 & 33.83 \\
28N & 1.251 & 0.979 & 0.051 & 0.030 & 0.021 & 0.015 & 0.012 & 8.13 & 35.88 \\
32N & 1.650 & 0.990 & 0.051 & 0.028 & 0.020 & 0.016 & 0.012 & 10.70 & 36.25 \\
36N & 2.451 & 0.997 & 0.084 & 0.027 & 0.019 & 0.016 & 0.018 & 15.91 & 36.50 \\
38N & 2.881 & 1.008 & 0.084 & 0.026 & 0.019 & 0.018 & 0.023 & 18.69 & 36.91 \\
40N & 3.651 & 1.051 & 0.097 & 0.025 & 0.018 & 0.021 & 0.025 & 23.69 & 38.48 \\
41.1N & 5.082 & 1.053 & 0.113 & 0.024 & 0.017 & 0.024 & 0.035 & 32.98 & 38.59 \\
\end{array}
\]

Table 3 Metal extraction from fly ash with varied $\text{H}_2\text{PO}_4$ concentration
(Solid : Liquid =1:1, metal concentration in g/L)

The Al and Fe dissolution using $\text{HNO}_3$ are
significantly lower than those obtained using $\text{HCl}$
\(^{20}\). As the extraction of iron is more than extraction
of aluminium in both the acids, $\text{HCl}$ and $\text{HNO}_3$, as
leachant are effective in recovering iron from fly
ash than aluminium. Iron occurs as iron oxides, i.e.
$\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$ and does not present in matrix,
therefore are easily dissolved out. The dissolution of
aluminium is less due to its presence as aluminium
silicon crystalline phase. Other elements like Ti,
Ca, Mg, K, Na and their salt, which generally lies
on the surface of the glassy phase, are also
dissolved to some extent.

**Leaching with ortho-$\text{H}_2\text{PO}_4$**

In order to study the effect of $\text{H}_2\text{PO}_4$ on the
extraction of aluminium from fly ash different
K are leached out and their concentrations are
given in the Table 3. The extraction of aluminium at
an initial concentration (4N) of ortho-phosphoric acid
is 1.68% and the percentage of extraction increases gradually with the increase in concentration of acid. Using 41.1N ortho-
phosphoric acid, the extraction value of aluminium
reaches 32.98%. In all the cases, considerable
amount of iron is extracted and the extraction value
varies from 4.51 % to 38.59 %. On comparison with
$\text{HCl}$ and $\text{HNO}_3$, ortho-phosphoric acid is found to
be strong and effective leachant, which enters into
the matrix of the aluminium silicate \(^{22,23}\). Results on
the extraction of various metal values show a
gradual increasing tendency with the increase of
acid concentration except calcium and magnesium.
The metal in fly ash dissolve forming mono metal
phosphate whereas, the increasing concentration of Ca and Mg may be attributed due probably to the formation of di- and tri calcium and magnesium phosphates.

**Leaching with H_2SO_4**

The dissolution of aluminium along with the other elements with different concentration of sulphuric acid are summarized in Table 4. The concentration of different metals have an increasing tendency with the increasing concentration of the acid used. It is observed that there is a gradual increase in aluminium extraction with the increase in acid concentration. The extraction of aluminium with 3N H_2SO_4 is found to be 2.66% whereas at 36N H_2SO_4 it is 41.3%. Similarly, iron extraction varies from 13.33% to 53% with 3N to 36N H_2SO_4 respectively. In all the cases, along with aluminium and iron, the other metals Ca, Mg, Na, K and Ti are also leached out to some extent. Aluminium and iron dissolves as Al³⁺ and Fe²⁺ in sulphuric acid whereas calcium precipitates as CaSO_4 causing particles inhibition effect. It is assumed that initial dissolution of aluminium is from glassy phase only and more stable quartz-mullite phase dissolves in the latter stage.

**Post leached Ash studies**

The post-leached samples have been characterized for particle size distribution, XRD and SEM in order to compare and detect the changes in the content of many strategic metals already leached out. Leached residues are washed thoroughly with distilled water, dried at 110°C, and then subjected to physical and mineralogical characterization.

**SEM Studies**

The SEM photomicrographs of the pre and post leached TTPS fly ash are given by Fig. 1 a and b. These photographs depict the leaching behaviour of fly ash with of H_2SO_4. SEM photomicrographs of pre leached fly ash show a smooth surface with an abundance of extremely small (submicron) dust like flecks located on or slightly embedded in the surfaces. Ash particle contains an exterior glass hull with some salt grain deposits, then a near surface layer of crystalline phases i.e. mullite and an interior glass matrix. In the post leached ash (Fig. 1 b) the photograph shows corroded surface, predicting the acid attack on the smooth surface during leaching. The attack of H_2SO_4 on the aluminosilicate matrix is prominent. The presence of some unattacked particle suggests that the total recovery of metal values can be attributed to the crystalline as well as amorphous phase.

<table>
<thead>
<tr>
<th>H_2SO_4 Concentration</th>
<th>Al</th>
<th>Fe</th>
<th>Ti</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>% Extraction of Al</th>
<th>% Extraction of Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N</td>
<td>0.410</td>
<td>0.364</td>
<td>0.014</td>
<td>0.040</td>
<td>0.010</td>
<td>0.002</td>
<td>0.024</td>
<td>2.66</td>
<td>13.33</td>
</tr>
<tr>
<td>6N</td>
<td>0.588</td>
<td>0.491</td>
<td>0.044</td>
<td>0.043</td>
<td>0.012</td>
<td>0.002</td>
<td>0.022</td>
<td>3.82</td>
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<td>9N</td>
<td>0.694</td>
<td>1.032</td>
<td>0.101</td>
<td>0.078</td>
<td>0.012</td>
<td>0.003</td>
<td>0.033</td>
<td>4.51</td>
<td>37.80</td>
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<tr>
<td>12N</td>
<td>1.163</td>
<td>1.077</td>
<td>0.111</td>
<td>0.089</td>
<td>0.012</td>
<td>0.002</td>
<td>0.039</td>
<td>7.55</td>
<td>39.45</td>
</tr>
<tr>
<td>15N</td>
<td>1.574</td>
<td>1.133</td>
<td>0.109</td>
<td>0.104</td>
<td>0.013</td>
<td>0.004</td>
<td>0.042</td>
<td>10.22</td>
<td>41.50</td>
</tr>
<tr>
<td>18N</td>
<td>2.358</td>
<td>1.138</td>
<td>0.117</td>
<td>0.132</td>
<td>0.013</td>
<td>0.005</td>
<td>0.053</td>
<td>15.31</td>
<td>41.69</td>
</tr>
<tr>
<td>21N</td>
<td>2.822</td>
<td>1.179</td>
<td>0.123</td>
<td>0.233</td>
<td>0.013</td>
<td>0.006</td>
<td>0.049</td>
<td>18.32</td>
<td>43.19</td>
</tr>
<tr>
<td>24N</td>
<td>3.174</td>
<td>1.199</td>
<td>0.129</td>
<td>0.350</td>
<td>0.013</td>
<td>0.006</td>
<td>0.063</td>
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<td>43.92</td>
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<tr>
<td>27N</td>
<td>4.040</td>
<td>1.247</td>
<td>0.138</td>
<td>0.497</td>
<td>0.013</td>
<td>0.008</td>
<td>0.075</td>
<td>26.23</td>
<td>45.68</td>
</tr>
<tr>
<td>30N</td>
<td>4.964</td>
<td>1.301</td>
<td>0.177</td>
<td>0.520</td>
<td>0.014</td>
<td>0.009</td>
<td>0.077</td>
<td>32.23</td>
<td>47.66</td>
</tr>
<tr>
<td>33N</td>
<td>5.406</td>
<td>1.403</td>
<td>0.228</td>
<td>0.532</td>
<td>0.015</td>
<td>0.010</td>
<td>0.082</td>
<td>35.10</td>
<td>51.39</td>
</tr>
<tr>
<td>36N</td>
<td>6.362</td>
<td>1.447</td>
<td>0.258</td>
<td>0.530</td>
<td>0.017</td>
<td>0.012</td>
<td>0.100</td>
<td>41.30</td>
<td>53.00</td>
</tr>
</tbody>
</table>

Fig. 1 (a) Pre leached Fly ash and (b) post leached Fly ash with sulphuric acid

**Particle size**

The particle size and specific surface area of the pre and post leached ash using HCl, HNO_3, o-H_3PO_4 and H_2SO_4 at a ash : acid ratio (1:1) are described in Table 5. The particle size of the leached ash using sulphuric acid are less than the parent fly ash i.e.19.84 μ, where as the particle size of post leached fly ash using nitric, hydrochloric and phosphoric acid are more, mostly in D_90 micron size than the parent one. In case of nitric and hydrochloric acid, the reason for higher particle size...
and lower specific surface area may be due to formation of some insoluble compounds. On the other hand, orthophosphoric acid forms monometallic phosphate (with an \( \text{H}_3\text{PO}_4 \) anion), dimetallic phosphate (with an \( \text{HPO}_4^{2-} \) anion) and trimetallic phosphate (with an \( \text{PO}_4^{3-} \) anion)\(^{21}\). Of which di- and tri-substituted phosphates of alkaline earth metals have negligible solubility compared to other metal salts of mono-, di- and trisubstituted phosphates. This gives rise to a larger particle size and thus smaller is the specific surface area.

But with sulphuric acid the aluminium (alumino-silicate) along with other metals present in fly ash are dissolved. Thus, the particle size decreases with increasing specific surface area. It is also suggested that acid leaching removes most of the amorphous phase that surrounds crystals of the insoluble phases such as mullite and quartz. It is seen that the leached ash has a relatively high specific surface area. By dissolution of amorphous phase, high surface area crystalline phases are exposed\(^{32}\). The dissolution of the crystalline phases is further supported by XRD.

**X-Ray Diffraction Studies**

Comparing the leaching data of HCl, HNO\(_3\), \( \text{H}_3\text{PO}_4 \) & \( \text{H}_2\text{SO}_4 \) given in Table 1,2,3 and 4, sulphuric acid is found to be the best leachant with respect to aluminium extraction. This can be further confirmed by the X-ray diffractogram comparison of the post-leaching fly ash residues. The mineralogy of pre leached and post leached residues of HCl, HNO\(_3\), \( \text{H}_3\text{PO}_4 \) and \( \text{H}_2\text{SO}_4 \) of TTPS fly ashes are studied by X-ray diffractogram and are shown in Fig. 1. The mullite, magnetite and hematite peaks at (2θ - 26.3, 35.1 and 33.1) differ from each other. In HCl & HNO\(_3\) the mullite peak (2θ - 26.3) are not deformed and are same as the parent fly ash whereas in ortho phosphoric and sulphuric acid the mullite peak height (intensity) decreases. Some other mullite peaks (2θ - 54.5) shows similar trend, which differs from the singlet peak obtained for the parent one. At 2θ - 45.85 the quartz peaks of post leached residues of \( \text{H}_3\text{PO}_4 \) and \( \text{H}_2\text{SO}_4 \) are enriched due to increase in concentration through loss of other elements in the leached sample. Similarly, at 20 - 26.75 the intensity of the quartz peaks are found to be more distinct than the parent one. Considering the leachants HCl and HNO\(_3\) it is found that the only hematite and magnetite peaks are affected keeping the mullite peak intact, which confirms that extraction of iron is more than the aluminium. Thus, observing the change in peak intensity in the diffractogram it can be proved that \( \text{H}_2\text{SO}_4 \) is the best leachant when aluminium extraction is considered as evident by the published work\(^{16}\).

However, the slow dissolution of aluminium from the more stable quartz-mullite phase and rapid dissolution of glassy phase were strongly supported by SEM and XRD.

**Table 5** Particle size distribution of Pre and Post leached fly ash

<table>
<thead>
<tr>
<th>Particle Size Characteristics</th>
<th>TTPS (Pre leached)</th>
<th>TTPS (Post leached)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D50, Micron</td>
<td>19.84</td>
<td>17.51</td>
</tr>
<tr>
<td>D90, Micron</td>
<td>58.68</td>
<td>76.26</td>
</tr>
<tr>
<td>D10, Micron</td>
<td>5.89</td>
<td>3.43</td>
</tr>
<tr>
<td>Sp. Surface Area, m(^2)/cc</td>
<td>0.5509</td>
<td>0.6308</td>
</tr>
</tbody>
</table>

**Conclusion**

Leaching behaviour of fly ash with different mineral acids has been studied with respect to
percentage of extraction of aluminium and iron. The direct acid leaching at low concentration and ambient temperatures is not satisfactory for high recoveries of these metals from the fly ash. The rate of extraction of Al and Fe increased sharply with increasing acid concentration. The rate of extraction of Aluminium is slightly higher using HCl as the leaching agent than with HNO₃ at the same concentration but both the acids gives satisfactory result with respect to extraction of iron. However, o-phosphoric acid and sulphuric acid are proved to be suitable leaching agents for metal extraction. As the concentrations of the acids were varied from low to concentrated reagent, low to moderate recoveries of metal values from fly ash by direct acid leaching is not surprising since fly ash consists primarily of iron and aluminium silicates together with silica fused into a refractory glassy mullite material. However sulphuric acid is found to be effective leachant with respect to aluminium extraction due to dissolution of the stable glassy mullite phase. The leachability of metals from fly ash depends on the nature of leaching medium, solid: liquid ratio, temperature and leaching time. By acid routes silica remains substantially insoluble where as the aluminium is taken into aqueous solution as Al³⁺. The acid leaching is not selective for aluminium and iron as Ti, K, Na, Mg and Ca generally dissolve simultaneously. For any kind of specific use the impurities other than the desired metal need to be removed through a suitable process.

References
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Studies on the Effect of Montmorillonite clay in combination with Graphene oxide on the properties of Chitosan

Vijayalekshmi V & Chithra P G

Dept of Chemistry, S.N College for Women, Kollam, Kerala, 691001, India

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Abstract Three dimensional (3D) structures built from nanomaterials lead to exciting novel properties due to the synergistic effect of the material and thereby finding great use in energy storage, catalysis and sensors. The unique physical properties of two dimensional (2D) materials such as graphene make them promising building blocks in creating multifunctional 3D structures. However the low mechanical/thermal stability still remain a challenge. The use of biopolymers as components of composites for many applications is very popular because of the biodegradable, antimicrobial, better resistance to solvents, increased thermal stability and improved mechanical properties. In order to enhance the thermal and mechanical stability, graphene oxide was added with nanoclay in different proportions into the polymer by solvent casting. Characterization of chitosan (CS) / layered silicate nanocomposites obtained by solution-mixing technique, having different compositions including untreated montmorillonite (MMT) and graphene oxide (GO) has been performed. The optimum amount of MMT and GO on nanocomposite properties by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), UV-visible and thermogravimetric analysis (TGA) measurements have been established. The chitosan chains were inserted into silicate layers to form the intercalated nanocomposites. The interlayer distance of the silicates in the nanocomposites enlarged as their amount increased. The stiffness and thermal stability enhanced. Enhanced tensile properties were observed for nanocomposites.

Keywords Chitosan; Montmorillonite, Graphene oxide, nanocomposites

The traditional non-biodegradable polymers, which are derived from fossil fuels, have considerably disturbed and damaged the echo system of nature. For this reason there is an urgent need to develop renewable source-based biopolymer materials that would not involve the use of toxic or noxious components in their manufacture and could allow degradation via a natural composting process. Poly lactide and polysaccharides are most promising candidates because they are made or come from naturally abundant products and are readily biodegradable. However, in order to render biopolymers able to compete with stronger and more ductile commodity polymers such as polyethylene or polypropylene, there is still a need to improve their properties including thermal stability and mechanical properties. At this point it is noteworthy to point out that polymer-layer silicate nanocomposites (PLSNs) technology has already proven to be a good way to improve these properties significantly. Although much attention has been paid to polymer/clay nanocomposites, relatively little attention has been paid to biopolymer-clay nanocomposites. In particular, biopolymer-based antimicrobial films have been attracting much attention from the food industry with their potential application for a variety of foods including meat, fish, poultry, cereals, cheese, fruits, and vegetables.

Chitosan, a polysaccharide composed mainly of β-(1, 4)-linked 2-deoxy-2-amino-D-glucopyranose units, is the deacetylated product of chitin, poly(N-acetyl-D-glucopyranose). Nanocomposites based on the intercalation of chitosan, a cationic natural polymer, in Na+-montmorillonite are bidimensional nanostructured materials provided of anionic exchange sites (NH3+,X−). This fact is due to the special arrangement of the biopolymer as a bilayer when the amount of intercalated chitosan is higher than the cationic exchange capacity of clay (CEC) of the clay. Biopolymer-clay nanocomposites are used as electrochemical sensors for the...
Materials and Methods

Materials
Chitosan (CS) of medium molecular weight (average molecular weight M=92,700 g/mol\(^1\)) used in this work was brought from Aldrich Chemicals. This chitosan was obtained by deacylation of chitin from crab shells and it had a degree of deacylation of 82.5%. Glacial acetic acid (HAc) was supplied by Aldrich Chemicals, \footnote{Glycerol and Glycerol were obtained from Sigma Aldrich.} and Graphene oxide was synthesized from graphite power by the Tour method\footnote{\textit{nat} 2015 (Japan), TEM operating at an accelerating voltage of 800 kV. The composite samples were cut by ultra-cryomicrotomy using a Leica Ultracut UCT. Freshly sharpened glass knives with cutting edge of 45° were used to get the cryosections of 50-70 nm thickness. Since these samples were elastomeric in nature, the temperature during ultra cryomicrotomy was kept at \(-50\) °C (which was below the glass transition temperature of EVA). The cryosections were collected individually on sucrose solution and directly supported on copper grid of 300-mesh size.} Graphite powder was obtained from Aldrich Chemicals.

Preparation of nanocomposites
CS/MMT/GO nanocomposites: Chitosan solution were prepared by dissolving chitosan (CS) in a 1% (v/v) aqueous acetic acid solution at a concentration of 4g followed by centrifuging to remove the insoluble material\footnote{Antibacterial activity of the material was determined against Gram positive bacteria Bacillus cereus and Gram negative bacteria E. Coli. It was assayed by so called halo method as follows. A melted beef agar medium was poured into a Petri dish and solidified. Then, the medium containing bacteria (1x10\(^8\) cells of E.coli, Bacillus cereus per ml) was layered over it. The samples were poured into a well cut on the surface then incubated for one day at 37 °C. Antibacterial activity was evaluated by the transparent halo circle around the specimen after incubation. When an agent has antibacterial activity, a halo circle is formed along the periphery of the specimen. When material has an excellent antibacterial activity, the halo ring formed will be very wide.} Graphene oxide was synthesized from graphite power by the Tour method\footnote{UV- Visible spectroscopy \textit{nat} May 2015 \textit{nat} 2015 (Japan), TEM operating at an accelerating voltage of 800 kV. The composite samples were cut by ultra-cryomicrotomy using a Leica Ultracut UCT. Freshly sharpened glass knives with cutting edge of 45° were used to get the cryosections of 50-70 nm thickness. Since these samples were elastomeric in nature, the temperature during ultra cryomicrotomy was kept at \(-50\) °C (which was below the glass transition temperature of EVA). The cryosections were collected individually on sucrose solution and directly supported on copper grid of 300-mesh size.} MMT was first swelled by 50ml distilled water and then added to 50ml chitosan solution with MMT contents of 1, 3, 5 and 7 wt% and graphene oxide in the order of 0.001, 0.002, 0.003 and 0.004 wt% and followed by stirring at 40 °C for 48 h. The glycerol contents were optimized at a level of 0.7 g. All the nanocomposite films were dried at room temperature and CS films were made in the same conditions as their nanocomposites. Clay composition and GO composition were optimized. Studies were done using 5 wt% clay and 0.003 GO loading.

XRD and TEM
X-ray diffraction patterns were taken by using Rigaku D-Max using Cu Kα (λ =1.5418 Å) diffractometer. The polymer nanocomposite samples were scanned in step mode by 1.5 °/min scan rate in the range of 20<12°. The specimens of 1x1 cm sheets were used for the analysis. The microcopy was performed using a JEOL, JEM - 2010 (Japan), TEM operating at an accelerating voltage of 200 kV. The composite samples were cut by ultra-cryomicrotomy using a Leica Ultracut UCT. Freshly sharpened glass knives with cutting edge of 45° were used to get the cryosections of 50-70 nm thickness. Since these samples were elastomeric in nature, the temperature during ultra cryomicrotomy was kept at \(-50\) °C (which was below the glass transition temperature of EVA). The cryosections were collected individually on sucrose solution and directly supported on copper grid of 300-mesh size.

Thermal analysis
The thermal properties of nanocomposites and pure chitosan were investigated by thermogravimetric analyser Q-50 TA instruments. Thermogravimetric analysis(TGA)were performed under nitrogen atmosphere at room temperature at 800 °C at rates of 0.1 to 200 °C per min. For purging platinum the sample holder, nitrogen gas is used so as to study the oxidation, burning and thermal stability of the materials. The purge gas flows directly over the sample.

Antibacterial properties
Antibacterial activity of the material was determined against Gram positive bacteria Bacillus cereus and Gram negative bacteria E. Coli. It was assayed by so called halo method as follows. A melted beef agar medium was poured into a Petri dish and solidified. Then, the medium containing bacteria (1x10\(^8\) cells of E.coli, Bacillus cereus per ml) was layered over it. The samples were poured into a well cut on the surface then incubated for one day at 37 °C. Antibacterial activity was evaluated by the transparent halo circle around the specimen after incubation. When an agent has antibacterial activity, a halo circle is formed along the periphery of the specimen. When material has an excellent antibacterial activity, the halo ring formed will be very wide.

UV- Visible spectroscopy
The UV- Visible analysis of the samples was carried out using UV- Visible Spectrophotometer. UV- Visible Perkin Elmer Spectrophotometer (Lambda-850) was used to obtain the spectra of the samples. Data were collected in the absorbance mode in the wavelength range of 200-800 nm.

Tensile Properties
Tensile strength and Elongation at break of each film-type sample were determined with an Instron
Universal Testing Machine (model 5565, Instron Engineering Corp., Canton, MA). Rectangular specimens (2.54 x 15 cm) were cut using a precision double-blade cutter (model LB.02/ A, Metrotec, S.A., San Sebastian, Spain). Initial grip separation was set at 50 mm, and cross-head speed was set at 50 mm/min. The TS and E measurements for each type of film were taken as follows: three sheets of each film type were used, with seven specimens cut from each sheet of film; thus, the measurements were done on a total of 21 specimens per each film type, with the mean values for TS and E reported for each sample.

**FTIR**
The Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 IR spectrometer from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) with a 0.5 cm\(^{-1}\) resolution.

**Results and Discussion**

**XRD**

![XRD pattern of the nanocomposites](image)

**Fig. 1** XRD pattern of the nanocomposites

Fig. 1 shows the XRD pattern of NaMMT and nanocomposite with 5 wt% clay loading. The NaMMT clay shows a diffraction peak at 2\(\theta\) = 7.2\(^\circ\) that is assigned to an interlayer platelet spacing of 12.26 Å. For Chitosan based nanocomposites with 5 wt% NaMMT clay and 0.003 GO content, the 2\(\theta\) theta shifts to a lower value 4.3\(^\circ\) that is assigned to an interlayer spacing of 20.5 Å. It perhaps resulted in the interaction between Na\(^+\) ions of the Na-MMT and the free hydroxyl groups of chitosan. Because of the hydrophilic and polycationic nature of chitosan in acidic media, this biopolymer has good miscibility with MMT and can easily intercalate into the interlayer by means of cationic exchange.

**TEM images**

![TEM image of nanocomposites with 5wt% clay +0.003 GO loading](image)

**Fig. 2** TEM image of nanocomposites with 5wt% clay +0.003 GO loading

Fig. 2 shows the TEM image of nanocomposites with 5 wt% clay +0.003 GO loading, and it is observed that, partially intercalated and exfoliated structure is observed for the nanocomposites.

**SEM images**

![SEM image of (a) Pure Chitosan and (b) nanocomposites with 5 wt% clay loading](image)

**Fig. 3** SEM image of (a) Pure Chitosan and (b) nanocomposites with 5 wt% clay loading

Fig. 3 shows the SEM images of pristine polymer and 5 wt% filler loading. From the images (a) and (b) it is clear that the particles are well dispersed into the chitosan matrix.
**Thermogravimetric analysis**

Thermal stability of these nanocomposites was investigated by TGA recorded in the temperature range of 30-900 °C under nitrogen flow condition. The thermal degradation takes place at 229 °C and 238 °C for pure matrix and chitosan nanocomposites at 5 wt% respectively as seen in Fig. 4. Accordingly, the weight loss associated to the adsorbed water molecules at ~ 90 °C for pristine MMT increases to ~120 °C for Ch/MMT nanocomposites. This is due to H-bonding between water molecules and active functional groups of Ch. According to TGA results, the combustion of bulk chitosonium–MMT film was found at 238 °C. From the Fig. 4, higher thermal stability of Ch/MMT nanocomposites is evidenced by the elevated temperature required to eliminate the organic matter associated with MMT. This elimination occurs at 238 °C corresponding to the combustion of the intercalated Ch. The weight losses at 600-700 °C are referred to the combustion of some MMT residues.

![Fig. 4 TGA curve of pure Chitosan and its nanocomposites](image1)

**Antibacterial properties**

The organoclay nanocomposites possess antibacterial property against both Gram negative bacteria and Gram positive bacteria. More antibacterial property is exhibited by gram negative bacteria. Although the mode of action of cations against bacteria is not known, it was suggested that an adsorption of cations onto the negatively charged cell surface by electrostatic interaction. In Bacillus cereus, the UV irradiated sample is more resistant to bacterial attack when compared to unirradiated sample. In the case of E-coli, the unirradiated sample shows a better antibacterial property when compared to UV irradiated sample as shown in Fig. 5 (c,d).

The halo ring diameter is maximum for nanocomposites with 5 wt% Na⁺ loading in the case of E-coli when compared to Bacillus cereus as shown in Table 1. The better antibacterial property for E-coli may be due to the electrostatic interactions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>E.coli (mm)</th>
<th>Bacillus cereus (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan (CS)</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Ch + 1%Na⁺ + 0.03G0</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>Ch + 3%Na⁺ + 0.03G0</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>Ch + 5%Na⁺ + 0.03G0</td>
<td>20</td>
<td>16</td>
</tr>
</tbody>
</table>

**UV-visible spectroscopy**

The UV spectrum of the sample at room temperature with 1 nm resolution is shown in Fig. 6. An absorption band were observed in the 300-400 nm. The wavelength of chitosan and its nanocomposites were found to be 339 nm and 351 nm respectively. The band at 300-400 nm gives the absorption which is related to the direct electronic d-π* orbitals and is called the Soret band. From the figure it is clear that the absorption is maximum for the 5 wt% clay filled sample.

![Fig. 6 UV absorption spectrum of Chitosan and 5 wt % nanocomposites](image2)
In the Fig. 7 (a), CS shows a band gap of 2.7 eV and in Fig. 7 (b) CS nanocomposites shows a band gap of 2.1 which indicates that nanocomposites shows an improved conducting property when compared to pure matrix.

**Fig. 7** (a) Tauc’s plot of pure CS; (b) CS nanocomposites

**Tensile Properties**

<table>
<thead>
<tr>
<th>Film type</th>
<th>Tensile strength (MPa)</th>
<th>Modulus at 300% elongation (MPa)</th>
<th>Elongation at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat chitosan</td>
<td>32.4</td>
<td>1.68</td>
<td>59</td>
</tr>
<tr>
<td>Na-MMT 1% + 0.003% GO</td>
<td>35.2</td>
<td>2.23</td>
<td>54</td>
</tr>
<tr>
<td>Na-MMT 3% + 0.003% GO</td>
<td>36.9</td>
<td>2.56</td>
<td>53</td>
</tr>
<tr>
<td>Na-MMT 5% + 0.003% GO</td>
<td>38.2</td>
<td>2.98</td>
<td>51</td>
</tr>
<tr>
<td>Na-MMT 7% + 0.003% GO</td>
<td>36.5</td>
<td>2.71</td>
<td>52</td>
</tr>
</tbody>
</table>

The tensile properties of the nanocomposites are shown in Table 2. It is clear that for 5 wt% Na⁺ loading shows better tensile strength and modulus when compared to the other filler loadings. The enhanced modulus and tensile strength observed reflect a direct result of the better polymer-clay adhesion.

**IR spectra**

The spectrum of Chitosan (Fig. 8 a) showed peaks at 3375 and 3320 cm⁻¹ due to overlapping of O-H and N-H stretching bands, i.e., 2900 cm⁻¹ for aliphatic C-H stretching, 1652 and 1612 cm⁻¹ for N-H bending, 1434, 1386, and 1333 cm⁻¹ for C-H bending, and 1051 cm⁻¹ for C-O stretching. The spectrum of MMT/CS (Fig. 8 b) showed the combination of characteristic absorptions due to the MMT and amine groups of Chitosan. Peaks for the external vibration and interlayered stretching O-H groups in MMT and MMT/Chitosan were constant at 3630 and 3421 cm⁻¹. On the other hand, the peaks of aliphatic C-H and -NH₂ groups in pure Chitosan at 2900, 1652, and 1612 cm⁻¹ were shifted to 2925, 1644, and 1560 cm⁻¹ in the MMT/Chitosan, corresponding to deformation vibration of the amine group in Chitosan. This result reveals the better interaction of chitosan in the MMT structure.

**Conclusion**

The 2θ value and d-spacing of nanocomposites decreased by 2.9° and increased by 7.74Å respectively. From the SEM images it is observed that particles are uniformly dispersed, which means a better interaction between the filler and the matrix. A partially intercalated and exfoliated structure is observed from TEM images. A better UV absorption property is observed in nanocomposites when compared to the pure matrix. The wavelength of CS and nanocomposites are found to be 339 nm and 351 nm respectively. From the tauc’s plot, CS and CSNa⁺ indicate that nanocomposites show an improved conducting property when compared to pure CS matrix. From
IR studies, the peaks of aliphatic C-H and -NH2 groups in pure Chitosan at 2900, 1652, and 1612 cm$^{-1}$ were shifted to 2925, 1644, and 1560 cm$^{-1}$ in the MMT/Chitosan, corresponding to deformation vibration of the amine group in Chitosan. This result reveals the better interaction of Chitosan in the MMT structure. Antibacterial activity of Chitosan and its nanocomposites with varying clay loading was done with and without UV exposure and showed strong antibacterial activity against Gram-positive and Gram-negative bacteria. Higher thermal stability of CS/MMT nanocomposites is evidenced by the elevated temperature required to eliminate the organic matter associated with MMT.

References
Distance-based and Density-based Algorithm for Outlier Detection on Time Series Data

Maya Nayak* & Prasannajit Dash

Orissa Engineering College, Bhubaneswar, Odisha, India

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Abstract Outlier detection always plays a major role in different industrial domains ranging from major financial fraud detection to network intrusions and also major clinical diagnosis of different diseases. Over the years of research, distance based outlier detection algorithm and density based outlier detection algorithm have emerged as a viable, scalable, parameter-free alternative way to the very long before the traditional approaches. In this paper, we evaluate both the distance and density based outlier detection approach applying on a time-series data i.e. stock market data traded for three months. We begin by surveying and examining the design landscape of the above outlier detection approaches. Also implemented the outlier detection framework for the said design and analysis to understand the various pros and cons of various optimizations proposed by us on a real-time data set i.e. the current stock market data set. The combinations of optimization techniques (factors) and strategies through distance and density based outlier approaches always dominate on various types of data sets. So plays a dominant role on this real-time stock market data set.

Keywords Canonical Algorithm, Simple Nested Loop (SNL), Prunning, Approximate Nearest Neighbor (ANN), kNN, dbScan, complex, dimension, attribute, object, tuple

In a larger number of data, outlier detection is said as per layman’s terms, the noted physicist Stephen Hawkin’s definition as “an observation which deviates so much from the other observations as to arouse suspicions that it was generated by a different mechanism”. For over a century, the outlier detection is the prime focus in more research work in the fields of statistics. Here, the data is considered to follow a parametric distribution and the objects never confirmed to the parametric nature are considered as outliers. Several non-parametric approaches which could not rely on the non-parametric data distribution have been proposed. The first class of methods which confirms to the non-parametric nature is the clustering algorithms. Basically partition-based clustering (k-means, fuzzy c-means), hierarchical based clustering and density-based clustering i.e. dbscan etc. The idea comes as a label to create outliers having those points that were not a core part of any clusters. While going for discovering various tasks on knowledge based are classified broadly into categories like dependency detection, class description, class identification and exception outlier detection. In correspond to the first three categories, the task is applied to a large number of objects in the dataset. The referred tasks in data mining (e.g. association rules, data classification, data clustering etc.). The fourth category focuses on a very small percentage of data objects quite discarded as noise. For last four decades, computational geometry inspired for more on outlier detection. It is based on the depth and convex hull computations. Due to the computational power, outliers are calculated relying more on the principle of data lying in outer space of the data space. The dependency on convex hull calculation hampers the scalability of such outlier detection on high dimensional data and even on low dimensional data these methods are quite very expensive with very large datasets.

To address the scalability factor on high dimensional data as well low dimensional data, the density based outlier detection approach which determines the outliers by analyzing the object’s neighborhood density and presents the opportunity to identify the outliers that are missed by other

Corresponding Author:
Maya Nayak
e-mail: mayanayak3299@yahoo.com
Prasannajit Dash
e-mail: prasannajitdash11@gmail.com
methods. Here these methods give the idea of the distance that plays an important role in determining the neighborhood and local density. While these methods give assurance in improved performance compared to methods inspired on statistical or computational geometry principles, they are not scalable. The well known nearest-neighbor principle which is distance based was first proposed by N. and K. It employs a well-defined distance metric to detect outliers i.e. the greater is the distance of the object to its neighbors, the more likely it is an outlier. In data mining and data analytics, the distance based approach is a non-parametric approach which supports generally the larger dataset with high dimensionality. The basic algorithm for such distance-based algorithm is the nested loop (NL) algorithm. This nested-loop (NL) algorithm calculates the distance between each pair of objects and calculates the outliers in regards to those objects which are very far from the neighborhood objects. The NL algorithm is the quadratic complexity in nature with respect to the number of objects, making it mostly not fit for mining large database like government audit database, clinical trial data and network data. So looking into the prospect of designing of such algorithms, we have identified several important optimizations and algorithms such as the use of compact data structures. Hence, the fundamental optimization technique that should be followed by all such algorithms is to find out an approximate nearest neighbor search such that it should find out a point that is an outlier in the data set.

Related Works
For so many years the outlier tests have been conducted depending on the (i) data distribution, (ii) the distribution parameters like standard deviation, variance, mean etc.,(iii) the number of expected outliers including upper or lower outliers. There are two serious problems while testing these outliers, the first one is that all the outliers are considered as univariate (i.e. single attribute). The second one is that all of them are considered as distribution based. In some situations there is no idea that whether a particular attribute follows a normal distribution i.e. a gamma distribution such that we need to perform an extensive testing to search for a mathematical distribution that fits the attribute. So depth-based methods are not expected to be more practical for more than four dimensional large datasets.

The DB-based (distance-based) techniques for outlier detection have become popular due to non-parametric nature and the ability to scale to large datasets. There are three main definitions of outliers:

(a) Outliers are objects with less than k neighbors in the dataset, where a neighbor is an object within a distance R
(b) Outliers are having n objects giving the highest distance values to their respective k nearest neighbor
(c) Outliers having n objects presenting the highest average distance to their respective k nearest neighbors

All three definitions exemplify Hawking’s definition, that is, the greater is the distance of the object to its neighbors, the more likely it is an outlier. The first definition originally proposed by Knorr and Ng relies on both the definition of a neighborhood (R) as well as the number of neighbors k in order to determine whether a point is an outlier or not. The choice of R is an additional parameter that we will set to determine apriori.

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<td>Symbol</td>
<td>Description</td>
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<tr>
<td>N</td>
<td>Number of outliers in dataset to be identified in the database</td>
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<tr>
<td>K</td>
<td>Number of nearest neighbours to be considered</td>
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<tr>
<td>D^{k}(p)</td>
<td>Distance between point p and its k^{th} closest neighbour</td>
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<tr>
<td>D_{min}^k</td>
<td>Smallest distance between a point and its k^{th} nearest neighbour from data set</td>
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<td></td>
<td>P</td>
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<tr>
<td>R(P)</td>
<td>The MBR diagonal value of a partition P</td>
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<td>MINDIST</td>
<td>Minimum distance between an object and MBR structure</td>
</tr>
<tr>
<td>MAXDIST</td>
<td>Maximum distance between an object and MBR structure</td>
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In fact, for a useful selection of R, it is shown that Knorr and Ng’s definition leads to a quadratic algorithm where all distances between pairs of objects must be calculated in the worst case. Another measure that magnifies such data for each object p is D^k^k(p), which is the distance between the object p and its kth-nearest neighbor. This measure was proposed by Ramaswamy, and is the basis of the second definition of an outlier. Among the three, however, the kNN definition by Ramaswamy is definitely more frequently used and is the focus of the paper.

Distance Based Outliers Problem Domain
The distance based outlier is taken into consideration as an object P in the real time dataset R and it is DB (p,D). The DB (p, D) is an outlier when at least the fraction p of the total objects in R lies greater than the euclidean distance D from P. Whether being standardized or without standardized in some applications, the dissimilarity (or
similarity) between the objects is calculated by taking the distance between each pair of objects. The distance said above is the Euclidean distance measure which is defined as
\[ d(i, j) = \sqrt{(x_{i1} - x_{j1})^2 + (x_{i2} - x_{j2})^2 + \ldots + (x_{in} - x_{jn})^2} \] (1)
where \( i = (x_{i1}, x_{i2}, \ldots, x_{in}) \) and \( j = (x_{j1}, x_{j2}, \ldots, x_{jn}) \).

The euclidean distance satisfies the following mathematical requirements of a distance function:
(i) \( d(i, j) \geq 0 \): Distance is a nonnegative number
(ii) \( d(i, j) = 0 \): Distance of any object to itself is always zero
(iii) \( d(i, j) = d(j, i) \): Distance is symmetric in nature
(iv) \( d(i, j) \leq d(i, h) + d(h, j) \): Calculating the distance from object i to object j in space is no more than making a distance over any other object h.

The notation i.e. DB(p,D) means the shorthand notation for distance based outlier using the parameters p and D which is nothing but the Hawkins definition. The definition is well defined for k-dimensional datasets for any value of k. Anyhow, the DB-outliers are not restricted computationally to small values of k. Hence the DB-outliers rely on the computations of distance values based on a metric distance function.

**Properties of DB-Outliers**
Definition 1: The generalization of DB(p, D) brings another definition Def for outliers, if there are specific values for \( p_0 \) and \( D_0 \) so that the object i.e. O is a DB\((p_0, D_0)\) which is the outlier. Outliers are considered in a normal distribution as the observations that lie 3 or more standard deviations(\( \sigma \)) from the mean i.e. \( \mu \).

Definition 2: Let us define Def\(_{\text{normal}}\) as ‘t’ which is an outlier in a normal distribution with mean \( \mu \) and standard deviation \( \sigma \) if \( |t - \mu| / \sigma \geq 3 \). DB\((p, D)\) unifies Def\(_{\text{normal}}\) with \( p_0 = 0.9988 \) and \( D_0 = 0.13\sigma \) so that, t is an outlier according to Def\(_{\text{normal}}\) if t is a DB\((0.9988, 0.13\sigma)\) as an outlier. If the value \( 3\sigma \) is changed to some other value, such as \( 4\sigma \), the above definition should be modified with the related \( p \) and \( D \) to show that DB\((p, D)\) still unifies the new distribution of Def\(_{\text{normal}}\).

Definition 3: Let us define Def\(_{\text{normal}}\) shows that t is considered as an outlier in a Poisson distribution with parameter \( \mu = 3.0 \) if \( t \geq 8 \). DB\((p, D)\) unifies Def\(_{\text{poisson}}\) with \( p_0 = 0.9892 \) and \( D_0 = 1.0 \).

**A Simple Nested Loop Algorithm For Finding All DB(p,D)-Outliers**
The algorithm NL i.e. the nested loop algorithm given below uses the nested loop design in blocks oriented nature. Let us assume that the total size of the buffer of B% of the total dataset size, the algorithm divides the entire buffer space into two equally measured arrays as the first array and the second array where the whole dataset got divided into arrays. By doing this, it computes the distance between each pair of objects or tuples. For each object t in the first array, a count of its D-neighbors is maintained. The process of counting almost gets done for a particular tuple whenever the number of D-neighbors exceeds M.

**Pseudo-Code For Algorithm NL (Nested Loop)**
(a) The size that holds B/2% of the dataset will be filled with a block having tuples from T.
(b) In first array, for each tuple \( t_i \), steps to be followed:
   1. The counter is to be initialized i.e. count to 0.
   2. In the first array, for each tuple check \( t_j \) whether the \( \text{dist}(t_i, t_j) \leq D \).
   3. If the above distance happens to be less or equal to D, then increment the count, i.e. count, \( > M \) where we could mark \( t_i \) as a non-outlier and further proceed to the next \( t_i \).
   4. While the remaining blocks to be compared to the first array, then fill the second array with another block. For each unmarked tuple \( t_i \) in the first array where for each tuple \( t_j \) in the second array if \( \text{dist}(t_i, t_j) \leq D \).
   5. If it happens, then increment the count, by 1. So if count, \( > M \), mark \( t_i \) as a non outlier and proceed to next \( t_i \).
   6. For each unmarked tuple \( t_i \) in the first array, report \( t_i \) as an outlier.
   7. In the second array if it has served as the first array anytime before, then swap the names of the first and second arrays and go to step (b).

**Application of Stock Market Data As Time Series Data**
Sources: http://nseindia.com/live_market/dynaContnt/live_watch/get_quotes/GetQuote.jsp?symbol=TATAMOTORS
As stock market text dataset shown in Fig. 1, hold for the National Stock Exchange data of Tata Motors for a quarter, these dataset consists of the date of transaction, opening price of the day, high and low price for a day and the closing price for a day. Since the data is collected for three months, it is time-series data as the outliers are to be observed for multidimensional data i.e. attributes around five in the dataset. The data related to the opening and closing price is calculated in terms of euclidean distance for data in columns like open price and close price. The sum is taken of the euclidean distances (row-wise) between the contents in open price and close price. Hence the average euclidean distance is calculated for the total objects i.e. rows or records (tuples). Here the fraction of object is
calculated by taking the value of ‘p’ as 0.9. Since the total number of rows are 249 in the dataset, therefore the fraction of the object i.e. ‘f’ is calculated as \((249 \times (1-p))\) which produces 24.9. Here the one dimensional matrix i.e. C1 of rank 249×1 where it contains all euclidean distances (row or tuple wise) between open and close prices. While iterating through the records from 1 to 249, if the value in C1 is less than the average euclidean distance then if the count of the object is greater than the fraction of the object, then it is not an outlier otherwise it is an outlier as shown Fig. 2 and Fig. 3 respectively. If the calculated distance is greater than the average euclidean distance then also it is considered as the outlier. Then the Nested Loop (NL) is applied to calculate the non-outliers and outliers in respect to the date.

In the same way, the high price and low price are calculated in terms of euclidean distance row wise as it checks the euclidean distance measurement for columns like high price and low price. The sum is calculated for euclidean distances (row-wise) between the data in high price and low price. Hence the average euclidean distance is calculated for the total objects means rows or records (tuples). Here the fraction of object is calculated by taking the value of ‘p’ as 0.9. Since the total number of rows are 249 in the dataset, therefore the fraction of the object i.e. ‘f’ is calculated as \((249 \times (1-p))\) which produces 24.9. So that the one dimensional matrix of order or rank 249×1 i.e. C2 where it contains all euclidean distances(row wise or tuple wise) between high and low prices. While traversing through the records from 1 to 249, if the value in C2 is less than the average euclidean distance then if the count of the object is greater than the fraction of the object, then it is not an outlier otherwise it is an outlier as shown in Fig. 4 and Fig. 5 respectively. If
the distance is greater than the average euclidean distance, then also it is counted as outlier. Then the Nested Loop (NL) is applied to calculate the non-outliers and outliers in respect to the date.

![Fig. 2 Open_Close Non Outliers in respect to date](image2)

![Fig. 3 Open_Close Outliers in respect to date](image3)

In Fig. 2 and 4, it indicates the non-outliers as per the date against the euclidean distance difference between Open and Close Price column data. The x-axis is the date and the y-axis is the distance differences. So in Fig. 3 and 5, it indicates the outliers.

![Fig. 4 High_Low Non Outliers in Respect to Date](image4)

![Fig. 5 High_Low Outliers in Respect to Date](image5)

**Clustering-Based Techniques for Outlier Detection**

Clustering finds groups of strongly related objects. Outlier detection finds objects that are not strongly related to other objects. Thus, an object is a cluster-based outlier if the object does not belong strongly to any cluster. In detecting outliers, small clusters that are far from other clusters are considered to contain outliers. This approach is sensitive to the number of clusters selected. It requires thresholds for the minimum cluster size and the distance between a small cluster (with outliers) and other
clusters. If a cluster is smaller than the minimum size, it is regarded as a cluster of outliers. This paper presents a density-based clustering technique known as Density Based Spatial Clustering of Applications with Noise (DBSCAN). The detection of time series outliers using the DBSCAN technique is focused in the paper.

Density Based Spatial Clustering of Applications with Noise (DBSCAN)

It presents a density-based clustering technique which estimates similarities between points from a data set with respect to distance and partitions them into subsets known as clusters, so that the points in each cluster share some common trait. We use the clustering technique used in mining data known as Density Based Spatial Clustering of Applications with Noise (DBSCAN).

DBSCAN is designed to discover the clusters and the noise from a given set of points by classifying a point

(i) inside of a cluster (core point),
(ii) in the edge of a cluster (border point), or
(iii) as neither a core point nor a border point (noise).

DBSCAN requires two important parameters; Eps, which is a specified radius around a point to other points, and MinPts, which is the minimum number of points required to form a cluster.

Key Concepts

The following definitions are the key concepts in understanding the DBSCAN algorithm:

Definition 1 The Eps - neighborhood of a point p, denoted by NEps (p), is defined by 

\[ N_{Eps}(p) = \{q \in P \mid dist(p, q) \leq Eps \} \]

A point is a core point if it has more than a specified minimum number of points required to form a cluster (MinPts) within an Eps - neighborhood. These are points that are in the interior of a cluster. A border point has fewer than MinPts within an Eps, but it is in the Eps - neighborhood of a core point. A noise point is any point that is neither a core point nor a border point.

Definition 2: The density-based approach is an approach that regards clusters as regions in the data space in which the objects are dense and separated by regions of low object density (outliers).

Definition 3: Considering the points p1 and p2, if p1 is directly density reachable from p2 if points are close enough to each other such that dist(p1, p2) < Eps, as measured using Euclidean distance or using any other distance measure. There are at least MinPts points in its neighborhood. For example, if MinPts = 6, then p1 must have at least 6 points as its neighbors. This concept of direct density-reachability shows that p1 is density reachable from p2 because the dist (p1, p2) < Eps, and p1 has enough points as its neighbors.

Definition 4: A point p1 is density reachable from a point p2 with respect to Eps and MinPts if there is a chain of points p1, ..., pn, such that pi+1 is directly density-reachable from pi.

Definition 5: A point p0 is density-connected to a point pn with respect to Eps and MinPts if there is a point q such that both p0 and pn are density-reachable from q with respect to Eps and MinPts.

The Algorithm

In general, using parameters Eps and MinPts, DBSCAN finds a cluster by starting with an arbitrary point p from a set of points and retrieves all points density-reachable from p with respect to Eps and MinPts. Suppose p is a core point, if p has neighboring points greater than or equal to the value of MinPts, a cluster is started. Otherwise, the point is labeled as an outlier, and a new unvisited point is retrieved and processed leading to the discovery of a further cluster of core points. A point can be in a cluster, and it can be an outlier. After all the points have been visited, any points not belonging to any clusters are considered outliers. The formal details are given in Table 2, and Algorithm 1 presents pseudocode for the DBSCAN algorithm.

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<th>Table 2</th>
<th>DBSCAN Algorithm</th>
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<td>(a)</td>
<td>Select the values of Eps and MinPts for a data set P to be clustered</td>
</tr>
<tr>
<td>(b)</td>
<td>Start with an arbitrary point p and retrieve all points density-reachable</td>
</tr>
<tr>
<td>(c)</td>
<td>If p is a core point that contains at most MinPts points, then a cluster is formed, otherwise, label p as an outlier</td>
</tr>
<tr>
<td>(d)</td>
<td>A new unvisited point is retrieved and processed leading to the discovery of further clusters of core points</td>
</tr>
<tr>
<td>(e)</td>
<td>Repeat step (b) until all the points have been visited</td>
</tr>
<tr>
<td>(f)</td>
<td>Label any points not belonging to any cluster as outliers</td>
</tr>
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Algorithm 1

Aim: Clustering the data with Density-Based Scan Algorithm with Noise (DBSCAN)

Input: SetOfPoints (P) - data set (m,n); m-objects, n-variables
Eps : neighborhood radius
MinPts : minimal number of objects required to form a cluster

Output: A vector specifying assignment of a point to certain cluster for example: 1st and 3rd points can be in cluster No. 1 and 2nd and 4th points can be in cluster No.2
(a) As a function in MATLAB, the function DBSCAN takes three parameters i.e. SetOfPoints, MinPts and Eps where the output is the parameter i.e. IsPointAnOutlier.

(b) Call the Normalize method which takes input as SetOfPoints and set the output to ‘SetOfPoints’

(c) Assign the Clusterid as zero

(d) For each and every unvisited point p in a ‘SetOfPoints’, mark p as visited

(e) After that the method ‘getNeighbors’ passes the parameters as SetOfPoints, P, Eps, the output gives the list of neighbors i.e. PListOfNeighbors.

(f) If the size of ‘PListOfNeighbors’ is less than the minimum point i.e. ‘MinPts’, then mark ‘p’ as the outlier

(g) Then iterate the loop like the next cluster is assigned it to ‘Clusterid’

(h) Further the method i.e. ‘expandCluster’ passes the parameters as SetOfPoints, P, N, Clusterid, Eps, MinPts, so add the ‘p’ to the cluster having the Clusterid

function expandCluster(SetOfPoints, P, N, Clusterid, Eps, MinPts)
add p to cluster Clusterid
WHILE there is unvisited point p’ in ListOfNeighbors
mark p’ as visited
PListOfNeighbors’ = getNeighbors(p’, Eps)
IF PListOfNeighbors’ <= MinPts
PListOfNeighbors = PListOfNeighbors joined with PListOfNeighbors
add p’ to cluster Clusterid
ENDIF
ENDWHILE
RETURN
ENDEXPANDCLUSTER

function = getNeighbors (SetOfPoints, P, Eps)
RETURN Eps-Neighborhood of p in SetOfPoints as a list of points
ENDDISCONNECT

DBSCAN has several advantages including its ability to find arbitrarily shaped clusters. It does not require the user to know the number of clusters in the data in advance. DBSCAN is very robust to outliers and requires just two parameters, Eps and MinPts. However, DBSCAN is highly affected by the distance measure used in finding the distance between two points. Its effectiveness in clustering data points depends on the distance measure used. The Euclidean distance measure is commonly used, but any other distance measure can be used. Also, before computing the distances between two points with different units, the data points must be normalized.

Selecting the Parameters Eps and MinPts

The DBSCAN algorithm requires two user-defined parameters Eps and MinPts. The values of these parameters have a big impact on the performance of the DBSCAN. For instance, if Eps is large enough, then all points form a single cluster, and no points are labeled as outliers. Likewise, if Eps is too small, majority of the points are labeled as outliers. There are several approaches that can be used to determine the values of Eps and MinPts.

The first approach uses the parameters specified by the experts. The parameters are provided by an expert who is very familiar with the data set to be clustered. An expert can provide the parameters and run the DBSCAN algorithm, which provides graphs showing which points from the data sets are considered to be outliers. Using visualization, an expert looks at the graphs, adjusts the parameters, and runs the algorithm until he/she gets good results. Good results are determined by the expert knowledge of the data set. An expert selects parameters that can be used as default parameters for that data set.

The k - dist approach looks at the behavior of the distance from a point to its kth nearest neighbor. If k is not larger than the cluster size, the value of k - dist is small for points that belong to the same cluster. The k - dist for points not in the cluster is relatively large. The idea is to pick a value of k to be the MinPts. The following steps are performed to find the value of k:

1. Compute the k - dist, (distance to its kth nearest neighbor) for each of the data points.
2. Sort k - dist measures in increasing order.
3. Plot the sorted k - dist values. We expect to see a sharp change at the value of k - dist that corresponds to a suitable value of Eps.

![Fig. 6 Outliers of high and low price in respect to date](image-url)
Fig. 7 Outliers of open and close price in respect to date

The Fig. 7 shows that the objects are encircled in the plotted graph shows the outliers of Open Price and Close Price against the corresponding dates as this has gone through the dbscan algorithm.

**Conclusion**

The nested loop (NL) algorithm avoids the explicit construction of any indexing structure and its time complexity is $O(kN^2)$. Compared to a tuple-by-tuple brute force algorithm that pays no attention to I/O’s. Algorithm Nested Loop (NL) is always superior because it tries to minimize I/O’s.

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