MATERIALS AND METHODS
Before proceeding for detailed studies, it was thought worthwhile to observe the adsorptive activities of the shells of Unio & Pila, a preliminary investigation was undertaken. The shells were collected from a local river. They were washed, dried, ground & sieved to 100 mesh and activated. The activated powders of the shells were taken as adsorbents in aqueous and alcoholic media. The aqueous medium contained 5 percent potassium iodide (KI). 50 ml. of each of 0.02 M, 0.15 M and 0.01 M aqueous and alcoholic solution of Iodine were separately taken and tested for adsorption on 2 g samples of the powdered adsorbents at 25°C. After 2 hours contact period, the solutions were filtered and the equilibrium concentration of Iodine in the filtrate was determined by titration against Sodium thiosulphate solution.

Encouraged from the results of preliminary work, the detailed studies were planned. It is needless to emphasise the abundance and easy availability of vast natural resources in the sphere of flora and fauna. The hard protective shells, the creatives of water dwelling animals : Unio & Pila conform to this category too.
The fresh water river PAHOOJ, originating from Jhansi district, almost the demarcating line between Uttar pradesh and Madhya Pradesh, flows up to Jalaun district where it falls in the pious water of legendary river YAMUNA, together with other three rivers. The confluence of these five rivers is known as PANCHNADA, attracts the large gathering of far and near people, to take holy dip. The great suntemple of Balaji at village Unnao (District - Datia, Madhya Pradesh) is situated on the bank of Pahooj, where pilgrims offer prayers only after taking dip in its sacred water.

The shells of Unio and Pila are found in plenty in and around the Pahooj, throughout its whole stretch. The river leaves a wide area along its two sides. The shells were easily collected from the various places of this river, in Jalaun & Jhansi districts (Uttar Pradesh) and Datia district (Madhya pradesh). The shells collected were of white & pink colour and ranged from 1 cm. to 5 cm. in size. The shells were gently washed with fresh water repeatedly to make them free from dust & sand and then they were passed through the process of boiling with water in order to remove the sticky materials. The shells were dried completely in sunlight. They were
broken to small pieces by mortar and pestle and then ground to fine powder. Powders of both the shells were passed through 120 mesh and 80 mesh sieves. The uniform fractions of all these powders were activated by heating in muffle furnace at 400°C for 4 hours. The activated powders were stored in marked, stoppered glass bottles which were kept in a desiccator at room temperature, to avoid the contact with moisture.

The adsorptive capacities of these powders as adsorbents were studied with the solution of chemically pure grade colouring materials (without further purification) & coloured effluents collected from different textile dyeing industries. The following colouring materials were used as adsorbates:--

1. Toluidine blue:

\[ \text{CH}_3 \quad \text{N} \quad \text{Cl}^- \]

\[ \text{H}_2\text{N} \quad \text{S} \quad \text{N} \quad \text{N(CH}_3\text{)}_2 \]

Toluidine blue
2. Crystal violet:

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+ N(CH₃)₂
C

(CH₃)₂N
| 
| 
| N(CH₃)₂
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Crystal violet

3. Trypsan blue:

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CH₃

NH₂ OH
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Trypsan blue
4. Rhodamine B:

\[
\begin{array}{c}
\text{Rhodamine B} \\
\end{array}
\]

5. Methylene blue:

\[
\begin{array}{c}
\text{Methylene blue} \\
\end{array}
\]
6. Methyl red:

![Methyl red molecule structure](image)

Methyl red

The aforesaid solid adsorbates were weighed accurately and their stock solutions of 1000 µg/L were prepared in warm double distilled water. All the solutions contained 10 percent ethyl alcohol to facilitate the solubilities of the adsorbates in water. The stock solutions were kept overnight to get stabilise and acquire room temperature. The stock solutions were covered with a double layer of black cloth to protect them from the effect of sunlight. These solutions were diluted to 800 µg/L, 600 µg/L, 400 µg/L & 200 µg/L
respectively by addition of water. 20 ml each of the above mentioned test solutions were pipetted out in order to make two sets in duplicate, into a series of numbered and stoppered pirex glass conical flasks, for comparative study of Unio & Pila shell powders (particle size : 120 mesh) at 10°C. Similar series of sets were taken for adsorption experiments at 25°C.

500 mg activated powder of 120 mesh of each of the adsorbents was weighed in stoppered glass tubes and put into numbered conical flasks of the series containing the adsorbate solutions. The flasks of duplicate series were placed systematically in thermostating condition in B.O.D. incubator at 10°C (±1°C) and another series in duplicate at 25°C (±1°C) for 2 hours. The flasks were shaken serially at frequent intervals for ascertaining proper contacts of all the particles of adsorbents with adsorbates. Immediately after incubation the equilibrated solutions were decanted into the graduated and numbered centrifuging tubes and centrifuged for 10 minutes at 10,000 r.p.m. The supernatant solutions were taken into the clean tube serially and amounts of adsorbates, adsorbed were calculated from the difference in initial
and the equilibrium concentrations of these solutions, measured spectrophotometrically by SPECTONIC-20 colorimeter.

With the rise of living standard and population explosion, the problem of pollution has been creating disturbances in the environmental equilibrium. Chemical pollution in air, water and soil is becoming a challenging task to the mankind. Untreated industrial wastes discharged into lakes and streams result in serious problems of water pollution. Few unwanted dissolved minerals cause hard water problems for industrial and municipal water supplies. Biological activity of the streams may be altered by toxic chemicals and many chemicals cause to rise the acidity and alkalinity in reaction with water, to the point where the water becomes corrosive; thus living organisms are killed. Chemicals which need more oxygen, give room to the problem of deoxygenation. Water purification represents the main, well established and refined technology. Possibly the most recent technology that has and will contribute in the future to lessening water pollution is that of water reuse: the recycling and in-plant treatment of water for manufacturing and processing purposes.
The industries discharge untreated water on land and in natural streams. The textile industries are one of them. The waste waters of varying colours come out of the textile industries. Many people who perform the dyeing works at small and large scale, manually, allow the untreated water, containing the different dyes, to flow in the drains which ultimately go to the rivers, lakes and ponds, resulting to water pollution. Dyes are the major constituents of these colouring matters of effluents. The samples of effluents of six open drains of local textile dyeing industries were collected. The effluents were of Red, Violet, Sky blue, Yellow, Green & Orange in colour respectively. The samples were dark coloured and foul smelling. They were filtered through whatman no.40 filter paper. The filterates were stored in stoppered and marked measuring flasks. The filtrates of these flasks were termed as stock solutions. They were kept for overnight at room temperature and covered with a double layer of black cloth to prevent them from the effect of sunlight. Double distilled water was added with these solutions for diluting them to 20.0, 40.0, 60.0 & 80.0 percent respectively. For performing comparative adsorption experiments of Unio & Pila shell powders at
temperature of 10°C, 20 ml. of each of the solutions were pipetted out into a stoppered and numbered conical flasks in 2 sets of duplicate series. For adsorption studies at a temperature of 25°C, the series of sets were arranged similarly. In stoppered glass tubes, 500 mg activated powders of 120 mesh of each of the adsorbents were weighed and put into each flasks of the series. The serially arranged flasks were placed in the mostating conditions for incubation at 10°C (±1°C) and 25°C (±1°C) in B.O.D. incubator for 2 hours. To ascertain the proper contacts of the particles of adsorbents with the solutions, the flasks were shaken simultaneously at frequent intervals. The graduated and numbered centrifuging tubes were taken and just after incubation, the equilibrated solutions were decanted into them. These solutions were centrifuged at 10,000 r.p.m. for 10 minutes. The supernatant solutions were taken into the clean tubes and the amounts of dyes adsorbed were calculated by difference of their initial and final concentrations, measured spectrophotometrically by SPECTONIC - 20.

Adsorption is a surface phenomenon, depends upon the surface area of the adsorbents, at the given time, temperature & pressure.
The extent of adsorption for the solid adsorbents increase with an increase in their accessible surface area. The external area will be greater for finer powder of the adsorbent. The size and distribution of pores within the solid adsorbents are responsible for accessible surface area for a given particle size. When the solid adsorbents are crushed to smaller particles, new pores are opened. By diffusion through capillaries filled with the solvent, the adsorbates in the solutions reach the inner surface of the porous adsorbents, thus the amount of adsorbates, adsorbed will be dependent on the nature of pores and capillaries of the adsorbents. Obviously, the size of particles of the adsorbents has a significant relation with their external area for their given quantity. To assess the effectiveness of particle size of Unio & Pila shells, the adsorption experiments were undertaken. For this purpose 500 mg activated powders of particle size 80 mesh of Unio & Pila shells were weighed in stoppered glass tubes. All the sets of flasks were arranged in the similar ways as was done for conducting the studies with 120 mesh powders. The test solutions of adsorbates, viz. Dyes and Effluents were also taken likewise and were treated in the same manners and the experiment:
were carried out at 10°C & 25°C. For calculating the amounts of dyes adsorbed, the earlier procedure was adopted.

Bailey et al. [212] have determined partial molar free energy of macroscopically homogeneous open thermodynamic system [213] by means of expression:

\[ -\bar{G} = RT \ln \frac{Ce}{Co} \]

Where; \( R \) = Molar gas constant

\( T \) = Absolute temperature

\( Ce \) = Equilibrium concentration and;

\( Co \) = Initial concentration of the adsorbate solution prior to adsorption.

By using the above relationship the values of partial molar free energy were obtained and arranged in the tabular form.

The values of adsorptions in terms of percentage were calculated and recorded in the tables. A graphical study was also undertaken by plotting the amount of different dye adsorbed per 500 mg of each of the adsorbents against equilibrium concentrations at 10°C and 25°C for varying particle size.