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Hydrothermal treatment of effluent affected polluted soil of Nanjangud, Mysore district, India

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The polluted soils from the major textile, distillery and food industries located on a high-grade rock terrain (Nanjangud, Mysore district, India) were treated under hydrothermal conditions using water as a solvent. The electrical conductivity and *N*, *P*, *K* content have been studied before and after the hydrothermal treatment for these soil samples. Characterization of these soil samples was carried out through powder X-ray diffraction, thin section and infrared spectroscopic studies.

1. Introduction

Nanjangud located at 25 kms away from the south-east of Mysore city has several industries like textile, pharmaceutical, distillery, automobile, paper and so on. This area forms the high-grade rock terrain essentially made up of amphibolites, quartzites and a wide range of manganiferous calc silicates. This terrain also has a rich mineral assemblage consisting of rare carbonate silicate minerals, feldspathoids and banded iron ore formation [1–3]. All these rock types have undergone gradual weathering and erosion from the geological past. In the present study, soil samples have been collected from different areas adjacent to textile, distillery and food industries. The local population claims that these industries discharge the effluent either fully or at least partially into the ground. Hence the soil from this area has been found to be highly degraded by the effluent action. As per the geological studies carried out some 50 years ago, the area had the following minerals like quartz, feldspar, hornblende, garnet, chlorite as major minerals and sphene, rutile, zircon, topaz as minor minerals. After the establishment of these industries some 25–30 years ago the mineralogy of the soil has changed significantly and several minerals have formed as a result of alteration of the feldspar, hornblende, quartzite and other primary minerals. A comparative study of the mineralogy and *N*, *P*, *K* content in the soils are given for both the types of soil which indicates the stability of the soil. The hydrothermal treatment of the 3 soil samples collected from the areas affected by the industrial effluent has been carried out under hydrothermal conditions at different temperature and pressure range under the action of steam. The results are interpreted with reference to the effluent property.

2. Methodology and characterization

Soil samples from the land were excavated by 1 ft × 1 ft, then representative sample from that area was collected by cone and quartering method. The soil samples collected were kept in a clean and dry place free from contaminants like dust or gases, and later dried in the air to remove moisture content in the soil. The soil samples were processed with the help of proper sieves to remove the coarse portion. For the sake of convenience, the samples are labeled as textile, distillery, food and agricultural soil samples. The samples were subjected to various studies like thin section study through petrological microscope, powder X-ray diffraction to know the mineral composition, FTIR study, and volumetric analysis to estimate the *N*, *P*, *K*.

The thin section study was carried out for the raw soil samples collected from field using Leitz Petrological microscope, Germany.

The electrical conductivity measurement was carried out using a conductivity meter: Salvin Process Instrument Co., Model SP 1000A. About 10 mg of the dry soil sample

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TABLE I Mineralogical assemblages of the respective industries

Soil sample	Mineralogical assemblages
Textile soil	Quartz, hornblende, pyroxene, rutile, plagioclase and biotite
Distillery soil	Feldspars, sphene, garnet, biotite, hornblende, quartz, hematite, magnetite
Food industry soil	Quartz, plagioclase, hornblende, sphene, biotite
Agricultural soil	Quartz, kaolinite, illite, chlorite, cerussite, feldspars

was taken and 100 ml of the distilled water was added into it to prepare a solution. The instrument was calibrated using 0.01N KCl solution kept at different conductivity range (1468–2000 α Siemens) at room temperature.

The hydrothermal treatment of the soil samples was carried out using the SS 316 General Purpose Autoclaves of 30 ml capacity provided with Teflon liners. The required amount of the soil was taken in the Teflon liner and a calculated amount of the solvent (water) was added into this Teflon liner. The liner was placed inside an autoclave and then heated at a predetermined temperature for a period of 24 hours. After the hydrothermal treatment, the soil sample was taken out from the liner and dried in an oven at 30°C. Then the hydrothermally treated soil samples were subjected to various studies.

The nitrogen content in the soil samples was estimated by Kjeldhal method [4]. The reagents used for the estimation were catalytic mixture of sulphuric acid, sodium hydroxide solution, zinc granules, boric acid cum indicator solution and hydrochloric acid. Then the available nitrogen present in the samples was calculated as follows:

$$\text{Available nitrogen} = \frac{(A-B)\times 280}{\text{Volume of Sample}}$$

Where A is the volume of 0.02 N sulphuric acid required for titrating the sample and B is the volume of 0.02N sulphuric acid required for blank titration.

Nitric acid and perchloric acid were used in the estimation of phosphorus content [4]. The amount of phosphorus present in the soil samples was calculated using the equation:

$$PO_4 = \frac{Pd \times V}{100 \times X}$$

Where Pd is the amount of PO_4 ingested, V is the volume of the solution and X is the weight of air-dried soil used for the estimation of phosphorus.

The Flame Photometer 128 and FPM compressor 126, Systronics Co., was used for estimating potassium [4]. The reagents used were ethyl alcohol, ammonium acetate and standard KOH solution. The air pressure was maintained at 15 lbs using a filter of 769 nm. The extract of the soil sample was observed under flame photometer and potassium content in the soil sample was calculated using the equation:

$$K = \frac{Y \times V}{W \times 100}$$

Where Y is the potassium content of the soil extract, V is the total volume of soil extract and W is the weight of the soil taken for the extraction.

The powder X-ray diffraction patterns for the dry soil samples were recorded using Bruker AXS X-ray diffractometer system D8 ADVANCE. The X-rays used were CuKα with $\lambda = 1.5404$ Å having a nickel filter. The powder X-ray diffraction patterns were indexed and the *d*—spacings of all the peaks were identified and compared with the JCPDS files.

The FTIR spectra were recorded in the range of 4000–400 cm^{-1}(JASCO-460 PLUS, Japan). The soil sample was blended with potassium bromide in the ratio of *1 : 150* for the FTIR study.

3. Results and discussion

Table I gives the mineralogical assemblages encountered from the above-mentioned soil samples before the hydrothermal treatment.

The powder XRD patterns recorded for all the four treated and untreated soil samples are shown in Fig. 1. Here for the sake of convenience the powder X -ray diffraction patterns of the soils treated hydrothermally at 200°C are given along with the untreated soil samples. The untreated textile soil contains the following minerals as evident from XRD data (Fig. 1a): quartz, rutile, orthoclase, sphene, hornblende, garnet that in turn after hydrothermal treatment at 200°C shows the following mineral assemblage: quartz, rutile, goethite, gibbsite, etc. (Fig. 1b). The mineralogy of the untreated distillery soil has the following minerals as supported by the XRD data (Fig. 1c): sphene, quartz, orthoclase, tremolite which in turn after hydrothermal treatment at 200°C shows minerals like gibbsite, quartz, microcline and rutile (Fig. 1d). Similarly the mineralogy of the untreated food industry sample contains minerals like garnet, hornblende, biotite, tremolite and orthoclase (Fig. 1e), after hydrothermal treatment at 200°C it results in the following mineral assemblage: quartz, microcline, goethite and revdite (Fig. 1f).

As evident from the X-ray data the less stable minerals like biotite, hornblende tremolite, etc, under hydrothermal conditions dissociate completely. The stable oxides remain intact even after hydrothermal treatment at 200°C.

The FTIR spectra were recorded for all the treated and untreated samples in the range 4000–400 cm^{-1}. The Fig. 2 shows the representative FTIR spectra of raw and hydrothermally treated ($T = 200$°C; $P = 80$ bars) distillery

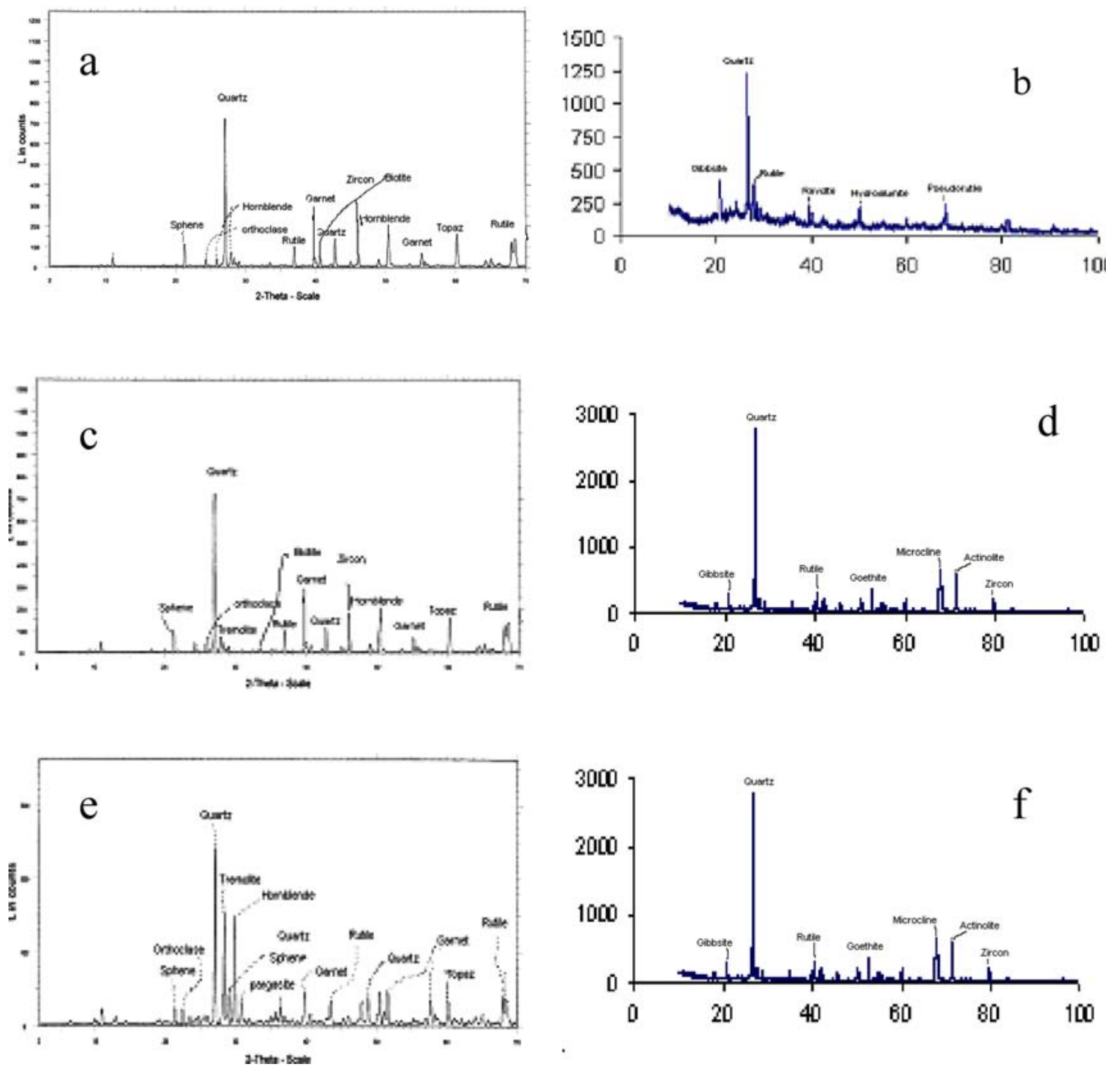

Figure 1 XRD patterns of soils: a) raw textile soil; b) treated textile soil; c) raw distillery soil; d) treated distillery soil; e) raw food industry soil; f) treated food industry soil.

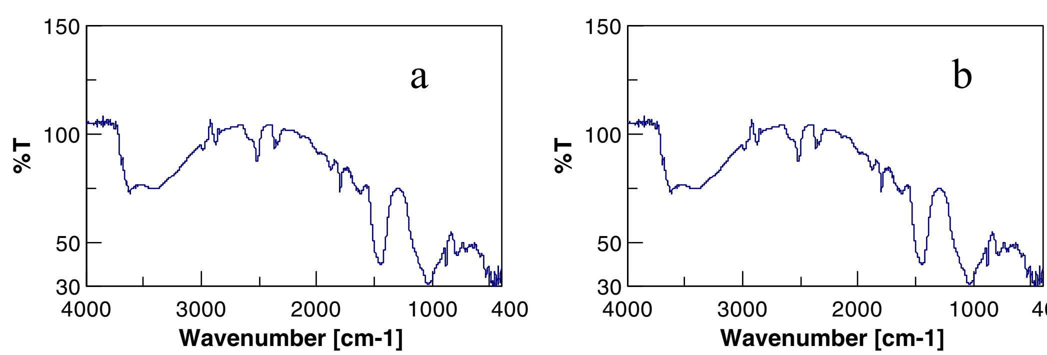

Figure 2 FTIR spectra of : a) raw food industry soil; b) treated food industry soil.

samples. The raw sample has a more complex spectral absorption bands because of the presence of a large variety of mineral assemblage whereas the treated distillery soil shows more sharp and intense absorption bands with some complexity in the lower wave numbers. Similar results were observed for the other samples also. The lesser splitting is observed particularly in the 2000–400 cm^{-1} wave number region. This type of sharp and intense absorption bands with less complexity is observed for the other treated samples also. These results match the XRD data.

TABLE III Fertility levels of the industrial soil samples

	Before hydrothermal treatment (mg/l)			After hydrothermal treatment (mg/l)								
				100°C			150°C			200°C		
Soil sample	*N*	*P*	*K*	*N*	*P*	*K*	*N*	*P*	*K*	*N*	*P*	*K*
Textile	0.39	16	80	0.32	13.9	71	0.27	10.09	63.7	0.12	8.67	61.9
Distillery	0.78	15	97	0.61	12.7	88	0.59	9.9	89.8	0.38	6.77	85.9
Food industry	0.5	25	200	0.47	26.2	197	0.37	24.2	194	0.22	21.3	189.7
Agricultural land	1.85	20	265	1.2	16	240	0.9	17.9	227	0.65	15	205

TABLE II Electrical conductivity data*

Soil sample	A	B	C	D
Textile soil	0.1	0.42	0.48	0.74
Distillery soil	0.23	0.18	0.18	0.44
Food industry soil	0.2	1.8	0.8	0.78
Agricultural soil	0.21	0.29	0.52	0.97

*Electrical conductivity of : A) raw soil sample; B) soil treated at 100°C; C) soil treated at 150°C; D) soil treated at 200°C (dsm^{-1}).

The electrical conductivity measurements carried out for the raw and treated textile, distillery and food industry soil yielded interesting results which correspond to the X-ray data. The electrical conductivity values are shown in Table II. The electrical conductivity values increase with an increase in the temperature of the hydrothermal treatment. The probable reason for such an increase in electrical conductivity with temperature of hydrothermal treatment is that the soluble ions like potassium, sodium, lithium, etc. which are in the stable complex form bonded firmly forming minerals like hornblende, biotite, feldspars, are in turn dissociate under hydrothermal conditions and present in the sample as soluble species resulting in the higher electrical conductivity. The electrical conductivity at 200°C for agricultural soil is very high because of larger concentration of soluble species.

The presence of *N*, *P*, and *K* components in the soil is an indication of the fertility of the soil (Table III). It is observed that the *N*, *P*, *K* in all the four types of soil decrease which indicates the drop in the fertility level of the soil. The values of *N*, *P*, *K* decrease with an increase in the hydrothermal treatment temperature, and which is responsible for the transformation of less stable minerals like biotite, feldspars, hornblende, rutile, goethite, etc. which contain less alkali and alkaline earth metals.

4. Conclusions

The untreated raw agricultural, distillery, textile and food industry soils show a wide range of mineralogical associations. The untreated soil samples show higher values of *N*, *P*, *K* and lower electrical conductivity because of the presence of lesser soluble species that are usually bonded to other cations forming hydrous ferromagnesium minerals. The treated soils show simple mineralogy. Mineral assemblages like biotite, hornblende, tremolite, etc., readily transform into other more simple and stable oxides and hydroxides. The treated soils show higher electrical conductivity than the untreated soils because of the presence of larger soluble species. The ferromagnesium minerals undergo easy transformation in the presence of chemical species from the effluents. These chemical species from the effluents cannot be easily recognized by the XRD or through thin section studies. The hydrothermal treatment helps to understand the role of chemical species from industrial effluents in the alteration and degradation of the soil.

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