Photocatalytic activity of Cr(VI) and Mn(VII) loaded $CaCO_3$ under sunlight radiation

A thesis

Submitted in the partial fulfilment of the requirements for the award of degree of

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Submitted by
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Under the supervision of

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Certificate

I hereby certify that the work presented in this thesis entitled "***Photocatalytic activity of Cr(VI) and Mn(VII) loaded $CaCO_3$ under sunlight radiation***" submitted in partial fulfilment of the requirements for the award of degree of Master of Science in Chemistry submitted to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my own work carried out under the supervision of Dr. Bonamali Pal and Dr. Satnam Singh. The matter embodied in the thesis has not been submitted to any other University for the award of any other degree or diploma. Works of other authors cited in this thesis have been duly acknowledged under reference section of this thesis.

Date: 15/7/19

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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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Davinder Kaur

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List of Abbreviations

RT	Room Temperature
$CaCO_3$	Calcium Carbonate
RB	Rhodamine B
UV	Ultraviolet
Wt %	Weight percent
DRS	Diffuse reflectance spectrophotometer
DLS	Dynamic Light scattering
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray
XRD	X-Ray Diffraction
Cr^{+6}-$CaCO_3$	Cr^{+6} metal ions doped over $CaCO_3$
Mn^{+7}-$CaCO_3$	Mn^{+7} metal ions doped over $CaCO_3$
DI	Deionized water
$KMnO_4$	Potassium permanganate
$K_2Cr_2O_7$	Potassium dichromate

List of Symbols

°C	Degree Celcius
Mg	Milli gram
Ml	Milli litre
Rpm	Revolutions per minute
µm	Micro meter
µM	Micro molar
Min	Minute
mV	milli Volt
a.u.	Arbitrary unit

Abstract

This study demonstrated the extraction of $CaCO_3$ from boiling tap water followed by its calcination at 900°C. Two metals ions with different oxidation states (Cr^{+6}, Mn^{+7}; 1wt%) were deposited over the surface of $CaCO_3$ (RT, 900°C) to study the adsorption and photo catalytic degradation of RB dye. Different techniques like DLS, XRD, DRS, SEM and UV-Vis spectrophotometer were used to characterize as-prepared photocatalysts. The DRS spectra revealed that $CaCO_3$ (900°C) shows absorption spectra at 245 nm which was red shifted to 364 nm and 531 nm after deposition of Cr^{+6} and Mn^{+7} respectively. The average hydrodynamic size of bare $CaCO_3$ (900°C) is 0.63 μm which is increased to 1.34 μm for Cr^{+6}-$CaCO_3$ (900°C)and 1.48 μm for Mn^{+7}-$CaCO_3$ (900°C) after metal ion impregnation. The hierarchical morphology was observed and the EDX-mapping studies revealed the presence of Cr^{+6} and Mn^{+7} ions doped on $CaCO_3$. The crystalline size of Cr^{+6}-$CaCO_3$ (900°C) (101 Å) and Mn^{+7}-$CaCO_3$ (900°C) (127 Å) was calculated using FWHM. The adsorption behaviour of RB dye follows Freundlich adsorption isotherm with $R^2 = 0.99$ and n=0.47. It was found out that Mn^{+7}-$CaCO_3$(900°C) showed enhanced degradation efficiency (92%) compared to $CaCO_3$(900°C) (73%) with higher rate constant (k) value of 4.6×10^{-2} min^{-1}.

1.INTRODUCTION & LITERATURE REVIEW

Calcium carbonate ($CaCO_3$) has gained significant attention in the area of catalysis and photocatalysis. The higher catalytic performance of $CaCO_3$ arouse due to its high surface area and narrow sized pore distribution. $CaCO_3$ also used for various industrial applications like cement making, paper production, adsorbents and adhesive or sealants etc [1]. Naturally $CaCO_3$ found in gypsum, plagioclases, dolomite, pyroxenes, and garnets and synthetically, it is found in chalk, limestone, and marble, produced by the sedimentation of the shells of small fossilized snails and shellfish [2-3]. Nowadays, it has been widely used in adsorption and photo degradation of hazardous organic pollutants (azo dyes) present in water. Bathla *et.al* reported extraction of $CaCO_3$ from tap water and used it as adsorbent and photo catalyst for degradation of malachite green dye with maximum degradation of dye after 60min[4]. $CaCO_3$ core shell microspheres had been used for removal of anionic dyes. Different parameters like amount of adsorbent, contact time were studied and it took 2 min to remove 99-100% anionic dye from solution [5]. The monolayer process of absorption for removal of methylene blue and congo red dye was done with $CaCO_3$ modified with bentonite showed by Zhang *et.al* [6]. Various parameters like SDBS and pH were studied for removal of Methylene blue and Congo red dye The maximum adsorption capacity of MB and CR lies in range of pH 2~10. To increase its adsorption and photocatalytic properties, amalgamation of transition metal dopants on $CaCO_3$ can increase its photocatalytic activity.

Many methods have been reported for the extraction of $CaCO_3$ such as flocculation, precipitation and gas diffusion methods [7]. Nowadays, recyclable and cheaper bioactive materials are used in synthesis method to make more it environment friendly. The $CaCO_3$ can be extracted from natural resources such as egg shells, mollusk shells and bones of dead animals. $CaCO_3$ can also be extracted using tap water. One of the method which is generally used to extract $CaCO_3$ is from hard water which is used in household, laboratories etc. The deposition of metal ions on the surface of $CaCO_3$ further enhance its photocatalytic efficiency. Li *et.al* reported the doping of Mn^{2+} and Co^{2+} on ZnO nanowires without changing its morphology and crystalline structure. The photocatalytic activity of Mn-doped and Co-doped ZnO nanowires showed higher activity than undoped ZnO nanowires [8]. Mn, Cr, Co-doped TiO_2 electrodes were prepared for the photocatalytic degradation of acid red G dye under UV light. Mn^{2+} showed the most photocatalytic efficiency. Different parameters like adsorption equilibrium constant, rate constant, initial degradation rate were determined for different electrodes [9].

In recent years, photo catalysts are being used for the removal of toxic dye pollutants from industrial waste water by converting them into simpler molecules like H_2O, CO_2, mineral acids [10-11].Many techniques have been used to treat dye effluents from water bodies like precipitation, ultra filtration, reverse osmosis, adsorption [12-13]. These techniques have not worked correctly as they simply convert non-biodegradable waste into sludge, creating another type of pollution requiring treatment [14].

Paola *et.al* investigated the photo catalytic property of TiO_2 by loading various transition metals (Co, Cr, Cu, Fe, Mo, V, and W) by wet impregnation method for the degradation of 4-Nitrophenol. It was revealed out the recombination rates were higher for impregnated metals than that for bare TiO_2 [15]. Eyasu *et.al* loaded Cr (0.05, 0.1, 0.2 and 0.3mol %) on ZnS nanoparticles via wet impregnation method. Methyl orange dye was degraded photocatalyticaly via synthesized nanoparticles in visible and UV light. The other factors such as dopant concentration ,pH, dye initial concentration were also investigated [16]. Rhodamine B dye was photo catalytic degraded using $NaBiO_3$ under visible light. It took around 30 min to completely decolourized the dye under provided conditions [17]. Jain *et.al* reported the removal of Rhodamine B dye from wastewater via photocatalytic and adsorptive method by using TiO_2 photo catalyst. Decrease in COD values confirmed the effective degradation of dye. Other parameters such as pH, concentration of dye, temperature, amount of catalyst were observed [18].

Rhodamine B dye is used as colorant in textile industry, as a tracer dye to check water flow and direction, stainer in biological uses. It is highly soluble in water ~15 g/L and suspected to be carcinogenic [19-20]. It has become highly important to degrade this dye using photo catalyst to remove its toxicology.

Though several photocataysts have been doped with different transition metal ions to increase its photocatalytic activity but no work has been done on doping of $CaCO_3$ for its higher degradation efficiency. In present study, the doping of $CaCO_3$ calcined at 900°C with transition metals Cr^{+6}, Mn^{+7} and to study its photcatalytic activity on RB dye.

2. OBJECTIVE

Our aim is to extract $CaCO_3$ from tap water and load it with different transition metals to study its photocatalytic activity.

- Extraction of $CaCO_3$ from boiling tap water and to study the effect of calcinations at high temperature (900°C).
- To study the effect of $Cr^{+6}$and Mn^{+7} metal ions impregnation onto $CaCO_3$ for improved adsorption and photocatalytic activity for degradation of Rhodamine B dye under sunlight.

3. MATERIALS AND METHODS

3.1 Materials

$CaCO_3$ was extracted from tap water using double distillation method in TIET laboratory. Rhodamine B dye ($C_{28}H_{31}N_2O_3Cl$), ethanol (C_2H_5OH), acetone (CH_3COCH_3), $KMnO_4$, $K_2Cr_2O_7$ were purchased from Loba Chemie, India. DI water was obtained from distillation plant. All chemicals were used as received without any further purification.

3.2 METHODS

3.2.1 Method of Extraction of Calcium Carbonate ($CaCO_3$) from tap water:

In double distillation method, tap water was first boiled for six hours at high temperature in round bottom flask. After boiling, the residue left in round bottom flask contains calcium carbonate which was used after centrifugation at 8000 rpm for 5 min at 25 ˚C and washed twice/thrice with water and ethanol respectively. Later, the residue was dried at RT. Then the powder form obtained is further calcined at 900°C for 4 hours in muffle furnace.

3.2.2 Wet impregnation method for loading $Mn^{+7}$and Cr^{+6}

Mn-doped $CaCO_3$

In 100 mL beaker, $KMnO_4$ (29mg) was dissolved in DI water (10mL).In another beaker (100 mL), $CaCO_3$(RT) (1g) was dissolved in known volume of DI water. After small regular intervals of time, $KMnO_4$ solution was added to the CaCO3 solution drop wise placed on magnetic stirrer. The solution was stirred for 24 h. The obtained solution was centrifuged (10 min, 8000 rpm) and washed with water and ethanol. The precipitate was dried for overnight at room temperature.

$K_2Cr_2O_7$ (57mg) was dissolved in distilled water(10mL) .Similar procedure was done for impregnating Mn^{+7}-$CaCO_3$(900˚C), Cr^{+6}-$CaCO_3$(RT, 900˚C) as mentioned above.

3.2.3 Characterization techniques

A variety of techniques have been used for the characterization of $CaCO_3$ (RT,900°C), Cr^{+6}-$CaCO_3$(RT,900°C), Mn^{+7}-$CaCO_3$(RT,900°C). The detailed study of used techniques is as follows:

Dynamic Light scattering (DLS) analysis and Zeta potential: The average hydrodynamic particle size distribution and surface charge on prepared catalysts were determined by taking 3 ml of the solution (2 mg catalyst in 10 ml ethanol) using Malvern ZEN3600 particle size analyser.

X-Ray Diffraction (XRD): For the identification of crystal structure and its size of prepared catalysts was determined by PAN analytical- Xpert High score with a diffraction angle of 20-90˚ at 5˚ rise/min.

Scanning electron microscope (SEM) analysis and elemental mapping: To determine the size and surface morphology and elemental examinations, a pinch of powder form of prepared catalysts was placed on a 300 mesh copper grid coated with a carbon film. JSM-6510LV, electron microscope working at 30 kV was used for analysis.

Ultraviolet-Visible (UV-Vis) Spectrophotometric analysis: was used to monitor the change in absorbance after regular intervals during dark adsorption and photocatalytic degradation reactions. It was recorded with the help of Shimadzu Corporation TW223L UV-Vis spectrophotometer.

DRS (Diffuse reflectance spectrophotometer): was used to study the spectral characteristic absorbance peaks of prepared catalysts before and after photocatalytic degradation. The change in the absorbance spectra of different catalysts) before and after photocatalytic degradation were depicted by Avntas DRS instrument, using $BaSO_4$ as a reference.

Dark adsorption behaviour of $CaCO_3$ (RT, 900°C), Cr^{+6}-$CaCO_3$(RT, 900°C), Mn^{+7}- $CaCO_3$ (RT, 900°C)

A stock solution of (0.01mM) RB dye was prepared by dissolving 1.2 mg of dye in 250 ml DI water. 10 ml of solution was taken from it and added to three test tubes each. 5 mg of $CaCO_3$ (RT) was added to each test tube and stirred on magnetic stirrer placed in dark for 5,10 ,15 min respectively. After regular interval of time, test tube was taken out and centrifuged (8000 rpm, 10 min, 25°C). The UV- Visible spectra of supernatant solution was recorded for the study of dark adsorption. Similar procedure was followed for the dark adsorption of $CaCO_3$ (900°C), Cr^{+6}, Mn^{+7}- $CaCO_3$ (RT, 900°C).

Photocatalytic degradation of RB dye under sunlight

Same procedure was followed for preparation of stock solution of RB dye (0.01mM) as above. Same amount of catalyst and dye was taken in three test tubes and was first stirred on magnetic stirrer in dark for 15 min then placed under direct sunlight. After regular interval of time, each test tube was taken out and centrifuged (8000 rpm, 10 min, 25°C). The UV- Visible spectra of supernatant solution was recorded for the study of photocatalytic degradation of RB dye under sunlight. Similar procedure was followed for the photocatalytic degradation of RB dye under sunlight using $CaCO_3$ (900°C), Cr^{+6}, Mn^{+7}-$CaCO_3$(RT, 900°C). The UV-Vis spectra of different catalysts with RB dye is shown in figure 8.

4. Result and discussion

4.1 Structural and Optical characteristics

The average hydrodynamic particle size distribution on $CaCO_3$(RT, 900°C), Cr^{+6}-$CaCO_3$(RT, 900°C), Mn^{+7}-$CaCO_3$ (RT, 900°C) illustrated in figure 1(a,b,c) were determined by taking 3 ml of the solution (2 mg catalyst in 10 ml ethanol) and ultrasonic treatment was given for 1 hour to disperse $CaCO_3$ particles completely in the solution. The average hydrodynamic size of $CaCO_3$ (RT) was found to be 1.34 and $CaCO_3$(900°C) 0.63 μm respectively. There was a gradual increase in size of Cr^{+6}, Mn^{+7}-$CaCO_3$(900°C) particles due to deposition of 1wt% Cr^{+6},Mn^{+7} metal ions on $CaCO_3$(900°C) and found to be 0.27 μm for some particles and 1.34 μm for large range of particles for Cr^{+6}-$CaCO_3$(900°C). Similarly for Mn^{+7}-$CaCO_3$ (900°C) some particles were of size 0.32 μm and rest had size of 1.48 μm. The average size for Cr^{+6}, Mn^{+7}-$CaCO_3$ (RT) was 0.33 and 0.38 μm respectively.

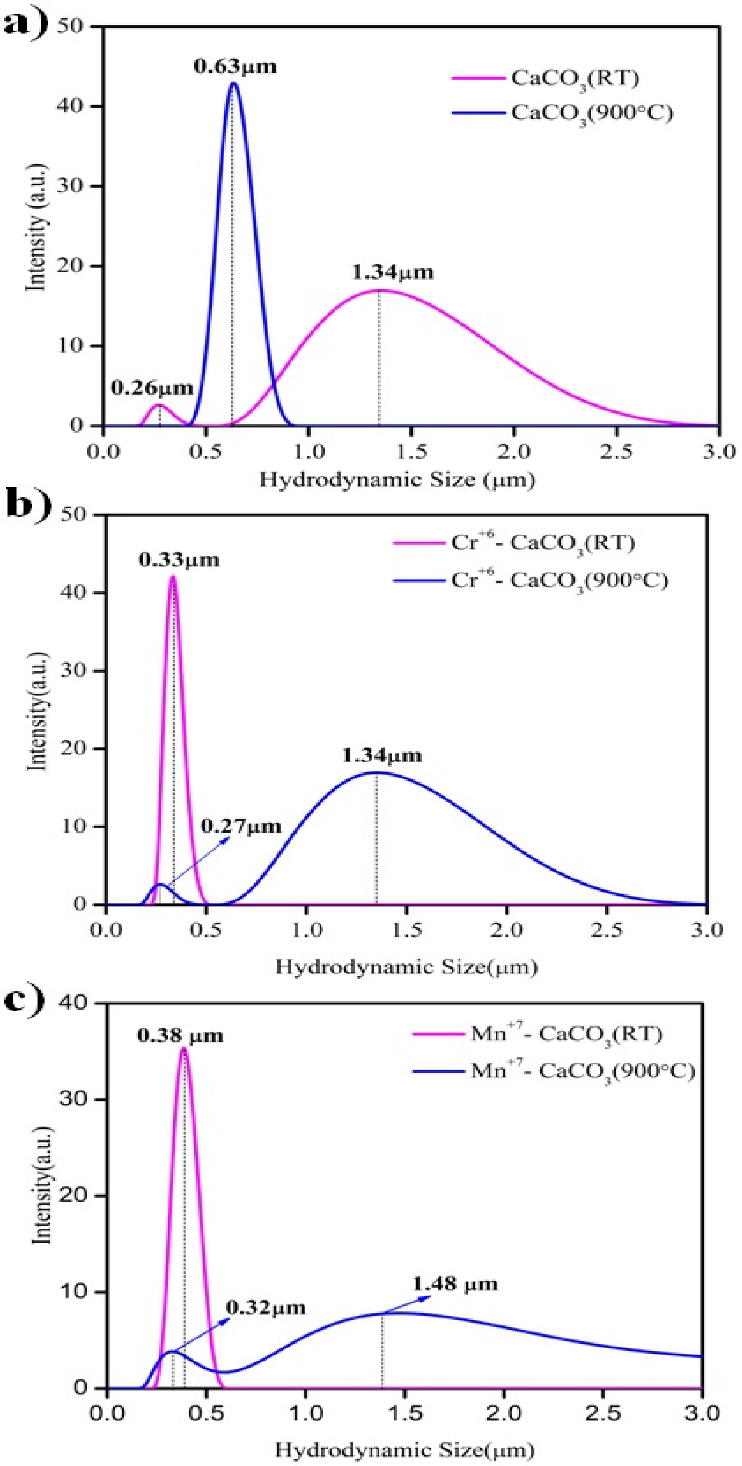


Figure 1: Dynamin Light Scattering (DLS) particle size distribution of a) bare $CaCO_3$, b) Cr^{+6}-$CaCO_3$, c) Mn^{+7}-$CaCO_3$ at different temperatures (RT and 900°C).

The surface charge of the catalyst was measured by zeta potential. . The surface charge on $CaCO_3$(RT,900°C),Cr^{+6}-$CaCO_3$(RT, 900°C), Mn^{+7}-$CaCO_3$(RT, 900°C) was detemined by dispersing 3 mg $CaCO_3$ in 10 ml ethanol. Ultrasonic treatment was given for 1 hour so that prepared catalysts gets completely dispersed in the ethanol. It was found out that the surface charge on $CaCO_3$(RT), Cr^{+6}-$CaCO_3$(RT), Mn^{+7}-$CaCO_3$ (RT) was 0.87 mV,0.47 mV and 0.15 mV respectively and on $CaCO_3$(900°C), Cr^{+6}-$CaCO_3$(900°C), Mn^{+7}-$CaCO_3$(900°C) was -7.06 mV, -0.10 mV, -0.49 mV shown in figure 2. The highly negative surface charge at 900˚C catalysts is due to the formation of Ca(OH)2 in water, which is negatively charged.

$CaO + H_2O \longrightarrow Ca(OH)_2 + CaCO_3$ (undecomposed)

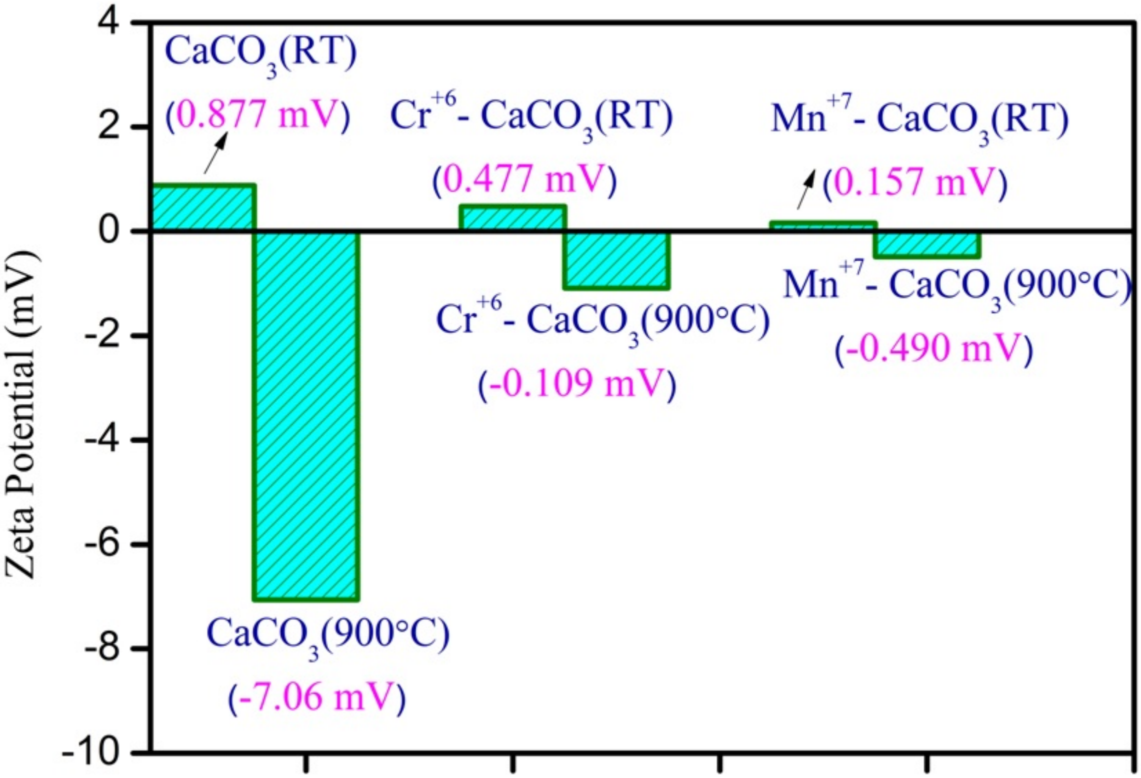
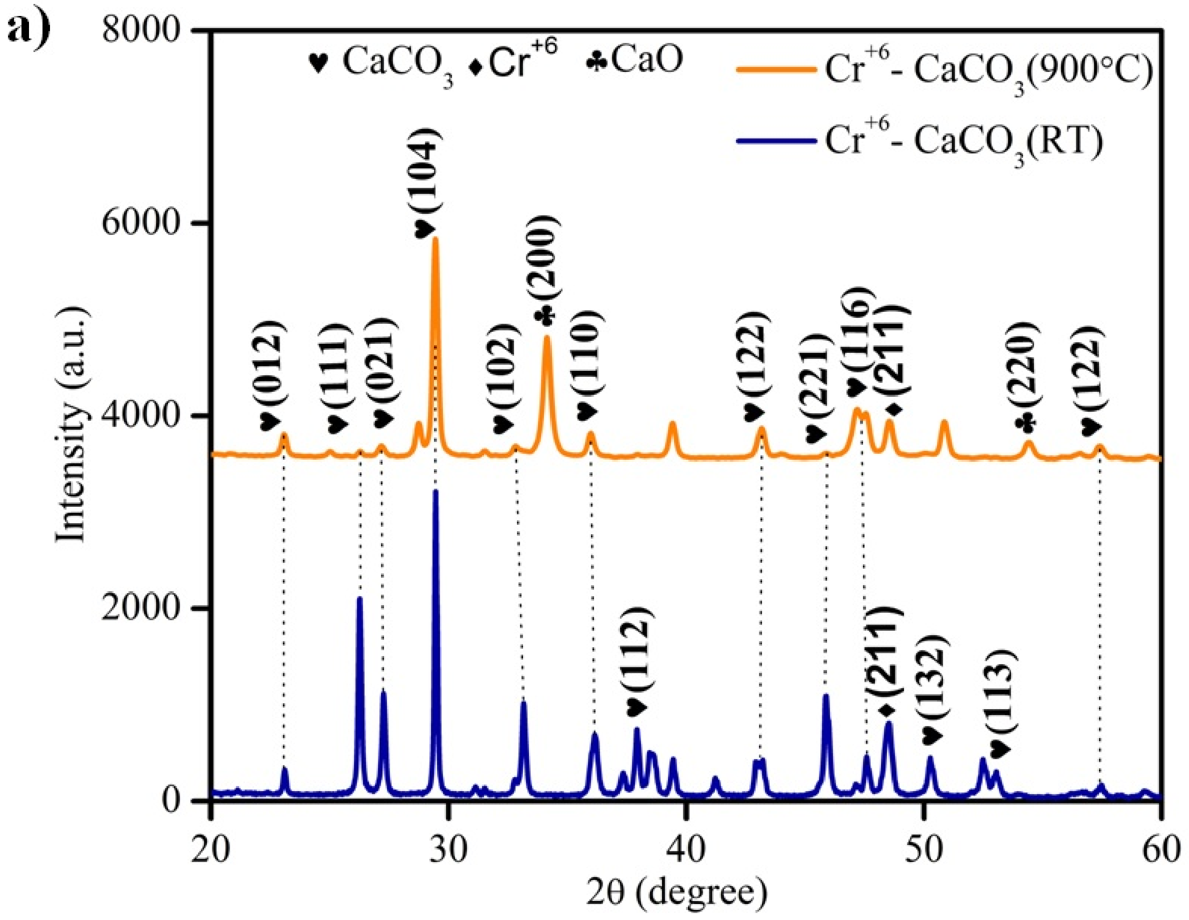


Figure 2: Surface charge distribution on $CaCO_3$, Cr^{+6}- $CaCO_3$, Mn^{+7}- $CaCO_3$ at different room temperatures (RT) and 900°C.

To determine the crystallinity and composition of the elements present in the Cr^{+6}-$CaCO_3$(RT, 900°C), Mn^{+7}-$CaCO_3$ (RT, 900°C) , XRD spectra was analyzed as shown in figure 3. It was found out that both Cr^{+6}-$CaCO_3$(RT), Mn^{+7}-$CaCO_3$ (RT) contains planes (021), (104), (102) ,

(221) showing high intensity peaks at 2θ = 27.25° ,29.43°,33.15°,45.83° and low intensity peaks at 2θ = 23.05°, 36.14°, 43.08°, 47.60°, 57.38° corresponding to planes (012), (110), (122), (116), (122) respectively of $CaCO_3$ (JCPDS Card no.01-075-2230). Cr^{+6}-$CaCO_3$ and Mn^{+7}-$CaCO_3$ (900°C) shows the peaks of CaO (JCPDS Card no.00-037-1497) at 2θ = 26.28°, 34.12°, 54.39° corresponds to (111), (200), (220) orientation planes respectively along with $CaCO_3$ orientation planes. There were more sharp peaks in Cr^{+6}, Mn^{+7}-$CaCO_3$ (900°C) indicating that doping of metal(Cr^{+6},Mn^{+7}) on $CaCO_3$ has increased the crystallinity of samples. Cr^{+6} showed its peak matching plane (211) at 2θ=48.5° in Cr^{+6}-$CaCO_3$(RT,900°C) (JCPDS Card no.00-027-0380) and Mn^{+7} showed its peak matching planes (211), (122) at 2θ=28.7°39.3° in Mn^{+7}-$CaCO_3$(RT,900°C) (JCPDS Card no.01-0725). The crystalline size of Cr^{+6}-$CaCO_3$ (900°C) and Mn^{+7}-$CaCO_3$ (900°C) was calculated to be 101 Å and 127 Å respectively using FWHM.



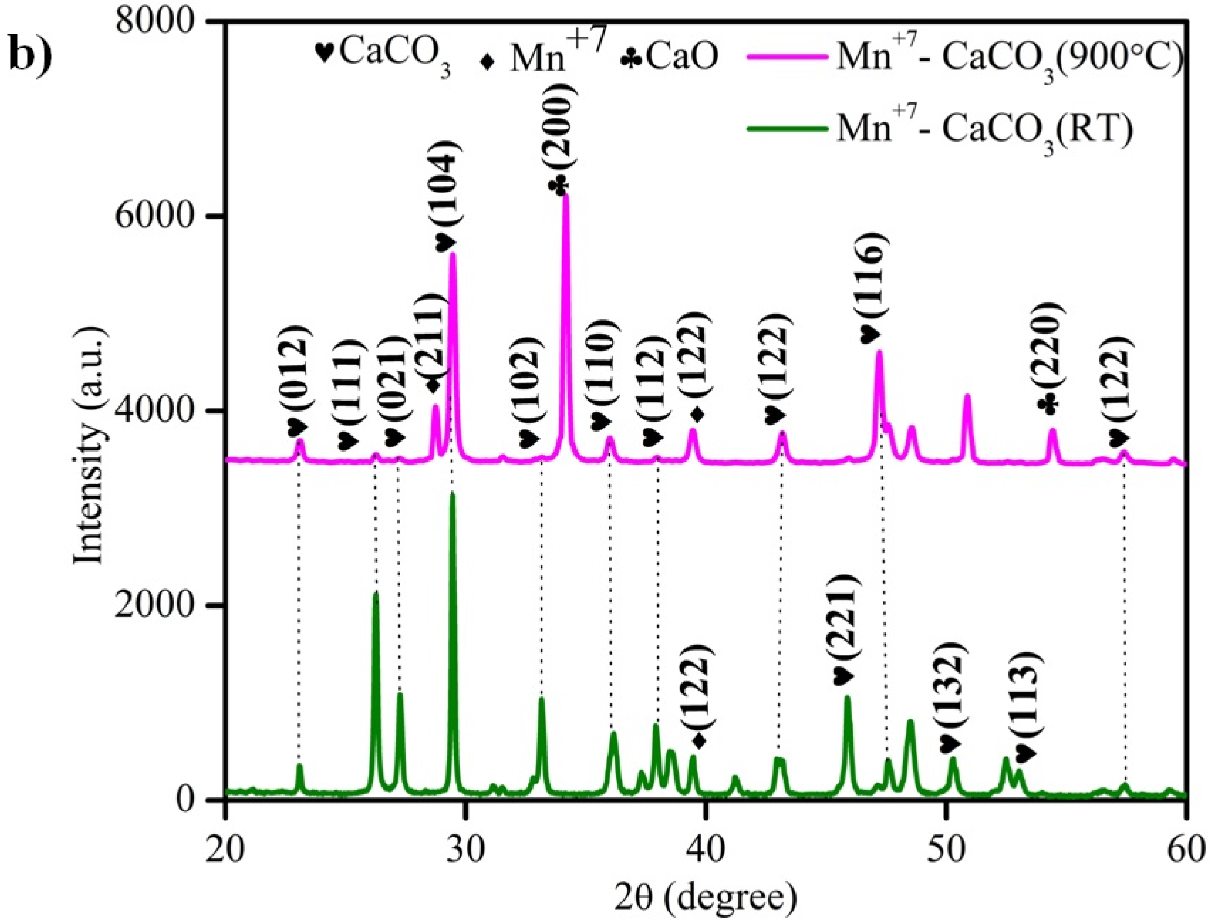
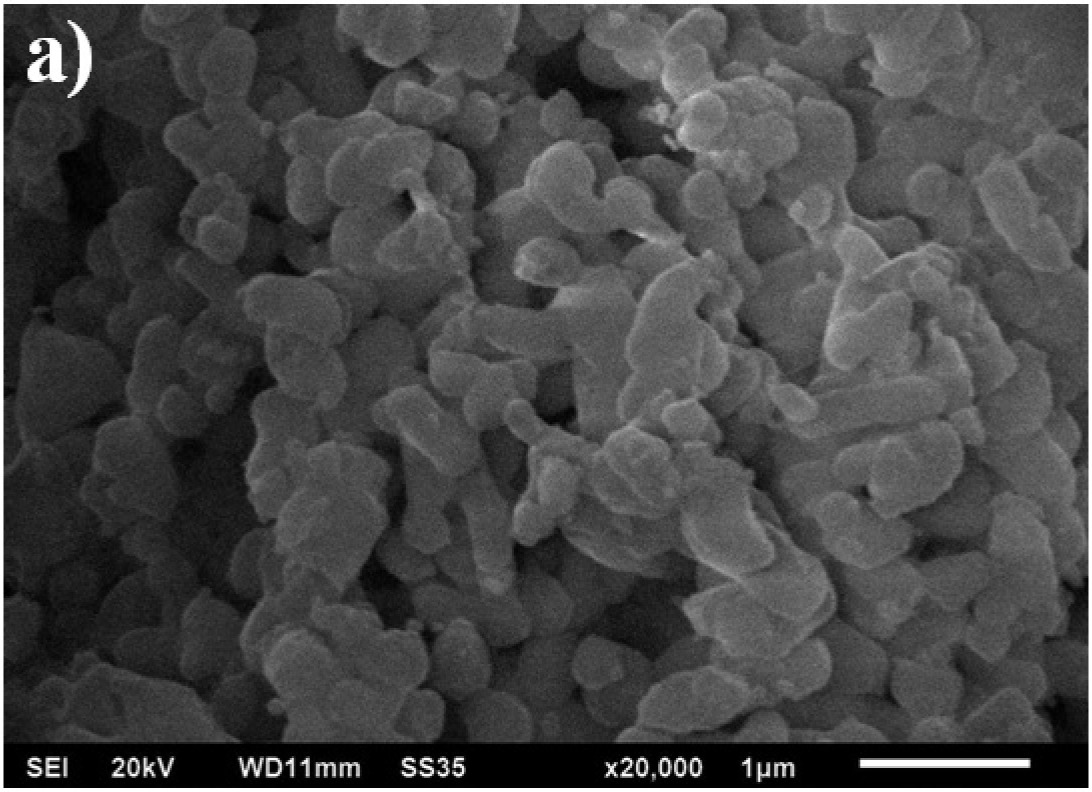


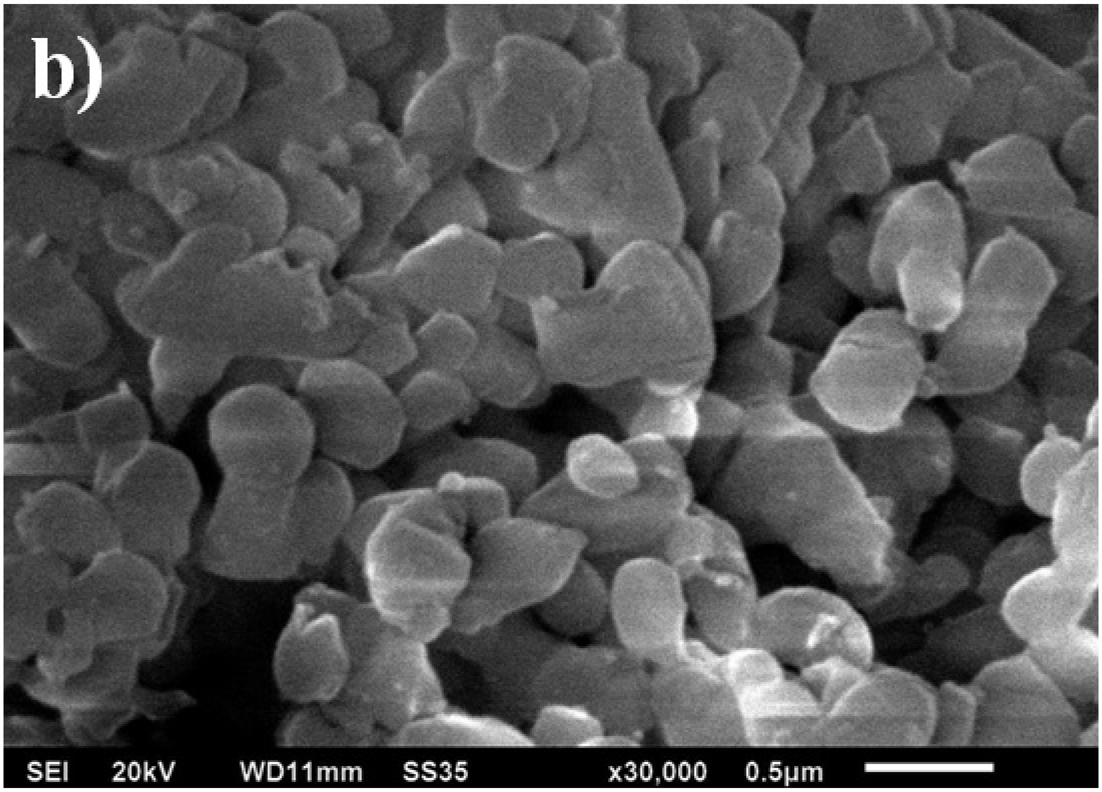
Figure 3: X-ray diffraction (XRD) patterns of a) Cr^{+6}-$CaCO_3$, b) Mn^{+7}-$CaCO_3$ at different temperatures (RT and 900°C).

SEM studies confirmed the uniform dispersion of Cr^{+6}, Mn^{+7} metal impregnated over $CaCO_3$ (900°C).It also revealed the size of the Cr^{+6}- $CaCO_3$(900°C), Mn^{+7}- $CaCO_3$ (900°C) lies between 0-5 µm and shows the hierarchical like morphology shown in figure 4.

EDS spectra of Cr^{+6}- $CaCO_3$ (900°C) confirmed the presence of Cr^{+6} metal over $CaCO_3$ as the detected wt% of Cr was found to be 0.04% which was further confirmed by element mapping figure 5(a).

The presence of Mn^{+7} metal ion over $CaCO_3$ was confirmed as the detected wt% of Mn was found to be 0.13% which was further confirmed by element mapping shown in figure 5(b).


a)
SEI 20kV WD11mm SS35 x20,000 1μm


b)
SEI 20kV WD11mm SS35 x30,000 0.5μm

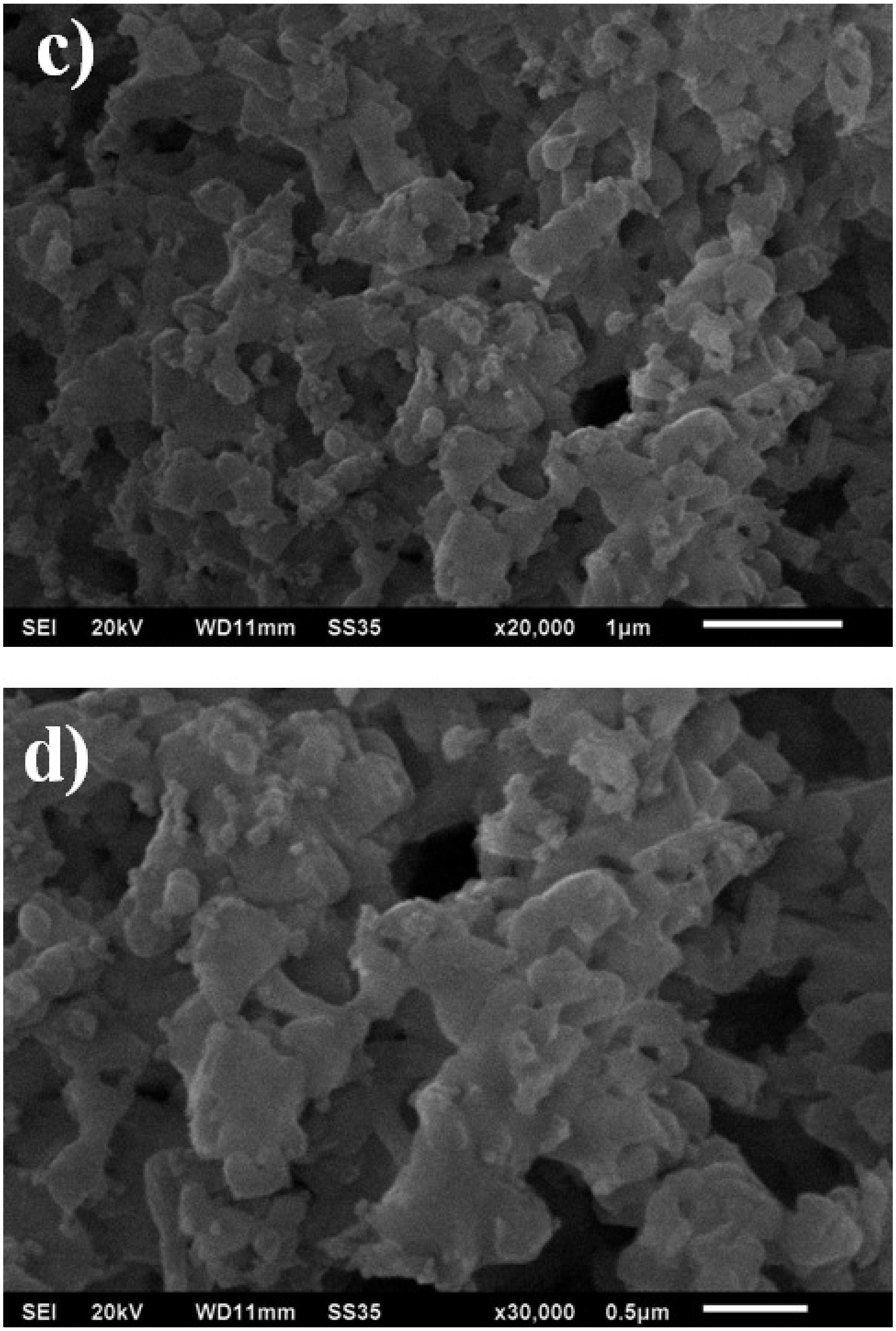
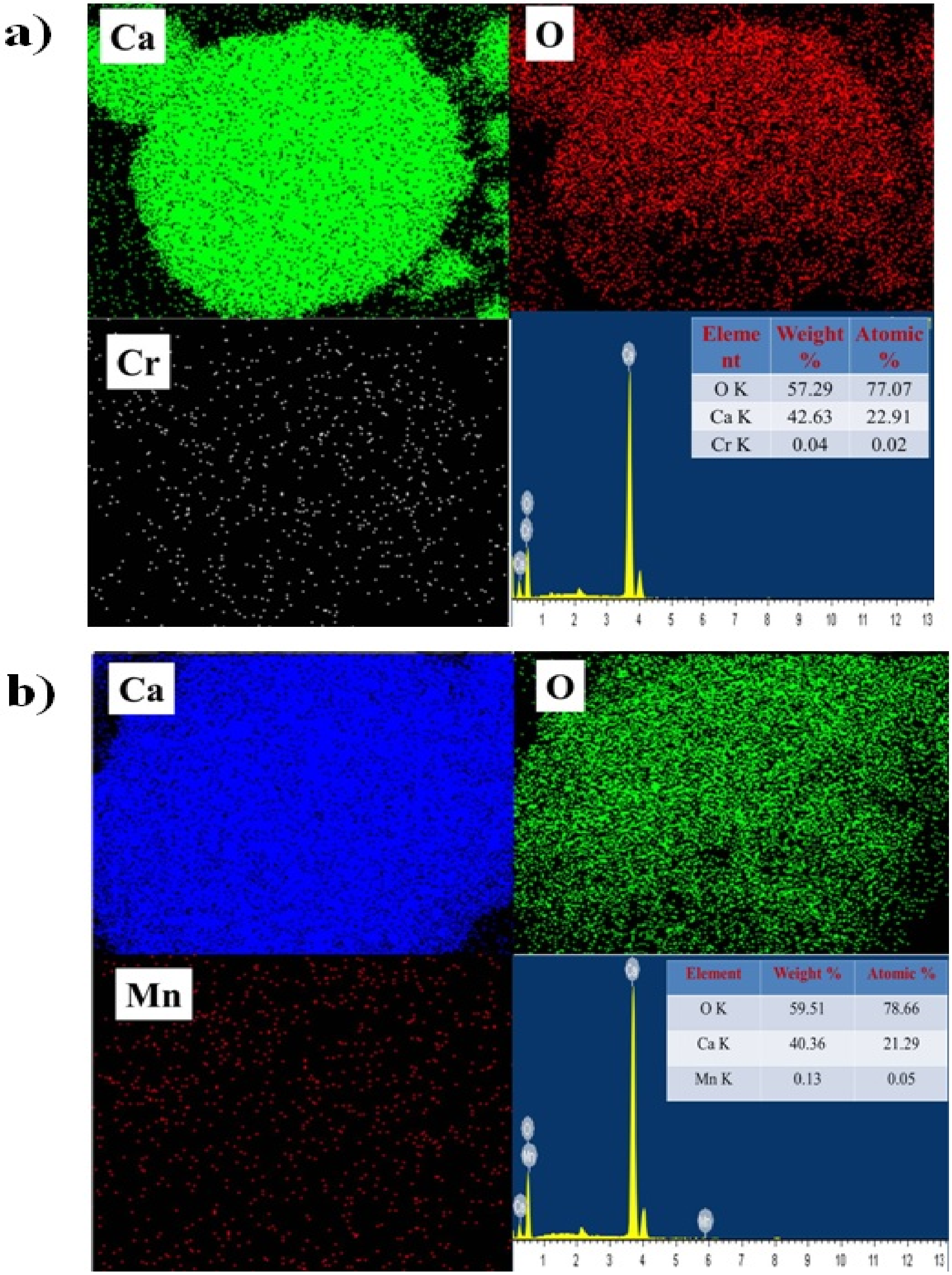


Figure 4: Scanning electron microscopy (SEM) of (a,b) Cr^{+6}-$CaCO_3$(900°C) , (c,d) Mn^{+7}-$CaCO_3$ (900°C) .



Element	Weight %	Atomic %
O K	57.29	77.07
Ca K	42.63	22.91
Cr K	0.04	0.02

Element	Weight %	Atomic %
O K	59.51	78.66
Ca K	40.36	21.29
Mn K	0.13	0.05

Figure 5: Element mapping and Energy-dispersive X-ray spectroscopy (EDX) analysis of a) Cr^{+6}-$CaCO_3$ (900°C), b) Mn^{+7}-$CaCO_3$(900°C).

4.2. Calibration graph of Rhodamine B dye

To assess the dark adsorption and photo catalytic degradation of RB dye, calibration graph was plotted for RB dye figure 6. Different concentration solutions of dye were prepared (0.0025, 0.003, 0.005, 0.08, 0.01) mM from stock solution of (0.01mM) RB dye, prepared by dissolving 1.2 mg of dye in 250 ml DI water. The absorbance Vs concentration was plotted and all the further calculations were done using this relationship.

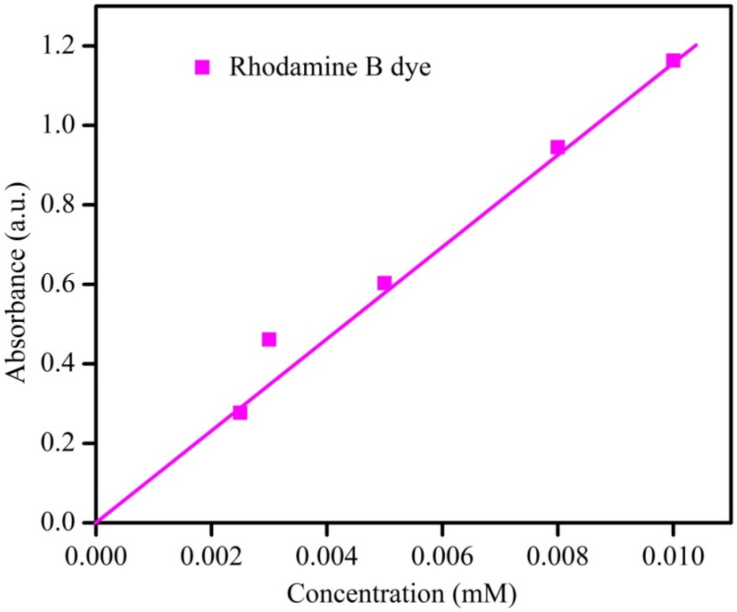


Figure 6: Calibration graph (Lambert-Beer's Law) of Rhodamine B dye (RB).

4.2. Section A: Dark adsorption

The absorption spectra of RB dye (0.01 mM, 5 ml) adsorbed in dark by $CaCO_3$(RT, 900°C), Cr^{+6}- $CaCO_3$(RT, 900°C), Mn^{+7}- $CaCO_3$(RT, 900°C) over regular intervals of 5, 10, 15 min was obtained as shown in figure 7. It was determined from the figure 8 that bare RB dye gives an absorption band at 554 nm and as the time of adsorption increased, a decrease in the intensity of absorbance band of dye was noticed. It was observed that $CaCO_3$ (RT,900°C) adsorbed more amount of dye than Cr^{+6}- $CaCO_3$(RT, 900°C).,Mn^{+7}- $CaCO_3$(RT, 900°C).The higher adsorption efficiency exhibited by the photocatalysts $CaCO_3$(RT, 900°C) can be attributed to large interfacial contact area .

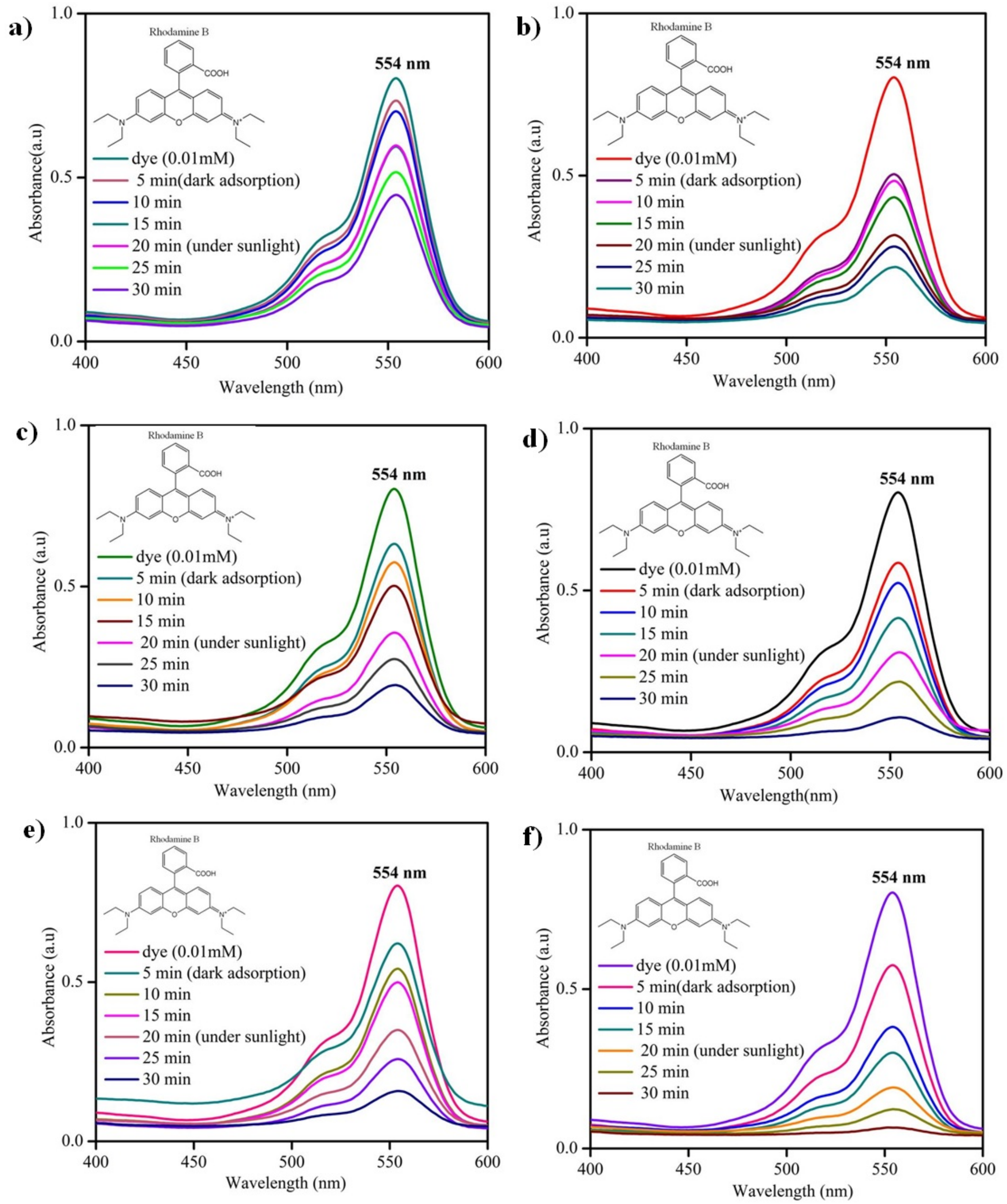


Figure 7: Dark adsorption followed by photo catalytic degradation under sunlight of RB dye(0.01mM) for 30 min by a)$CaCO_3$(RT) b)$CaCO_3$(900°C) c) Cr^{+6}-$CaCO_3$(RT) d) Cr^{+6}-$CaCO_3$(900°C) e) Mn^{+7}-$CaCO_3$(RT) f) Mn^{+7}-$CaCO_3$(900°C) .

The figure 8 shows that the log x/m Vs log Ce graph where x is the amount of adsorbent, m is mass of adsorbent and Ce is the concentration of adsorbate and the values of n and K are found by slope and intercept. Freundlich fitting curve was best fit for RB dye adsorption. Freundlich Adsorption isotherm is given by equation $x/m = k\ Ce^{1/n}$.

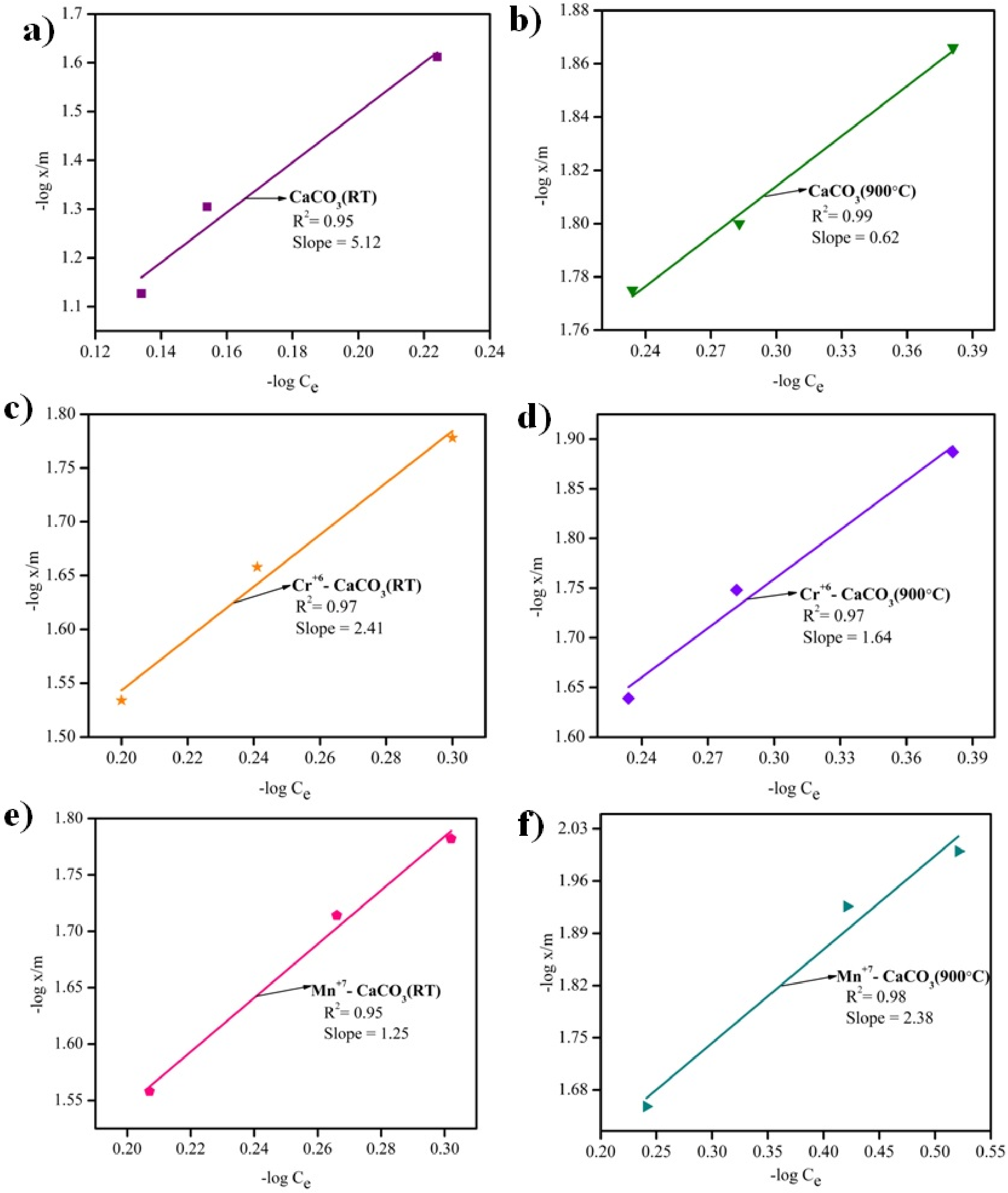


Figure 8: Freundlich adsorption isotherms for a) $CaCO_3$(RT) , b) $CaCO_3$(900°C), c) Cr^{+6}-$CaCO_3$(RT) , d) Cr^{+6}-$CaCO_3$(900°C), e) Mn^{+7}-$CaCO_3$(RT) ,f) Mn^{+7}-$CaCO_3$(900°C).

4.2. Section B: Photodegradation of RB dye

The absorption spectra of RB dye (0.01 mM, 5 ml) photocatalytically degraded by $CaCO_3$(RT, 900°C),Cr^{+6}-$CaCO_3$(RT, 900°C),Mn^{+7}-$CaCO_3$(RT, 900°C) over regular intervals of 20, 25, 30 min under sunlight was obtained as shown in figure 7. It was determined from the figure 8 that bare RB dye gives an absorption band at 554 nm and as the time of degradation increased, a decrease in the intensity of absorbance band of dye was noticed. It was observed that Mn^{+7}-$CaCO_3$(900°C) degraded more amount of dye than $CaCO_3$(RT,900°C), Cr^{+6}- $CaCO_3$(RT, 900°C).The higher degradation efficiency exhibited by the photocatalyst Mn^{+7}- $CaCO_3$ (900°C) can be attributed to that it doesnot adsorb dye over its surface it degrades the dye as it reaches over its surface.

Figure 9 shows the log C_0/C_t Vs time (min) graph where C_0 is the initial concentration and C_t is the concentration at different time intervals of RB dye photocatalytically degraded by $CaCO_3$(RT, 900°C), Cr^{+6}- $CaCO_3$(RT, 900°C)., Mn^{+7}- $CaCO_3$(RT, 900°C). Pseudo first order rate kinetics was observed according to the equation:

$$\mathbf{2.303 \log C_0/C_t = k\ t}$$

where, k is the rate constant for pseudo first order rate kinetics. The k values for $CaCO_3$(RT, 900°C) ,Cr^{+6}-$CaCO_3$(RT, 900°C) ,Mn^{+7}-$CaCO_3$(RT, 900°C) photocatalysts degraded RB dye for 30 min was 1.2×10^{-2} min^{-1}, 1.67×10^{-2} min^{-1} , 2.6×10^{-2} min^{-1} ,$4.6\times10^{-2}min^{-1}$,3.4×10^{-2} min^{-1} , 4.6×10^{-2} min^{-1} respectively.

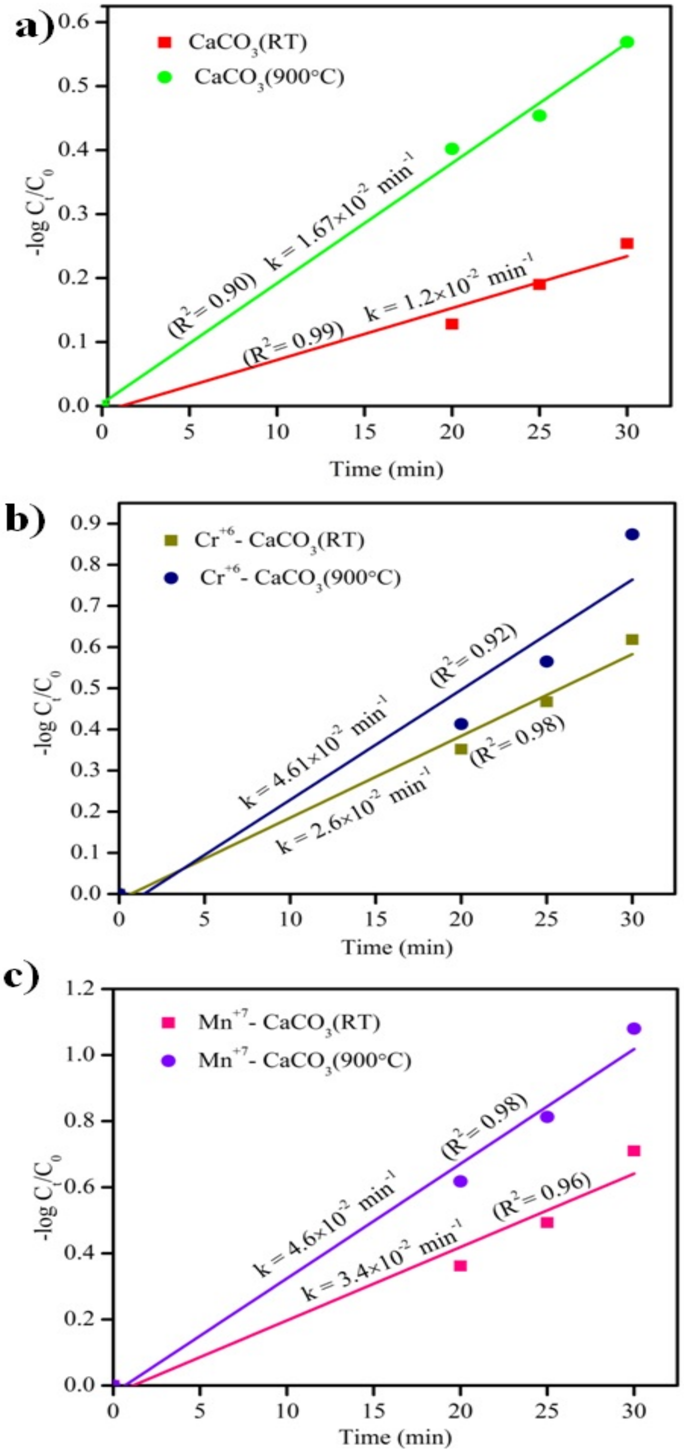


Figure 9: Kinetic studies showing the rate constant following pseudo first order for photo catalytic degradation of RB dye under sunlight for a) $CaCO_3$ (RT, 900°C), b) Cr^{+6}-$CaCO_3$ (RT,900°C), c) Mn^{+7}-$CaCO_3$(RT,900°C).

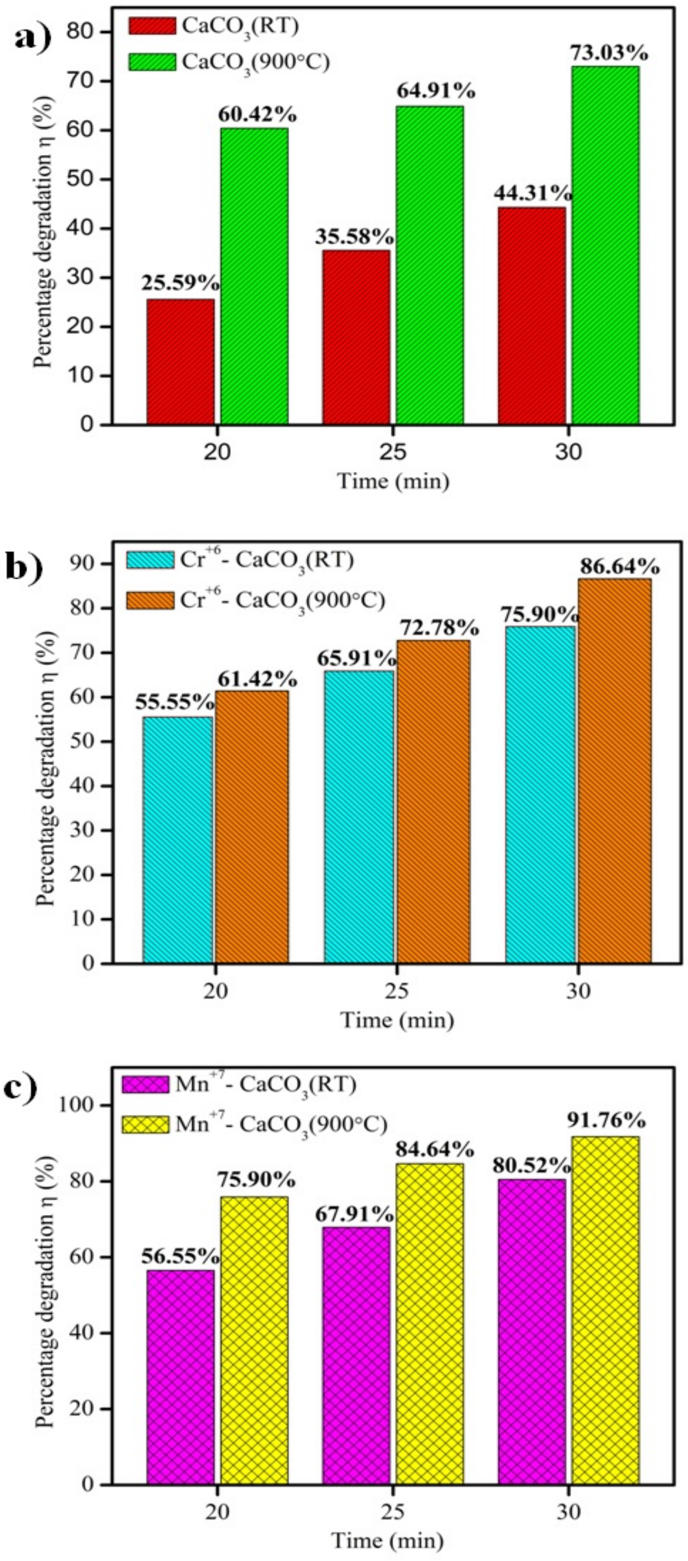


Figure 10: Percentage degradation of dye obtained for a) $CaCO_3$ (RT,900°C) b) Cr^{+6}-$CaCO_3$ (RT,900°C) c) Mn^{+7}-$CaCO_3$ (RT,900°C).

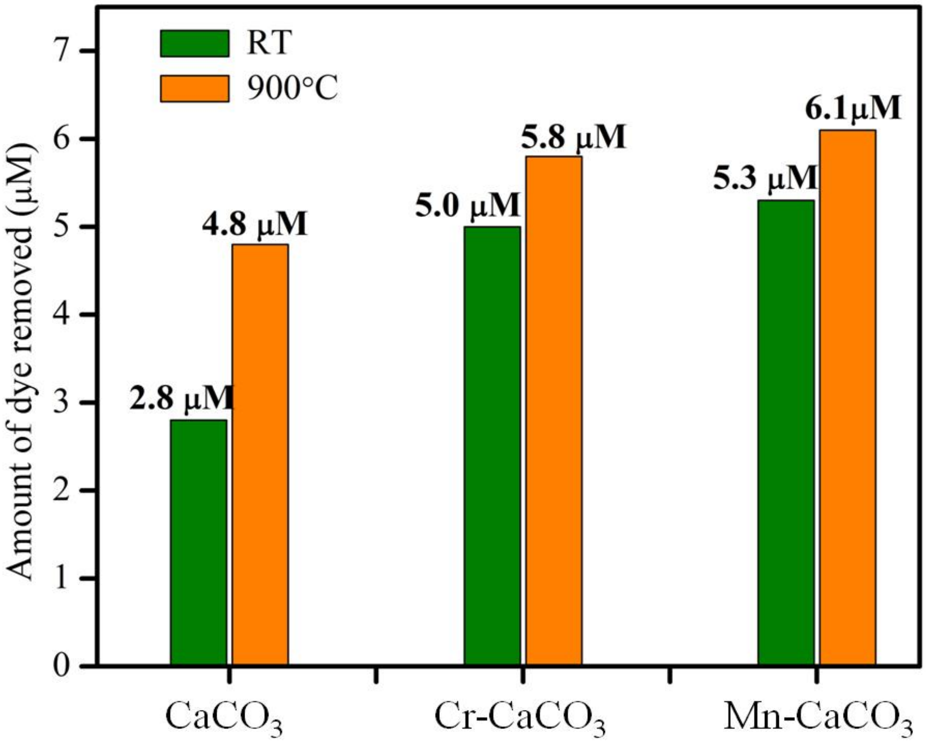
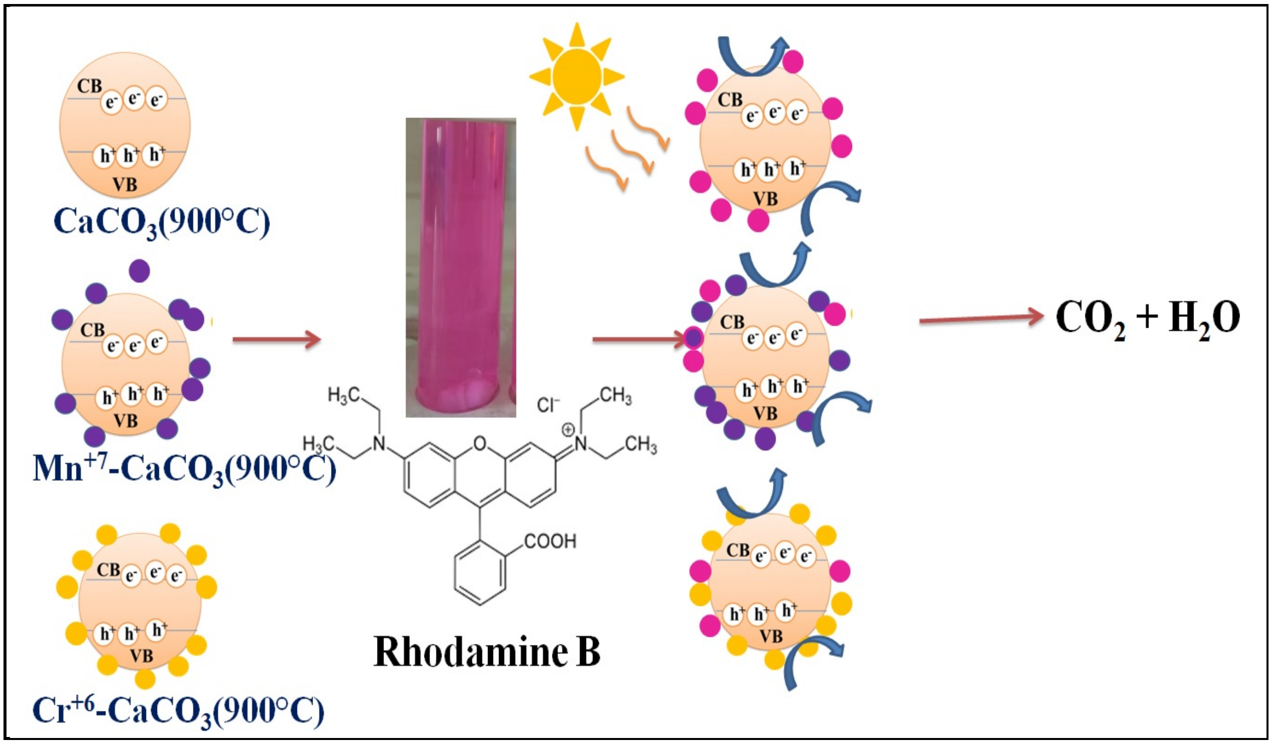


Figure 11: Comparative study of amount of dye removed Vs different catalysts $CaCO_3$,Cr^{+6}-$CaCO_3$, Mn^{+7}- $CaCO_3$ at (RT, 900°C) for photodegradation of dye (10μM) for 30 min.

From figure 10 , it can be seen that maximum amount of percentage degradation was done by Mn^{+7}-$CaCO_3$(900°C) which is ~92% . In terms of μM, out of 10 μM dye, 6.1 μM was removed by Mn^{+7}-$CaCO_3$(900°C) which was further supported by DRS. DRS absorption spectra was recorded to study the spectral characteristic absorbance peaks of $CaCO_3$(RT, 900°C),Cr^{+6}-$CaCO_3$(RT,900°C),Mn^{+7}-$CaCO_3$(RT, 900°C)catalysts before and after photocatalytic degradation shown in figure 12. It was revealed that $CaCO_3$ (RT,900°C) shows its characteristic peak at 245 nm and after photocatalytic degradation , its absorbance peak decreased to 270, 266 nm respectively. An additional peak of 554 nm was seen after degradation which suggests it could be due to adsorption of dye on its surface on $CaCO_3$(RT,900°C). Similarly for Cr^{+6}-$CaCO_3$(RT,900°C) a characteristic peak of Cr was observed at 256,364 nm and after photo degradation an additional peak of 554 nm was observed corresponding to dye peak. For Mn^{+7}-$CaCO_3$(RT, 900°C) absorbance peak of Mn was at 312,505 nm before degradation and at 327,531 nm after degradation indicating it degraded the dye as no peak of dye was observed compared to $CaCO_3$(RT, 900°C),Cr^{+6}-$CaCO_3$ (RT,900°C) shown in figure 12 and scheme 1.



Scheme 1: Adsorption and photocatalytic degradation of dye under sunlight using $CaCO_3$(900°C),Cr^{+6}-$CaCO_3$(900°C) , Mn^{+7}- $CaCO_3$(900°C).

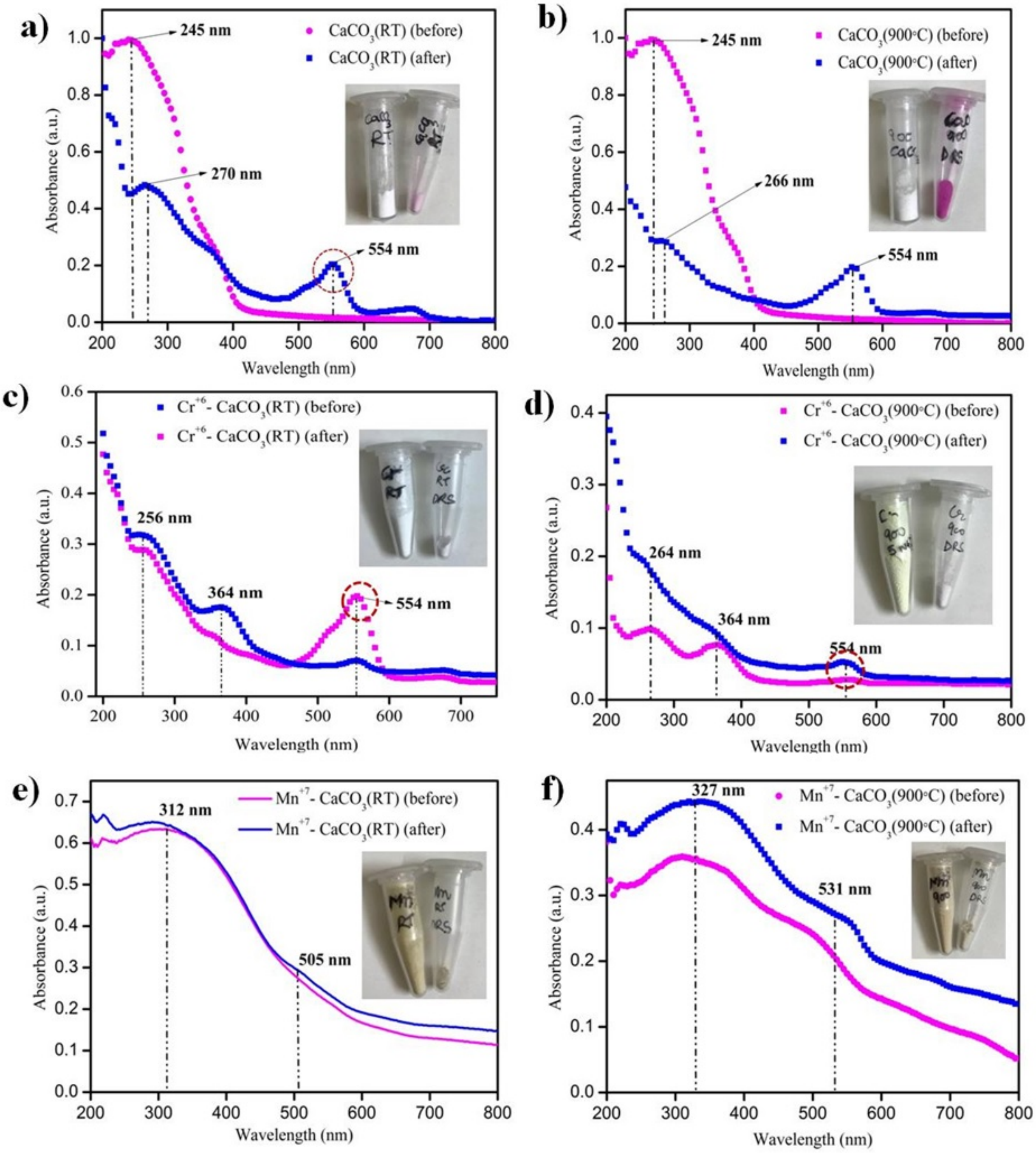


Figure 12: Diffuse reflectance spectroscopy (DRS) spectra before and after dye degradation for a)$CaCO_3$(RT), b) $CaCO_3$(900°C), c) Cr^{+6}- $CaCO_3$(RT), d) Cr^{+6}- $CaCO_3$(900°C), e) Mn^{+7}- $CaCO_3$(RT), f) Mn^{+7}- $CaCO_3$(900°C).

Comparative study

The rate constants were studied with different catalysts of RT, 900°C shown in figure 13. It was found out that Mn^{+7}-$CaCO_3$ (900°C) has maximum rate constant compared to other catalysts. It could be due to its high electron affinity which does not adsorb dye on its surface and reduce into small non harmful molecules as shown in scheme 1.

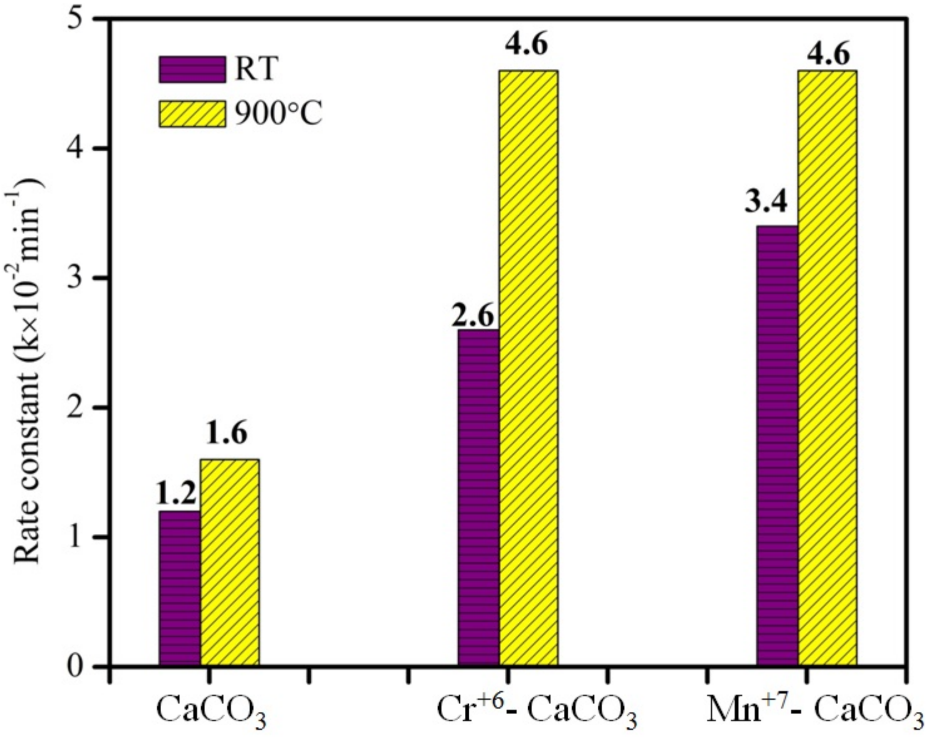


Figure 13: Comparative study of rate constant Vs different catalysts $CaCO_3$, Cr^{+6}-$CaCO_3$, Mn^{+7}-$CaCO_3$ at different temperatures (RT, 900°C).

5. CONCLUSION

In summary, $CaCO_3$ was extracted from tap water and calcined at 900°C. Cr^{+6} and Mn^{+7} were impregnated over $CaCO_3$ of room temperature and 900°C and its adsorption and photocatalytic properties were studied and compared with bare $CaCO_3$. The prepared catalysts were characterized using various techniques like DLS, XRD, DRS, SEM and UV-Vis spectrophotometer. It was found out that on loading $CaCO_3$ (900°C) with Mn^{+7}, the photocatalytic activity was increased. This method was useful as $CaCO_3$ obtained is cost effective, environmental friendly, non- hazardous in nature and photo degradation was done in sunlight, a natural source of light. In future, $CaCO_3$ can be impregnated with different metal ions at different temperatures and its photocatalytic activity can be used for degradation of various dyes.

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