

## **SUPPORTING INFORMATION**

# Surface engineered zeolite: An active interface for rapid adsorption and degradation of toxic contaminants in water

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**S 1:** It gives the Raman spectra of the Ze/ZnO CSPs. The peak at  $432\text{ cm}^{-1}$  correspond to the typical ZnO band edge. The small intensity peak at  $581\text{ cm}^{-1}$  is found in ZnO:N doped materials. Other peaks at  $508\text{ cm}^{-1}$ ,  $645\text{ cm}^{-1}$ ,  $854\text{ cm}^{-1}$  may be considered as local vibrational peaks of Raman and their intensities are related to the concentration of the nitrogen in the Ze/ZnO CSPs.

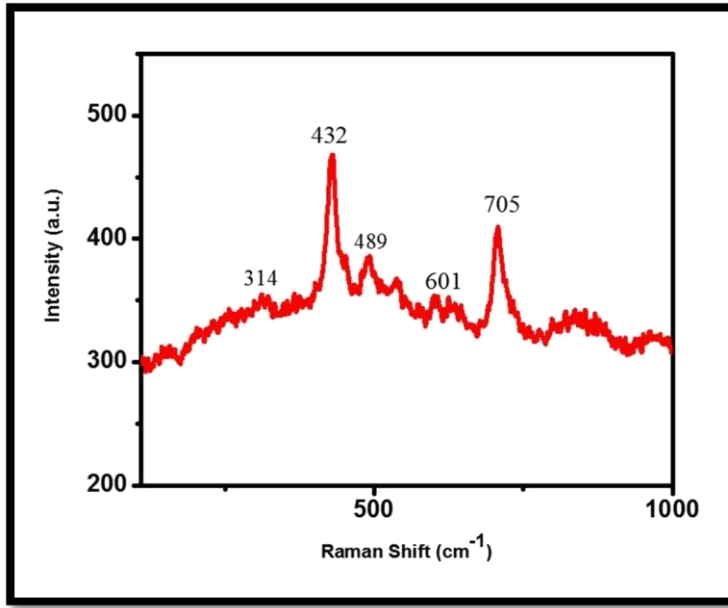


Figure S 1. Raman spectra of the Ze/ZnO CSPs

**S 2:** It gives the compositional analysis of the Ze/ZnO CSPs as compared to the pristine zeolite. The compositions of the materials has been studied using EDAX and ICP methods. It has been confirmed using both the studies that no traces of ZnO are present in the pristine zeolite (CBV 500).

Element	EDAX				ICP	
	Zeolite		Ze/ZnO CSPs		Zeolite	Ze/ZnO CSPs
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Weight %
OK	46.94	60.59	50.40	69.60	-	-
AlK	12.85	09.83	8.13	6.66	8.84	5.33
SiK	40.22	29.57	21.67	17.05	29.97	20.28
ZnK	0.0	0.0	19.80	6.69	0	4.40

Table S 1. Elemental composition of zeolite and Ze/ZnO CSPs particles taken using EDAX and ICP analysis.

**S 3:** It gives the BET adsorption isotherm for the Ze/ZnO CSPs and the zeolite. BET analysis confirms that there has been no change in the surface adsorption characteristics of the zeolite even after the formation of the ZnO thereby inferring that the porosity of the zeolite is maintained as such in the material

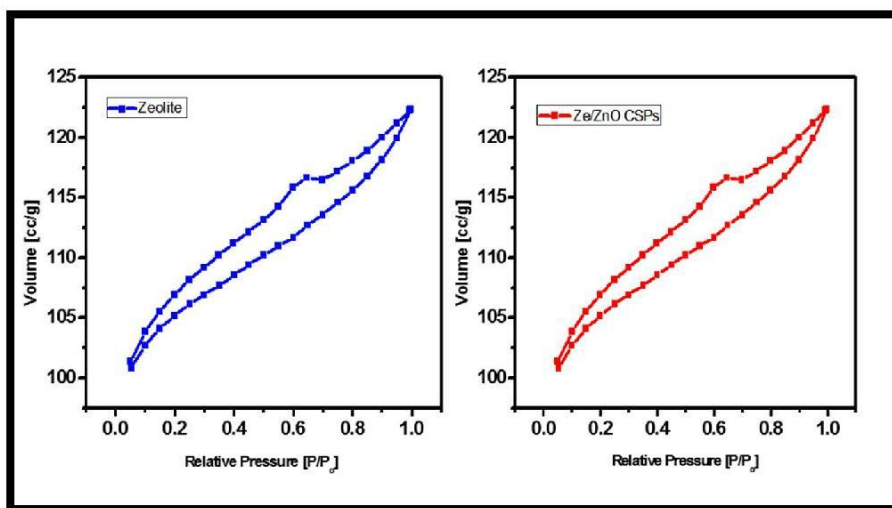
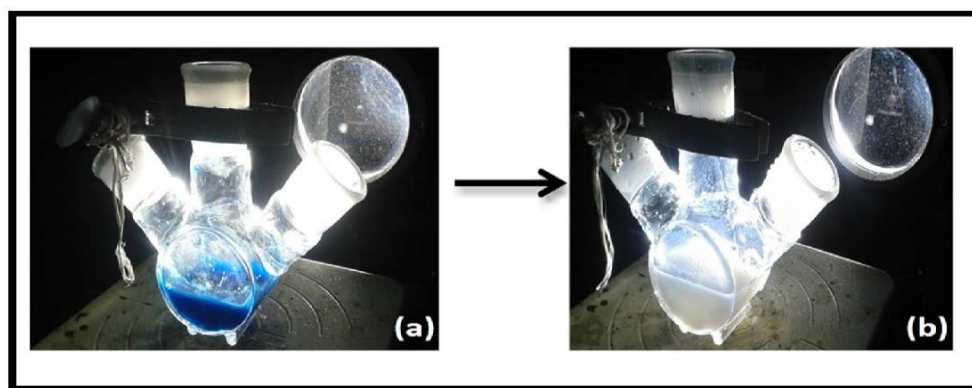


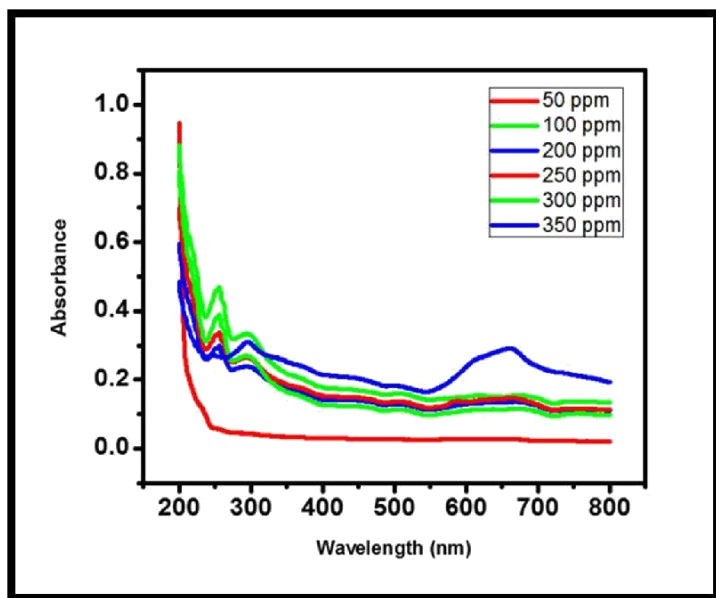
Figure S 2. BET adsorption isotherm of zeolite and ZnO CSPs

**S 4:** It describes the experimental setup used for the photodegradation process. Fig (a) shows the blue MB dye solution at the start of the process and Fig (b) marks the complete conversion of MB dye into its less harmful counterparts thereby changing the color of the solution from blue to milky white. Pure water is obtained by separating the CSPs thereafter from this solution.



**Figure S 3.** Photodegradation using solar simulator (a) before photodegradation (b) after photodegradation (75 mins)

**S 5:** It describes the UV spectra of the solutions taken after adsorption of the MB dye by the Ze/ZnO CSPs. It can be inferred from the spectra that the Ze/ZnO CSPs are able to adsorb upto 300 ppm of the dye solution after which the MB peak starts appearing.



**Figure S 4.** UV-visible spectra of the solutions after adsorption of MB dye by the Ze/ZnO CSPs.

**S 6.** It describes the length of zone of inhibition of the Ze/ZnO CSPs for E.Coli, S.Aureus and Pseudomonas.

Bacteria	Length of zone of inhibition
E.Coli	4.5 mm
S.Aureus	4 mm
Pseudomonas	4.5 mm

**Table S 2.** Length of zone of inhibition of Ze/ZnO CSPs.

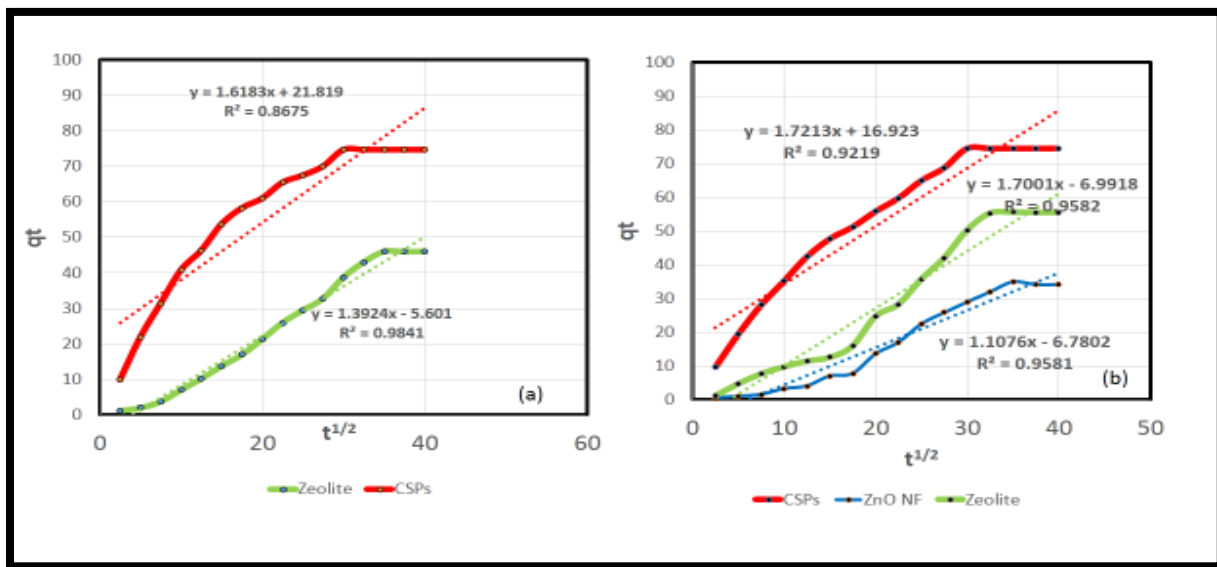
### **S 7. Diffusivity and Intra-particle diffusion model**

Adsorption kinetics is determined by four major steps which are diffusion of molecules from the bulk of the liquid towards the solid-liquid interface, thereafter diffusion inside the pores and diffusion of molecules along the surface and lastly the attainment of adsorption desorption equilibrium<sup>1</sup>. Thus, the overall adsorption process is generally controlled by one or more steps such as film diffusion, pore diffusion, surface diffusion or combination of these steps. The possibility of intra particle diffusion can be confirmed using intra-particle diffusion model. According to this model, the amount of material adsorbed at time t,  $q_t$  is:

$$Q_t = k_{id} * t^{1/2} + \Theta - (6)$$

Where  $k_{id}$  is the intra-particle diffusion rate constant ( $\text{mg}/(\text{g min}^{1/2})$ ) and  $\Theta$  ( $\text{mg/g}$ ) relates to the thickness of the boundary layer. The larger the value of  $\Theta$ , the greater is the boundary layer effect. A straight line in the plot of  $q_t$  vs.  $t^{1/2}$  suggests that the adsorption is taking place by intra-particle diffusion only whereas multiple linear plots tell that two or more steps are influencing the entire adsorption process<sup>2</sup>.

Fig S 5 (a) gives the plot of  $q_t$  vs.  $t^{1/2}$  for the adsorption of Pb (II) by the zeolite and the Ze/ZnO CSPs and Fig S 5(b) gives a plot of  $q_t$  vs.  $t^{1/2}$  for the adsorption of MB dye by the zeolite, ZnO NF and the Ze/ZnO CSPs. It is observed that in all the cases, the data plots are related by multi straight lines. The first straight line depicts the macro pore and the mesopores diffusion whereas the second straight line depicts the micropore diffusion<sup>2</sup>. Deviations from the origin as observed in the plots suggest the difference in the rate of mass transfer in the initial and the final stages of the adsorption and also that the pore diffusion is not the sole rate controlling step<sup>3</sup>. Probably, the diffusion of the ions from the adsorbent-solution interface as well as the adsorption on the available surface of the adsorbent is responsible for the overall adsorption process. The multilinearity associated with the plots indicate that initially the adsorption is governed by the film diffusion; boundary layer effect which is followed by intra-particle diffusion stage and the final uptake is governed by the pore-diffusion mechanism. The low  $R^2$  value for the plot of Ze-ZnO CSPs for Pb (II) and MB dye adsorption and intercept corresponding to the thickness of the boundary layer  $\neq 0$  also indicate that intra-particle diffusion is not the sole reason of adsorption. The slope of the plot gives the rate parameter and it was calculated to be  $1.3924 \text{ mg}/(\text{g min}^{1/2})$  for zeolite and  $1.6183 \text{ mg}/(\text{g min}^{1/2})$  for the Ze/ZnO CSPs in case of Pb (II) adsorption. For MB dye adsorption, the rate parameter was calculated to be  $0.9582 \text{ mg}/(\text{g min}^{1/2})$  for zeolite,  $0.9581 \text{ mg}/(\text{g min}^{1/2})$  for ZnO NF and  $0.9219 \text{ mg}/(\text{g min}^{1/2})$  for CSPs. It is the characteristic of the region where the intra particle diffusion is the rate controlling step. Thus it can be inferred that the adsorbent CSP follows both the diffusion as well as the adsorption of the analyte from the solution.



**Figure S 5.** Intra-particle diffusion plot for (a) for Pb (II) adsorption (b) for MB dye adsorption

## S 8. Possible mechanism for effective dye degradation

Adsorption is a pre-requisite for efficient photodegradation of dyes. Methylene blue dye having general formula  $(C_{16}H_{18}N_3S)^+Cl^-$  consists of a positive phenothiazine part which dissociates from the negative chloride ion in water in order to dissolve. Moreover, the surface of the Ze-ZnO CSPs is negatively charged with a zeta potential of -7. The negative surface charge attracts the positive phenothiazine part of the MB molecule. Because of organophilic nature of Zeolite, the aromatic MB molecules diffuse through the porous structure of the CSPs and adsorb on the surface of the zeolite. The synergy of zeolite core and ZnO shell play a significant role in enhanced adsorption of the MB dye. The adsorbed dye lies at the interface of core and shell. The lifetime decay data of the Ze-ZnO CSPs and the pure ZnO nanoflakes shows that the average lifetime of the CSPs to be 3.920 ns which is higher than that of the ZnO nanoflakes (0.1657 ns). The close proximity of adsorbed dye and enhanced life time of CSPs ensures high rate of decomposition of dye.

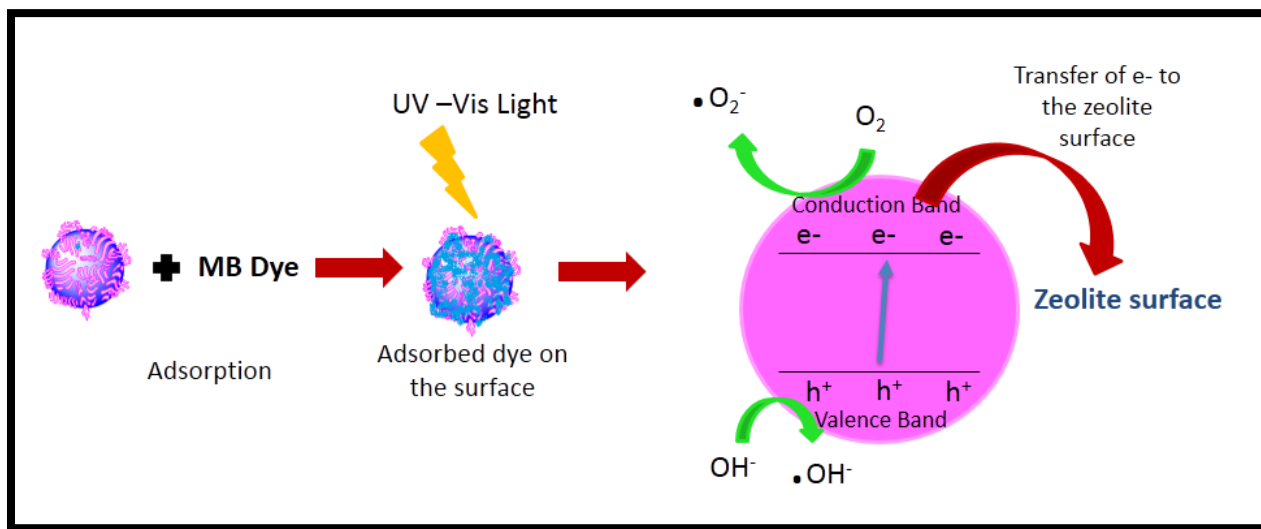


Fig S 6 Proposed mechanism for the photodegradation of the MB dye by the Ze/ZnO CSPs

## S 9. Mechanism of the anti-bacterial activity of the synthesized material.

Nano ZnO particles are reported for anti-bacterial activity<sup>12,13</sup>. The interaction of the ZnO nanoflakes with the cell membrane causes damage to the cell resulting in leakage of the bacterial cell components. Release of  $Zn^{2+}$  ions and production of highly reactive oxygen species such as  $H_2O_2$  oxidizes the cell components resulting in permanent damage to cells.

### S.10 Error analysis

Graphs with the error bars are attached below. These are also included in the supplementary information file. The standard deviation method was used for calculating the data error and the corresponding standard deviation values have been given in Table 5.

I. Error bar shown for Fig 4(a)  $t$  vs.  $q_t$  for Pb (II) adsorption by the zeolite and the CSPs

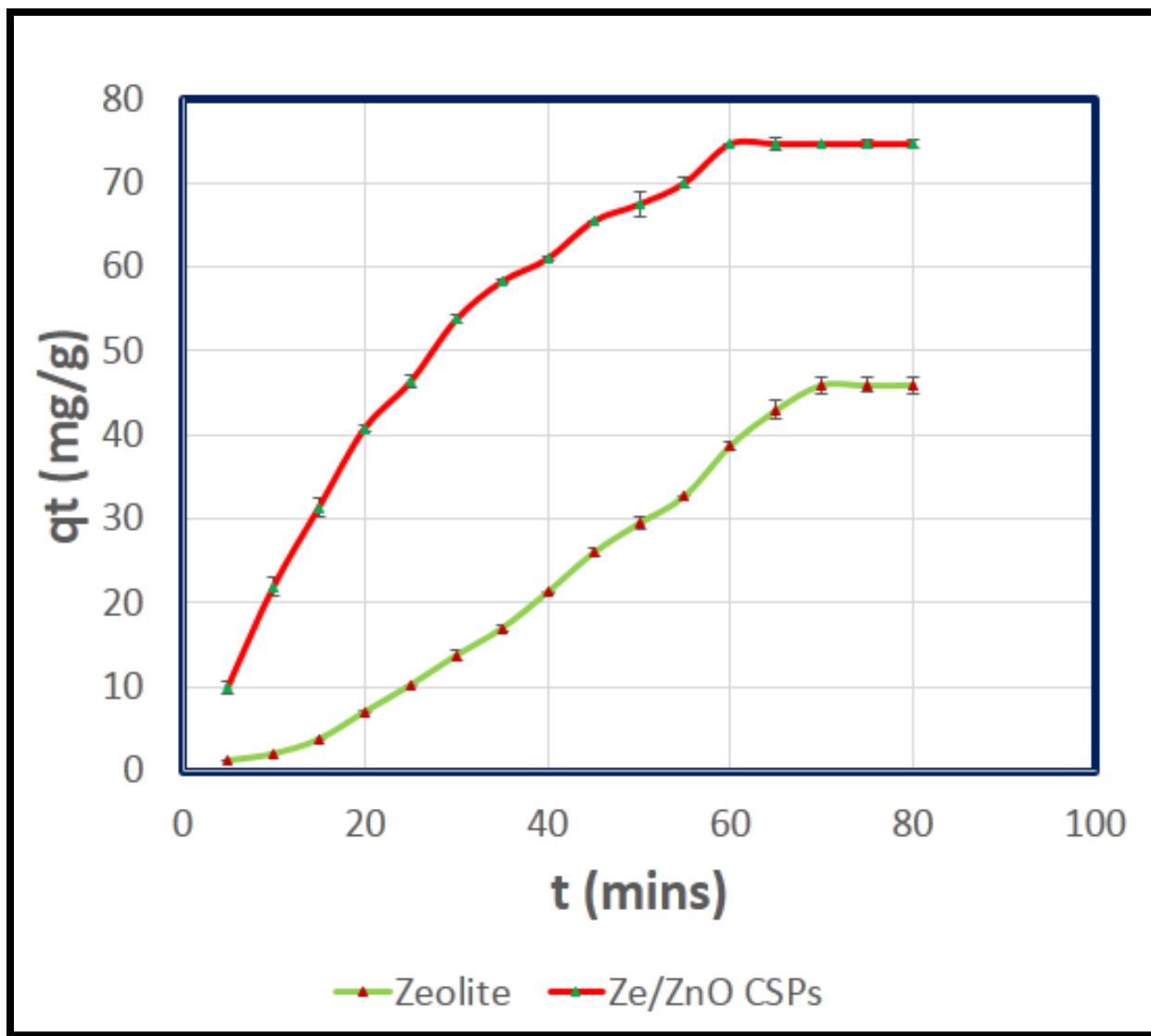


Fig 4 (a) in the main manuscript

<b>Ze/ZnO CSPs</b>		<b>Zeolite</b>	
Mean Qt value	Standard Deviation	Mean Qt Value	Standard Deviation
9.898	0.085	1.208	0.716
21.854	0.051	1.997	1.125
31.368	0.021	3.747	1.196
40.77	0.0583	7.019	0.328
46.3125	0.0112	10.2005	0.678
53.719	0.535	13.733	0.525
58.249	0.407	16.957	0.231
60.97	0.1344	21.268	0.156
65.421	0.519	25.945	0.056
67.452	0.763	29.457	1.591
70	0.0288	32.747	0.65
74.661	0.528	38.722	0.005
74.662	1.092	42.967	0.806
74.661	1	45.96	0.014
74.663	0.907	45.918	0.416
74.662	1.001	45.968	0.504

II. Error bar shown for Fig 5 (a) Ce vs. qe for Pb (II) adsorption by the zeolite and the CSPs

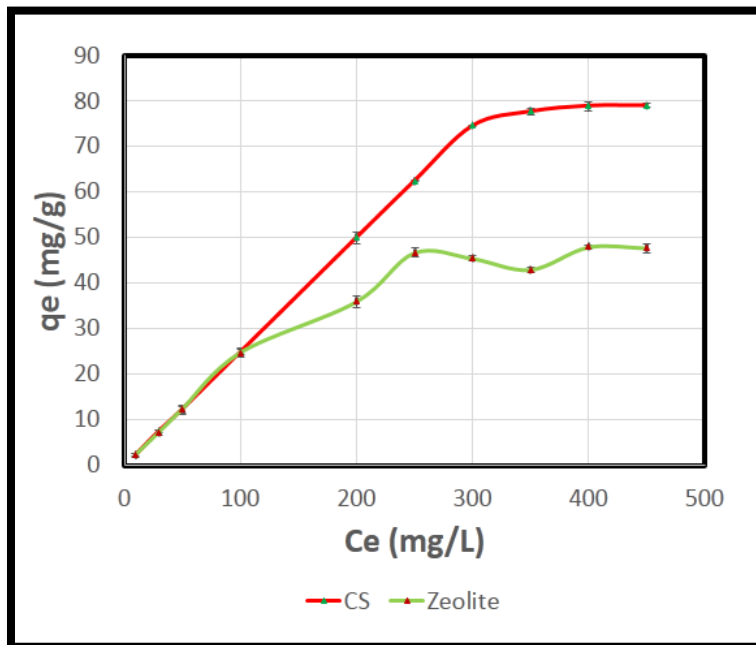


Fig 5 (a) in the main manuscript



<b>Ze/ZnO CSPs</b>		<b>Zeolite</b>	
Mean Qe value	Standard Deviation	Mean Qe Value	Standard Deviation
2.267	0.367	2.254	0.446
7.49	0.359	7.182	0.577
12.252	0.755	12.253	1.047
24.82	0.523	24.724	0.928
49.956	1.389	35.929	1.197
62.42	0.196	46.71	1.042
74.525	0.1504	45.457	0.659
77.67	0.628	42.99	0.5216
78.92	0.9937	47.973	0.5104
79.005	0.3919	47.752	1.0176

III. Error bar shown for Fig 6 (a) ; t vs. qt for the adsorption of MB dye by the zeolite, ZnO NF and the Ze/ZnO CSPs

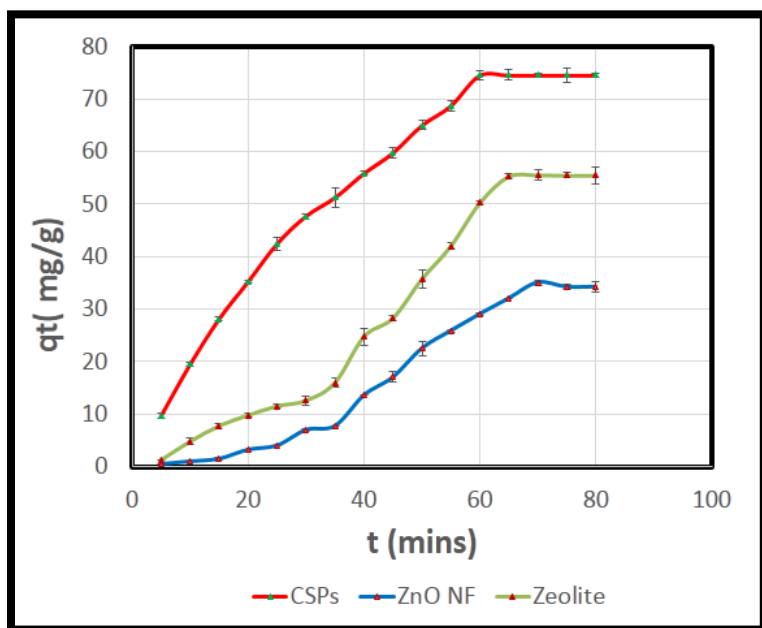


Fig 6 (a) in the main manuscript

Ze/ZnO CSPs		Zeolite		ZnO NF	
Mean Qt value	Standard Deviation	Mean Qt Value	Standard Deviation	Mean Qt Value	Standard Deviation
9.722	0.5144	1.2177	0.0616	0.47	0.0062
19.509	0.4251	4.762	0.6102	0.97	0.0086
28.14	0.4134	7.712	0.5206	1.474	0.1527
35.222	0.1786	9.749	0.3891	3.209	0.08775
42.46	1.2297	11.484	0.4194	3.999	0.0557
47.718	0.4916	12.545	0.83	6.969	0.1674
51.249	1.8604	15.012	0.8419	7.724	0.0585
55.855	0.4254	24.745	1.5942	13.57	0.0363
59.76	1.01	28.27	0.603	16.997	0.9992
64.999	0.8471	35.72	1.724	22.467	1.299
68.721	1.01	41.999	0.685	25.842	0.2992
74.532	0.956	50.219	0.3395	29.017	0.2644
74.531	0.9994	55.27	0.5412	31.993	0.10622
74.531	0.3059	55.547	0.9712	35.018	0.4627
74.531	1.303	55.477	0.5482	34.184	0.5063
74.532	0.4317	55.47	1.563	34.201	0.9644

IV. Error bar shown for the Fig 7 (a) ;  $C_e$  vs.  $q_e$  for the adsorption of MB dye by the zeolite, ZnO NF and the Ze/ZnO CSPs

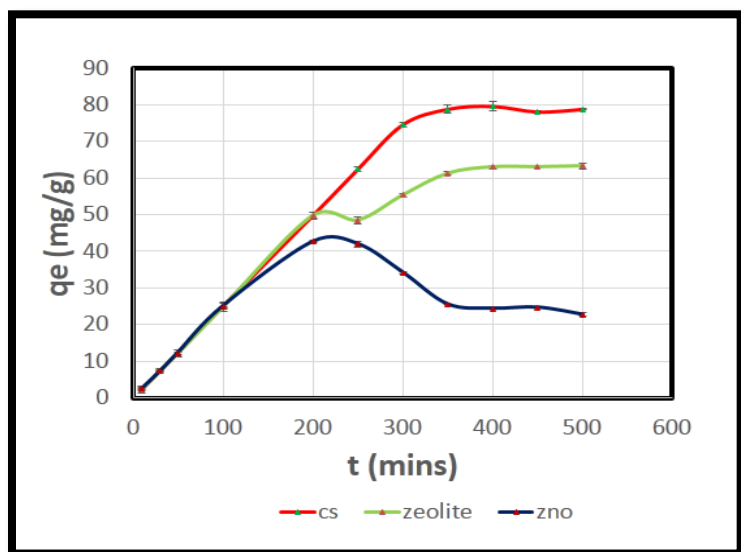


Fig 7 (a) in the main manuscript

Ze/ZnO CSPs		Zeolite		ZnO NF	
Mean Qe value	Standard Deviation	Mean Qe Value	Standard Deviation	Mean Qe Value	Standard Deviation
2.309	0.891	2.343	0.5151	2.471	0.0925
7.2815	0.1919	7.351	0.1504	7.179	0.6265
12.253	0.9584	12.185	0.276	12.253	0.951
24.952	0.7507	24.774	0.1107	24.979	1.2826
49.707	0.7901	49.701	1.0238	42.547	0.312
62.317	0.6517	48.445	0.9908	41.968	0.8312
74.53	0.5986	55.27	0.4417	34.184	0.3318
78.78	1.2237	61.195	0.4986	25.497	0.1302
79.567	1.3299	62.951	0.4229	24.347	0.1402
78.042	0.4292	62.99	0.1865	24.647	0.0984
78.76	0.109	63.223	0.6995	22.685	0.5501

V. Error bar shown for % photodegradation of MB dye by the Ze/ZnO CSPs

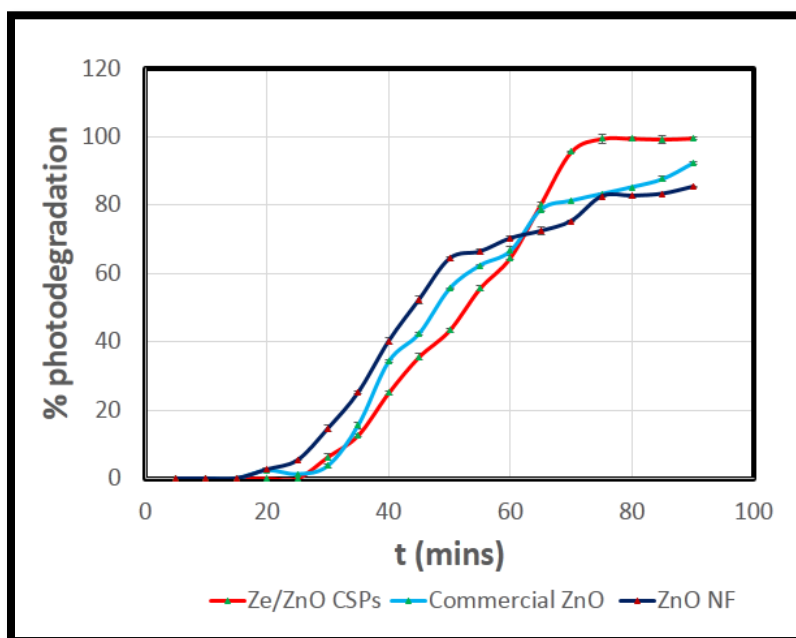


Fig 9 in the main manuscript

Ze/ZnO CSPs		Commercial ZnO		ZnO NF	
% photodegradation	Standard Deviation	% photodegradation	Standard Deviation	% photodegradation	Standard Deviation
0	0	0	0	0	0
0	0.0005	0	0.0003	0	0
0	0.0005	0		0.05	0.0374
0	0	2.36	0.5985	2.654	0.3985
1.00E-03	6.00E-04	1.238	0.36	5.328	0.0802
6.28	0.9248	3.687	0.6909	14.602	0.9184
12.625	0.4169	15.569	1.0233	25.215	0.2937
25.025	0.643	34.215	0.3143	40.201	1.0834
35.56	1.02	42.365	0.3863	52.364	1.0992
43.32	0.5004	55.521	0.336	64.325	0.6002
55.59	0.6871	62.312	0.1356	66.3654	0.8655
64.64	0.5382	66.556	1.147	70.254	0.6022
80.28	0.5889	78.659	0.3491	72.365	1.1795
95.62	0.0951	81.248	0.1131	75.321	0.1601
99.39	1.2143	83.234	0.2703	82.548	0.2772
99.46	0.5825	85.234	0.3005	82.654	0.4803
99.23	1.1172	87.569	0.796	83.265	0.2138
99.53	0.2446	92.238	0.3609	85.325	0.2354

#### VI. Error bar shown for the recyclability of the CSPs

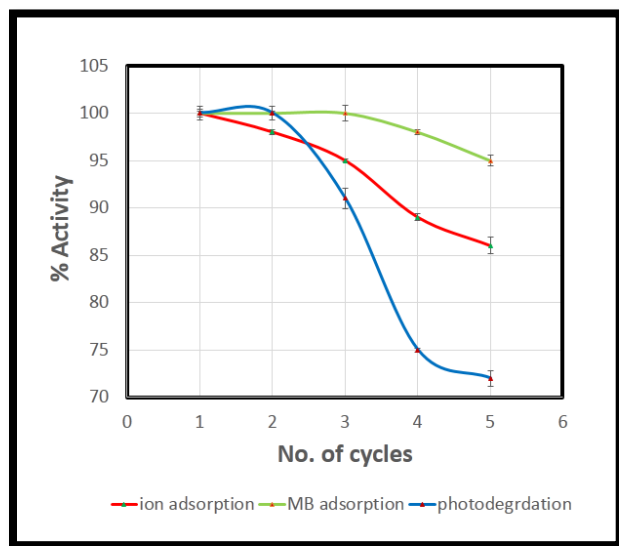


Fig 10 in main manuscript

Ion Adsorption		MB Adsorption		Photodegradation	
% Activity	Standard Deviation	% Activity	Standard Deviation	% Activity	Standard Deviation
100	0.4405	100	0.6975	100	0.1997
98	0.2416	100	0.202	100	0.6989
95	0.1883	100	0.7853	91	1.068
89	0.3465	98	0.2861	75	0.21388
86	0.8652	95	0.5511	72	0.8451

The error analysis for Table 1 could not be performed as the system for BET analysis is presently out of order and will take time to become operational.

### S 11. Studies on the change in pH of the solution after addition the adsorbents

The zeolite and the Ze-ZnO CSPs are insoluble in water and do not affect the pH of the solution. The zeolite Y (CBV 500) when dispersed in water shows a pH of 7.75. Ze-ZnO CSPs when dispersed in water gives a pH of 7.35. Solution of Pb (II) ions in water is mildly acidic in nature with a pH of 6.09. As zeolite and the CSPs do not affect the pH of the Pb(II) solution, the pH of Pb(II) sample solutions remained almost same after the addition of the adsorbent particles as indicated in table below . Also, no precipitation was observed after the addition of the adsorbents (zeolite/CSPs) into the Pb (II) solutions.

**Table S 3.**

Material	pH
Blank	7.02
Zeolite	7.75
Ze/ZnO CSPs	7.35
Pb (II) solution	6.09
Zeolite in Pb (II) solution	6.30
Ze/ZnO CSPs in Pb(II) solution	6.14

In order to study the effect of the pH on the adsorption of Pb (II) ions from water, pH variation study was conducted. The solutions were tested for adsorption by zeolite and CSPs at a wide pH range of 2-9. The pH of the test solutions were adjusted by using 0.1M HCl and 0.1M NaOH solutions. Complete adsorption of the Pb (II) ions takes place at a pH of 6.5-7.

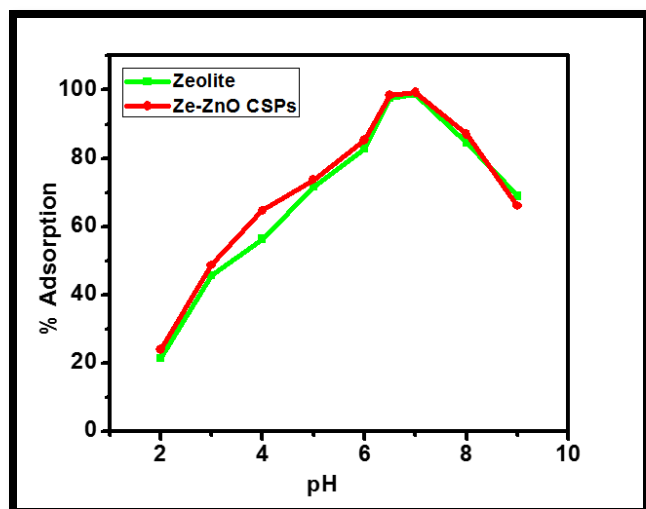


Fig S 7. pH variation plot for the adsorption of Pb(II) by the zeolite and the CSPs

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