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Research Article

A Comparative Study on the Sorption of Divalent ions by Bivalves Shells: Equilibrium and Statistical Studies

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Abstract

The present study aims at examining the potentiality of the identified no- cost sorbent i.e. Bivalves shells to remove Cu(II) and Zn(II) ions from the aqueous solutions. These shells are collected from seashores, washed with double distilled water, dried, crushed and treated using 0.1N HCl. The characteristics and functional groups present in the treated shells are supported by SEM, EDAX and Physio-chemical parameter analyses. Various operating factors influencing the adsorption of divalent ions onto the treated shells are experimentally verified by Batch Equilibration method. The experimental results derived the following optimized conditions : 0.18mm size, 1g dosage, 10 min agitation time, pH 7 environment for the trapping of Cu(II) ions (98.1% removal) and 0.18mm size, 1g dosage, 60 min agitation time, pH 5.5 environment for that of Zn(II) ions (97% removal) at an initial concentration of 1000 mg/L in both the cases. Statistical analysis using SPSS software is carried out to assess the correlation of experimental values for both the systems with the theoretical approach to justify the trapping ability of TMSP.

Keywords: bivalve shell, characterization, divalent ions, biosorption, statistical studies.

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Introduction

Utilization of heavy metals in industries viz., paints, pigments, batteries, ceramic glazes, electroplating and textiles [1], over the past few decades has led to serious environment problems on account of improper untreated disposal [2]. Copper is widely employed in mining/ metallurgical, paints, pigments and electroplating industries [3]. According to WHO standards, the permissible concentration of divalent copper in effluents and drinking water are 0.05 and 1.0 mg/L [4] respectively, beyond which it is carcinogenic and leads to several ailments viz., gastrointestinal problems, headache, fatigue, depression, skin rashes, learning disorders through the accumulation in kidneys, brain, skin, pancreas and heart [5].

Environmental Protection Agency (EPA) has declared Zn^{2+} to be one of the priority pollutant due to its nature, leading to dehydration, electrolyte imbalance, stomach ache, nausea and dizziness.

Various methods have been reported for the sorption of metal ions from aqueous solutions, the common being solvent extraction, filtration, coagulation, chemical precipitation, ion exchange, electrolysis, membrane process and adsorption. Adsorption is an effective process for the removal of heavy metal ions. Low cost materials prepared from a variety of raw materials as wood, peat and animal origin viz., chitin and chitosan have been employed in trapping toxic metal ions by many researchers [6].

The objective of the present study is to assess the adsorption capacity of Mussel shell for Cu(II) and Zn(II) ions. Mussel shell is belonging to the family bivalve molluscs from saltwater and freshwater habitats, is a waste product generated during shellfish processing.

Experimental Section

Preparation/Treatment of Adsorbent Materials

Mussel shells were collected from Sea shores, washed thoroughly with double distilled water and crushed partially using mortar and pestle. The crushed MSP were then soaked in 0.1 N HCl for 4 hours, washed with double distilled water and sun dried, thereafter referred to as TMSP. TMSP was ground well in a laboratory blender and sorted into varied particle sizes (85 BSS, 72 BSS, 52 BSS, 36BSS and 22 BSS) using standard test molecular sieves (JAYANT Scientific Instruments Co., Mumbai) and stored in air tight containers. The pictorial representations of the raw and treated MSP (85 BSS mesh size) are shown in **Figure 1.**

Figure 1

Particle Size Determination

The sieved MSP of varying mesh sizes were subjected to image microscopic analysis in order to determine the particle sizes using Binocular Microscope (OLYMPUS make, Model- CX21I). Fifteen different granular particles of each mesh size were chosen for the measurement of lengths and breadths to arrive at an average, as no two single particles are alike. By applying multiplication factors, the particle sizes were calculated. The calculated particle sizes corresponding to the mesh sizes of 85 BSS, 72 BSS, 52 BSS, 36 BSS and 22 BSS are 0.18 mm, 0.21 mm, 0.30 mm, 0.42 mm and 0.71 mm respectively. The microscopic structure of treated MSP (0.18mm particle size) is depicted in **Figure 2**.

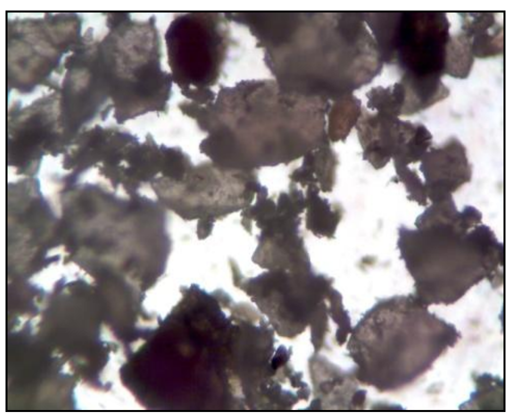

Figure 2

Physio- Chemical and Surface Characterizations (TMSP)

The physio chemical characteristic studies viz., pH (*DELUXE pH Meter (LABTRONICS*), Conductivity (*ELICO (CM 180) Digital Conductivity Meter*), Moisture content, (Xylene-extraction test method (ASTM D 2867-95), Bulk density, Specific gravity, Porosity and ash content were determined. The surface area and volume of the pores were obtained by N_2 physisorption at 77 K. These analyses were performed with a Micromeritics *BEL, Japan, Inc* Surface Area Analyzer using the BET method. The surface morphology was analyzed using Scanning Electron Microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDAX) (*JEOL JFM- 6390*).

Choice of Metal ions

The heavy metals of interest investigated for the present study include: Copper [Cu(II)] and Zinc [Zn(II)]. The choice of heavy metals was decided based on the literature collection conducted where the prevalence of these metals were observed in the effluents discharged from various electroplating industries in and around Coimbatore.

Batch Mode Adsorption Studies

The agitation of Cu(II) and Zn(II) ions with TMSP in a mechanical shaker (KEMI- KR3-1) was experimentally verified to define the role of variable parameters viz., particle sizes (0.71 mm, 0.42 mm, 0.30 mm, 0.21 mm and 0.18 mm), dosages of TMSP (200 mg, 300 mg, 400 mg and 500 mg), initial concentrations of the aqueous Cu(II) and Zn(II) solutions (100-1000 ppm: 100 ppm interval), agitation time intervals between the sorbate and sorbent species (30 min, 60 min, 120 min), pH environments (3, 5, 7, 9 and 11) and temperatures of the system (293- 333 K: 10 K interval) to optimize the conditions for the systems ensuring maximum sorption.
Duplicate experiments were conducted to ensure the reproducibility of values within ± 2%. The initial and residual concentrations of corresponding metal ions were analyzed using Atomic Absorption Spectrophotometer: *Shimadzu (AA 6200) Model*

Data Evaluation

The percentage of adsorption of metal ions from aqueous solutions was estimated by using the following equation [7].

$$\%\ \text{adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

The amounts of metal ions removed by adsorbent (q) were calculated using the mass balance

$$q = \frac{V(C_i - C_e)}{W} \qquad (2)$$

where, V is the volume of the solution (L), W is the mass of the adsorbent (g), C_i and C_e are the initial and equilibrium metal concentrations (mg/L) respectively.

Statistical Analysis

The relationship between adsorbed Cu(II) and Zn(II) ions and variable parameters was correlated using Pearson Moment Coefficient Method. The extent of statistical fit was verified using SPSS 20 software, the output variable being ANOVA, Pearson Correlation and descriptive analysis with a significance based on 95% confident level.

Results and Discussions

Surface Characterization

The sorption activity of any sorbent mainly depends on its chemical nature and pore structure. **Table 1** shows the various physiochemical properties of TMSP. The ash content of TMSP exhibits very less value, indicative of the least presence of inorganic matter and high quantity of carbon content (≈ 45%). The specific gravity of TMSP (1.86) is the ratio of the masses of equal volumes of biomass and distilled water. The lower bulk density (1.67) against the standard value of 2.20 shows that TMSP has a large number of pores, which are more suitable for adsorption. Since, the high pore size has a greater potential to store/ adsorb particles. The presence of water vapours considerably inhibits the sorption activity, wherein the calculated Moisture content for TMSP being 7.24%. The surface area of TMSP is 1.52 m^2/g, indicates that the extent of surface occupancy by adsorbate has a decisive influence upon the removal efficiency of TMSP. The porosity and mean pore diameter values implies that TMSP is mesoporous in nature [8].

Table 1 Physicochemical Characteristics of the Adsorbent.

Factors	Values
pH of 1 % solution	10.87
Conductivity	39.23
Moisture (%)	7.24
Bulk density (g/L)	1.67
Specific gravity	1.86
Porosity	10.22
Ash content (%)	4.3
Surface area (m^2/g)	1.52
Mean Pore diameter (A^0)	240
Carbon (%)	43.69
Nitrogen (%)	2.17
Hydrogen (%)	5.50
Sulphur (%)	-

SEM Analysis

The surface morphologies of the unloaded, Cu(II) / Zn(II) loaded TMSP are depicted in **Figures 3 (a-c)**. Figure 3a represents a highly porous nature of the unloaded TMSP surface with coarse textured pores of different shapes. The smooth covered pores on the surfaces after Cu(II) and Zn(II) sorptions as observed in Figure 3b and 3c respectively indicate the binding of the respective ions onto the surface active sites of TMSP, where the decline of ruggedness is visible. This can be evidenced from the presence of surface pores only in Figure 3a, not distinct in Figure 3b and 3c.

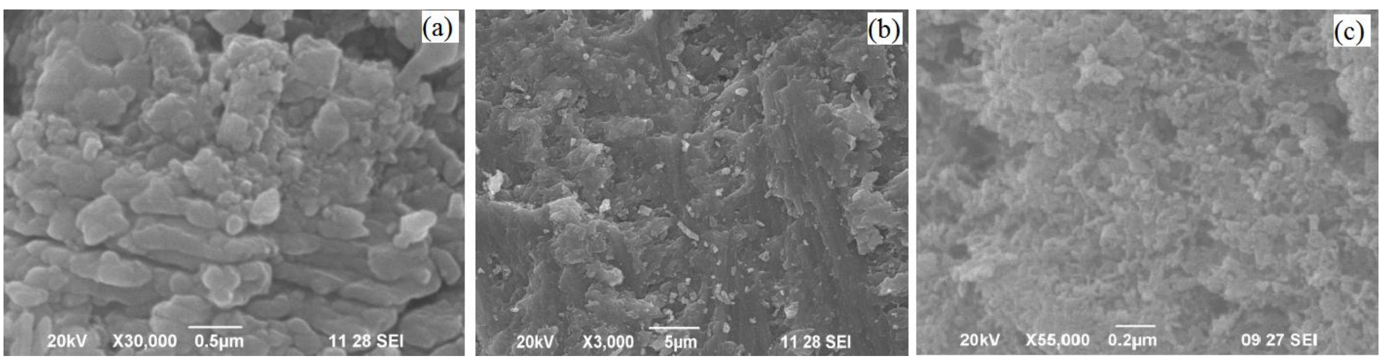

Figure 3 (a) Unloaded TMSP (b) Cu(II) loaded TMSP (c) Zn(II) loaded TMSP.

EDAX Analysis

The EDAX spectra were recorded to analyze the elemental constitution of TMSP qualitatively. The spectra of TMSP before and after adsorption are depicted in **Figures 4(a –c)** indicative of the presence of O, C, Ca and Cl, being reported as the principle elements of any adsorbent [9]. The appearance of new peaks at an energy range of 8-10 KeV (Figure 4b and 4a), confirms the Cu(II) and Zn(II) adsorption onto TMSP.

Effect of Particle Size

Figure 5 illustrates the adsorption of Cu(II) and Zn(II) onto TMSP under studied particle sizes. The smooth and steep declining of the curves indicate a systematic trend followed in the adsorption pattern, supported by the corresponding values given in **Table 2**. It is understood from the table that as the particle size increased from 0.18 mm to 0.71 mm, the amount of divalent ions adsorbed declined in both the cases. It shall be justified that the increase in sorption may depend on the large external surface area for smaller particle sizes [10]. Since 0.18 mm exhibited maximum amounts adsorbed of 86.09 mg/g and 83.76 mg/g for Cu(II) and Zn(II) ions respectively, this size (0.18 mm) is fixed as the optimized size for further experiments. The P-values of Cu(II)- 0.0137 and Zn(II)- 0.0260 at 95% confident level ($P<0.05$) emphasizes statistically that there is significant correlation in adsorption pattern. The negative correlation values of Cu(II)- r = -0.8624 and Zn(II)- r = -0.7395 observed between the particle sizes and amounts adsorbed confirms the decreased adsorption capacity as the sizes of the particles were increased.

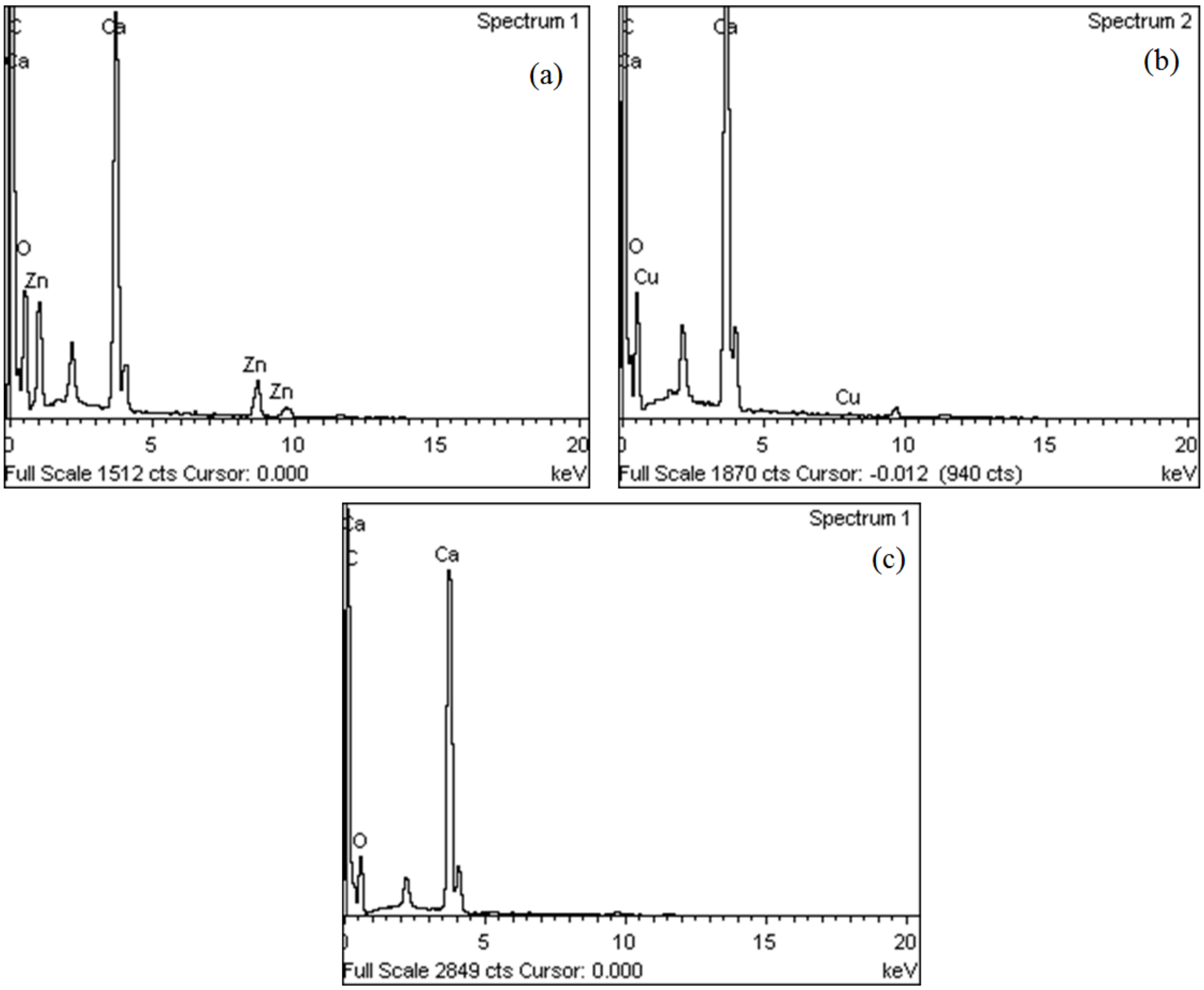

Figure 4 (a) Zn(II) loaded TMSP, (b) Cu(II) loaded TMSP, (c) Unloaded TMSP.

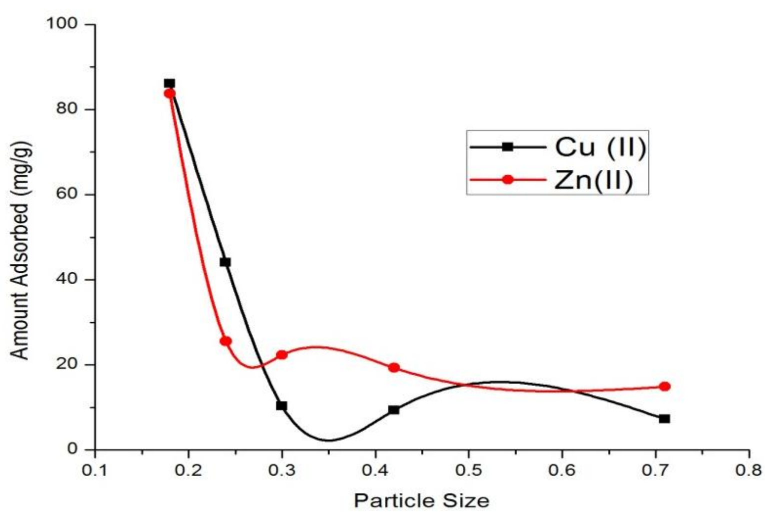

Figure 5 Effect of particle size.

Table 2 Effect of particle size.

S.No	Particle Size	Amount adsorbed mg/g	
		Cu(II)	Zn(II)
1	0.18mm	86.09	83.76
2	0.24mm	44.09	25.52
3	0.30mm	10.29	22.29
4	0.42mm	9.32	19.32
5	0.71mm	7.26	14.87

Effect of Dosage

The results for the influence of varied doses on the divalent ions – TMSP systems are presented in **Table 3** and depicted in **Figure 6**. The data revealed that a steady increase in the amounts of Cu(II) and Zn(II) adsorption upto 1000 mg dosage, beyond which a slight decline in the removal was registered [11]. This is obvious from the curve patterns henceforth, 1000 mg is fixed for further experiments. The P-values of Cu(II) = 0.0455 and Zn(II) = 0.02605 at 95% confident level ($P<0.05$) indicates statistically that there is extremely significant correlation in adsorption pattern. The positive correlation coefficients (for Cu(II)- r = 0.8858 and Zn(II)- r = 0.9942) indicating that the dosages and the amounts adsorbed are directly proportional to each other.

Table 3 Effect of Dosage.

S.No	Dosages	Amount adsorbed mg/g	
		Cu(II)-TMSP	Zn(II)-TMSP
1	100 mg	44.09	38.65
2	200 mg	38.83	46.87
3	300 mg	36.23	52.87
4	500 mg	41. 23	61.87
5	1000 mg	86.09	83.76
6	1500 mg	81.87	76.54
7	2000 mg	74.08	71.17

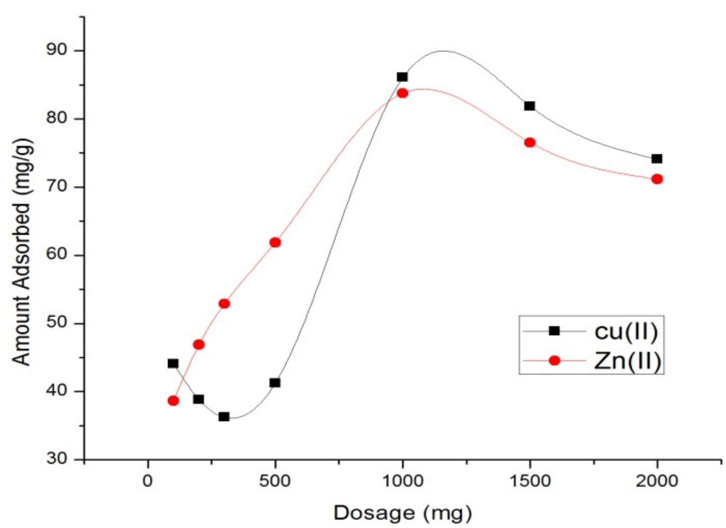

Figure 6 Effect of Dosage.

Effect of Initial Concentration and Contact Time

The data pertaining to the influence of the chosen material upon different initial concentrations agitated at predetermined time intervals is listed in **Table 4**. In the case of Cu(II) system, a contact time of 10 mins itself was found to be sufficient for adsorbing a maximum of 86.09 mg/g, but a contact time of 60 mins was observed for a maximum 83.76 mg/g amount of Zn(II) being adsorbed after the conductance of series of pilot studies. This can be due to Zn(II) ions produce net positive charge in the solution, therefore would make it difficult for negative electrons to dissociate, while comparing with Cu(II) ions [12]. A further increase in the contact time had resulted in a dip for all the concentrations of [Cu(II) and Zn(II)], as it is obvious from the curve pattern (**Figure 7**). This decrease can probably be due to the slow pore diffusion of the solute ion into the bulk of the adsorbent [13].

Table 4 Effect of Initial Concentration and Contact Time

	Time (min)	Amount Adsorbed (mg/g)				
		100ppm	**250ppm**	**500ppm**	**750ppm**	**1000ppm**
	10	20.19	35.05	43.06	54.09	86.09
Cu(II)-TMSP	20	9.82	24.75	32.87	42.99	78.28
	30	9.41	14.79	22.64	32.99	43.43
	30	45.87	17.98	41.98	60.98	64.87
Zn(II)-TMSP	60	56.81	25.87	52.98	70.87	83.76
	90	46.87	15.87	41.87	61.87	46.87

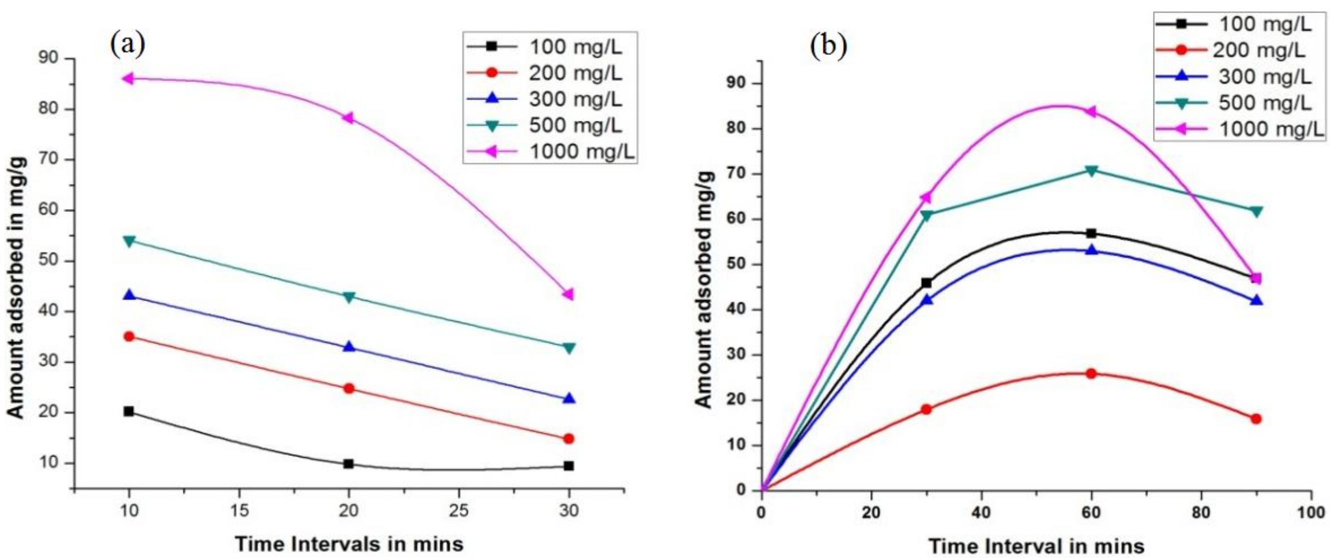

Figure 7 Effect of Initial Concentration and Contact Time (a) [Cu(II)], (b) [Zn(II)] .

Effect of pH

The pH dependence of Cu(II) and Zn(II) biosorption under so far optimized conditions is represented as bar chart (**Figure 8**). The reduction in the amounts of the adsorbed divalent ions can be attributed to the fact that the precipitation of ions as hydroxide ions might occur in alkaline solutions. Also, the lower q_e values observed in acidic conditions indicate the competence between the proton (H^+) and metal ions (Cu(II) and Zn(II)) to get sorbed on the surface [12] of TMSP. The calculated P-value (Cu(II) = 0.0387 and Zn(II) = 0.0455) at 95% confident level ($P<0.05$) statistically prove that there is significant correlation in adsorption pattern. From the observation, it is obvious that pH 7 and 5.5 recorded higher q_e values, thereby maintained in all further experiments.

Descriptive statistics are a set of brief descriptive coefficients that summarizes a given data set, which can either be a representation of the entire experimental work (**Tables 5** and **6**). The observed significant relationship between the parameters and the amounts of Cu(II) and Zn(II) adsorbed were substantiated by performing Pearson Correlation Analysis, indicated in **Tables 7** and **8**. The prediction of its relationship for both the ions with TMSP is verified through statistical analysis which can be a strong tool for monitoring heavy metal pollution.

Comparison of Preferential order of adsorption

The order of preferential adsorption of metal ions onto TMSP was found to be Cu(II)>Zn(II). The relative abilities of the solute- ion species to compete for surface sites of the sorbents are governed by intrinsic factors such as valence, ionic radius, pH, and the solution activities [14]. Both the employed ions being divalent in nature, the selectivity depends entirely on their hydrated ionic radii. Smaller the size of the ion, greater is the degree of hydration. Thus, for ions of similar charge, hydrated ionic radii determine the order of preference of adsorption. Cu(II) being smaller in size than Zn(II), its hydrated ionic radius is smaller (0.419 nm) than Zn(II) (0.430 nm) [15] leading to greater access of Cu(II) adsorption in preference to Zn(II).

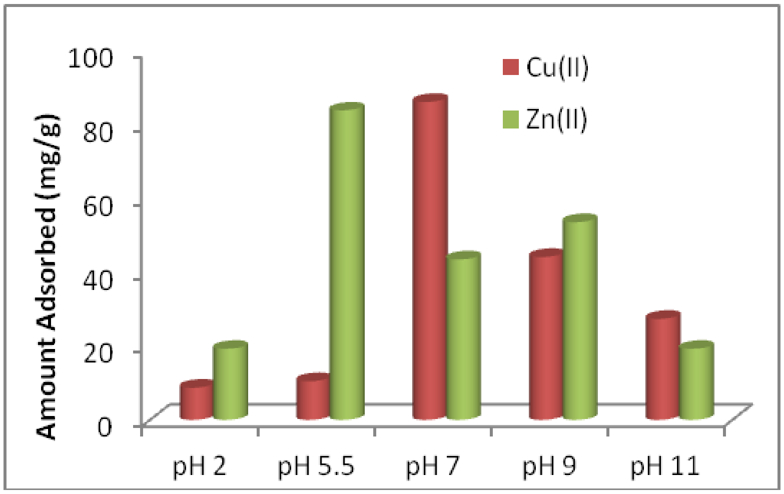

Figure 8 Effect of pH.

Table 5 Statistical Analyses [Cu(II)].

Descriptive	Parameters (Amount adsorbed in mg/g)			
	Particle Size	**Dosage**	**Initial Con.**	**pH**
Mean	37.448	55.4	42.43	71.24
SD	36.235	16. 92	31.69	20.99
Maximum	86.09	73.56	73.64	88.1
Minimum	9.325	28.15	13.45	57.3
Degrees of freedom	3	4	4	3
Sum of Squares	1006.5	12.788	558.61	812.1
Mean Square	503.25	4.156	292.87	706.07
Variance	948.38	269	350.26	110.84
Range	64.44	41.16	30.19	20.8

Table 6 Statistical Analyses [Zn(II)].

Descriptive	Parameters (Amount adsorbed in mg/g)			
	Particle Size	**Dosage**	**Initial Con.**	**pH**
Mean	37.72	56.8	52.43	81.24
SD	30.79	17.29	21.69	10.99
Maximum	83.76	83.76	83.64	98.1
Minimum	19.32	38.65	33.45	67.3
Degrees of freedom	3	4	4	3
Sum of Squares	1289.3	13.788	758.61	1812.1
Mean Square	644.66	4.596	252.87	906.07
Variance	948.38	299	470.26	120.84
Range	64.44	45.11	50.19	30.8

Table 7 Pearson correlation among selected parameters and amount of Cu(II) ion adsorbed.

	Particle size	Dosage	pH	Temperature
Pearson correlation	-0.739	0.994**	0.094	0.146
Sig. (2 tailed)	0.261	0.001	0.906	0.815
N	4	5	4	5

Table 8 Pearson correlation among selected parameters and amount of Zn(II) ion adsorbed.

	Particle size	Dosage	pH	Temperature
Pearson correlation	-0.786	0.984**	0.091	0.134
Sig. (2 tailed)	0.224	0.001	0.916	0.892
N	4	5	4	5

**Correlation is significant at the 0.01 level (2-tailed).

Conclusion

The selected animal waste (Mussel shells) was powdered and modified using 0.1 N HCl (TMSP) for trapping Cu(II) and Zn(II) ions. The physio chemical characteristic studies viz., pH, conductivity, moisture content, bulk density, specific gravity, porosity, ash content and elements (C,H,N,S) were determined for the prepared TMSP. The surface morphological changes, elemental constitutions and surface area of TMSP as observed from using SEM, EDAX and BET analysis respectively for unloaded / loaded material, registered a significant changes in porosity structure (SEM) and the appearance of Cu(II) and Zn(II) peaks in the EDAX images supporting the adsorption positively. The Batch equilibration conditions for maximum percentage removal (98.1%) of Cu(II)- TMSP system was optimized at: 0.18mm particle size, 1000 mg dosage, 10 minutes agitation time, 1000 mg/L initial concentration of Cu(II) ions, pH 7 of the solution medium at 30^0C and for Zn(II)- TMSP system (97%) was optimized at: 0.18mm particle size, 1000 mg dosage, 60 minutes agitation time, 1000 mg/L initial concentration of Zn(II) ions, pH 5.5 of the solution medium at 30^0C. The statistical output data for viz., particle sizes, initial concentrations of the metal ions (Cu(II) and Zn(II)), dosages and pH of the solutions had a significant effect on Cu(II) and Zn(II) adsorption. A very good correlation between the input and output variables is observed by applying SPSS 20 software.

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