**Supporting Information**

**Kinetics, Thermodynamics and Metal Separation Studies of Transition (Co2+, Ni2+, Cu2+, Zn2+) and Heavy Metal ions (Cd2+, Hg2+, Pb2+) Using Novel Hybrid Ion Exchanger- Zirconium Amino tris methylene phosphonic acid**

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***Section-1 Table Captions***

**Table-S1**: Parameters optimized for synthesis of Zr-ATMP [Shah et al. 2012]

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Parameters | No | Mole ratio  Metal: Anion  (M) | Volume ratio  Metal: Anion  (mL) | Temperature  (ºC) | Stirring Time  (h) | Aging Time  (h) | IEC  (meq/g) |
| Concentration | 1 | 0.1-0.1 | 50 : 50 | RT | 1 hr | 1 hr | 3.19 |
|  | **2** | **0.1-0.2** | **50 : 50** | RT | **1 hr** | **1 hr** | **3.61**\**\** |
|  | 3 | 0.2-0.1 | 50 : 50 | RT | 1 hr | 1 hr | 2.68 |
| Volume | 4 | 0.1-0.2 | 50 : 100 | RT | 1 hr | 1 hr | 2.46 |
|  | 5 | 0.1-0.2 | 100 : 50 | RT | 1 hr | 1 hr | 2.24 |
| Temperature | 6 | 0.1-0.2 | 50:50 | 70 | 1 hr | 1hr | 3.19 |
| Aging Time | 7 | 0.1-0.2 | 50:50 | RT | 1 hr | 15 hr | 2.99 |
|  | 8 | 0.1-0.2 | 50:50 | RT | 1 hr | 3 hr | 2.84 |
| Stirring Time | 9 | 0.1-0.2 | 50:50 | RT | 2hr | 1 hr | 2.61 |
|  | 10 | 0.1: 0.2 | 50:50 | RT | 3 hr | 1 hr | 2.94 |
| pH=1 | 11 | 0.1: 0.2 | 50:50 | RT | 1 hr | 1hr | 3.09 |
| Mode of addition | 12 | 0.1: 0.2 | 50:50 | RT | 1 hr | 1hr | 3.12\* |

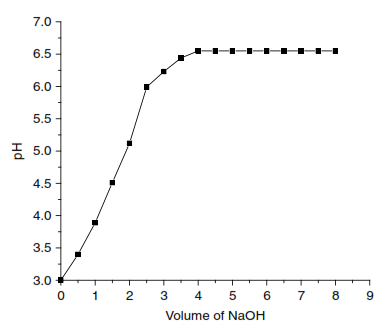
*\*Change in mode of addition-ZrOCl2 to ATMP, RT = Room Temperature (25 ºC)*

\**\*Optimum condition*

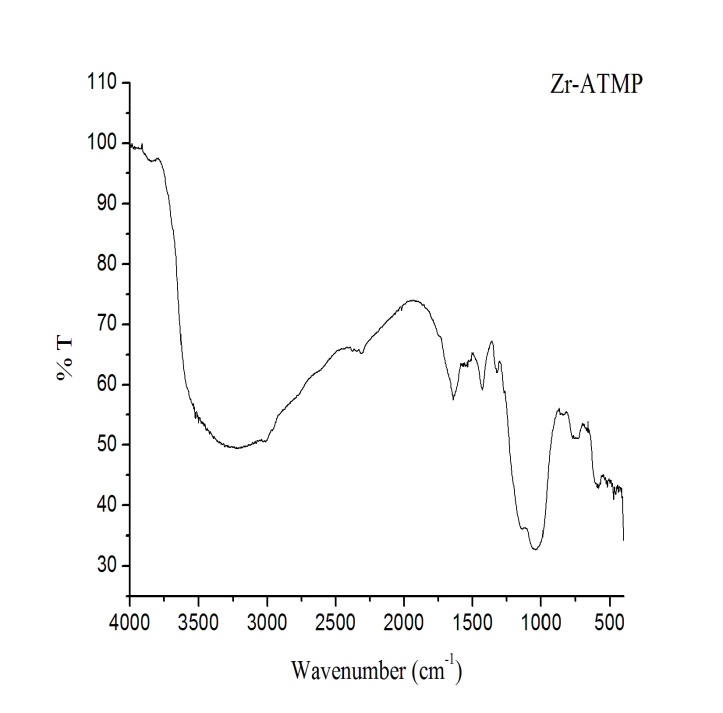
**Table S2:** Physical and ion exchange characteristics [31]

|  |  |
| --- | --- |
| Characteristics | Observation |
| Appearance | White hard granules |
| Particle size(range) | 250-590 µm |
| % Moisture content | 6.49 % |
| True density | 1.78 g∙mL-1 |
| Apparent density | 0.35 g∙mL-1 |
| Void volume fraction | 0.79 |
| Concentration of fixed ionogenic groups | 6.30 mmol∙g-1 |
| Volume capacity of resin | 1.26 meq∙mL-1 |
| Nature of Exchanger | Weak cation exchanger |
| CEC (RT) | 3.61 meq∙g-1 |
| 100°C | 2.93 meq∙g-1 |
| 200°C | 2.11 meq∙g-1 |
| 300°C | 2.26 meq∙g-1 |
| 400°C | 2.73 meq∙g-1 |
| 500°C | 1.76 meq∙g-1 |
| Chemical stability | Maximum tolerable limits |
| 1. Acids | 18 N H2SO4, 16.3 N HNO3, 11.3 N HCl |
| 1. Bases | 0.01 N NaOH, 0.01 N KOH |
| 1. Organic solvents | Ethanol, Benzene, Acetone, Acetic acid |

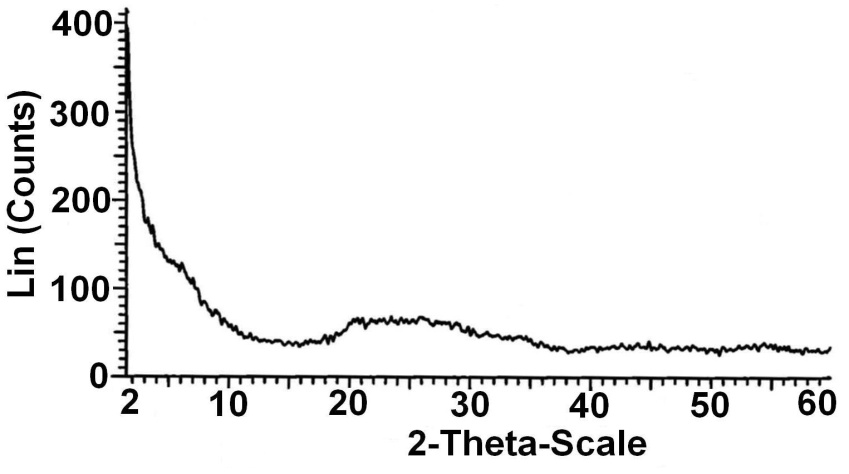
***Section-2Figure Captions.***

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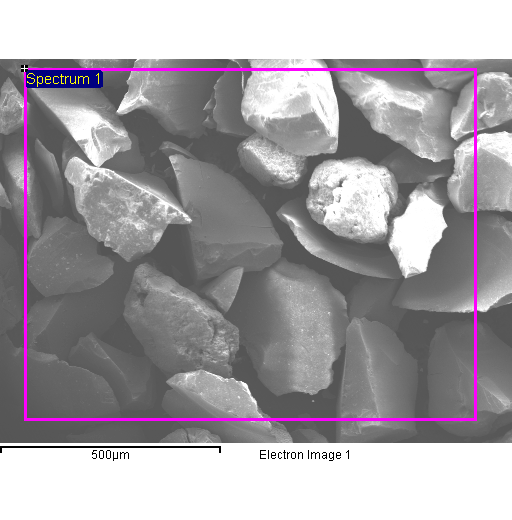
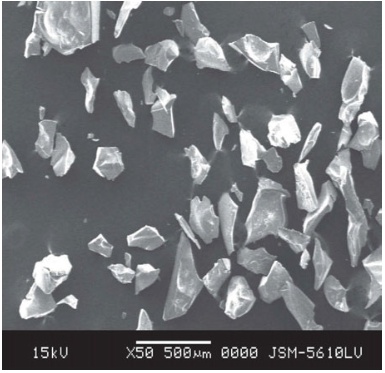
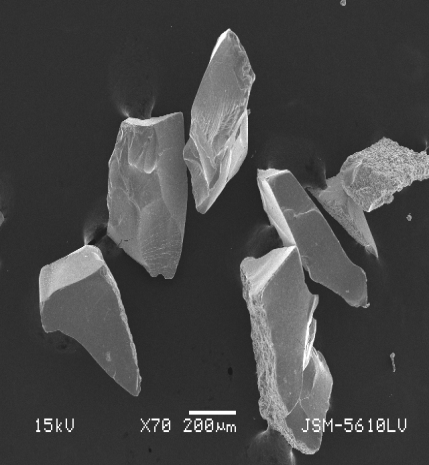
**Fig. S1**pH Titration Curve of Zr-ATMP

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**Fig. S2:** FTIR of Zr-ATMP

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**Fig. S3:** XRD of Zr-ATMP

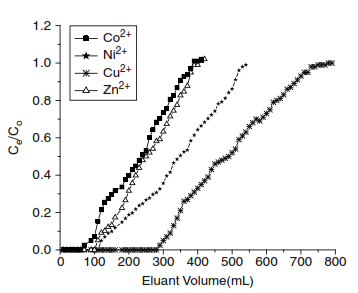
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**Fig. S4** SEM of Zr-ATMP

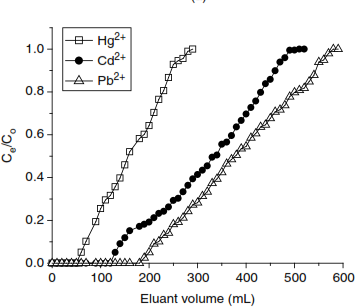
**Fig.** S5: *Plots of τ vs. time for Cu2+-H+ exchange for 0.014 M concentration using Zr-ATMP*

**Fig. S6:** τ vs. time plots for different temperatures for Cu2+-H+ exchanger using Zr-ATMP

**Fig. S7:** Arrhenius plots of *ln Da* versus *1/T* for Cu2+ metal ions using Zr-ATMP



**Fig. S8** Breakthrough curves for Transition metal ions using Zr-ATMP

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**Fig. S9** Breakthrough curves for Heavy metal ions using Zr-ATMP

***Section-3 Theory***

***S3.1 Explanation about the Thermodynamics parameters of ion exchange***

Negative Δ*G°* values indicate that the exchange process is feasible and spontaneous in nature. A negative enthalpy change (*ΔH°*) indicates that the exchange reaction is exothermic while a positive enthalpy change indicates that the exchange reaction is endothermic. The enthalpy change (*ΔH°*) for an ion exchange reaction can be either of the reasons or a net effect of the following factors: (1) the heat consumed in bond breaking, as H+ is released from the resin (2) the heat released in the formation of bonds with the incoming cation (3) the heat corresponding to the energy required for crossing the barrier (distance between exchange phase and solution phase) (4) the enthalpy change accompanying hydration and dehydration of exchanging ion in the solution. The entropy change (*ΔS°*) normally depends on the extent of hydration of the exchangeable and exchanging ions along with any change in water structure around ions that may occur when they pass through the channels of the exchanger, introducing a high degree of disorder into the resin matrix due to the ion exchange process.

***S3.2 Kinetics of Exchange***

Ion exchange was studied at 30◦C by varying the concentration of metal ions and effect of reaction temperature on ion exchange was studied in the temperature range 30◦C – 60◦C with 10◦C intervals for Cu2+, Zn2+, Ni2+,Co2+ (transition metal ions) and Pb2+,Cd2+,Hg2+ (heavy metal ions). The plots of ** versus *t* (Supporting Information Figure S6) for Cu2+ – H+ exchanges at different temperatures were linear. From the slope (*S*) of the **versus *t* plots, values of *DA*were calculated using the relationship *DA = S* × *r02* where, S= slope values (obtained from  versus t) and *r0=* bead radius. It is observed from (Supporting Information Figure S7) that the plots of *ln DA* versus *1/T* are linear, verifying the validity of the Arrhenius relation, *DA = D0 exp(-Ea/RT)*. The energy of activation (*Ea*) and the pre-exponential constant (*D0*) were evaluated from the slope and intercept of these plots. The entropy of activation (*ΔS\**) was then calculated using the equation *D0 = 2.72 d2 kT / h exp (ΔS\*/R)* where *d* is the average distance between two exchanging sites taken as 5 Å, while other terms have their usual meaning. Since the exchanger is not dynamic, ion exchange process depends on mobility of the exchanging ions. Self-diffusion coefficient (*D0*) gives an idea about the mobility of the migrating ions and depends on the size and charge of the ion and also on the extent of hydration in aqueous medium. During the exchange, the orientation of the exchanger sites and mobile ions are equally important and is expressed as the orientation factor. Orientation factor being related to randomness, is given by entropy of activation (*ΔS\**). The overall rate of exchange reaction thus depends on *D0*, *Ea* and *ΔS\**. It is thus expected that larger values of *D0* and *ΔS\**, and smaller values of *Ea* indicate a faster rate of exchange. The entropy reflects the changes in hydration sphere of the exchanging cation during the ion exchange process. When ion exchange occurs, cation of high entropy in the external aqueous phase, passes to one of lower entropy in the exchanger phase, which results in a significant negative contribution of entropy change.

***S3.3 Adsorption Isotherm***

Equilibrium behaviour is described in terms of equilibrium isotherms which depend on the system temperature, concentration of the solution, contact time, and pH. Adsorption equilibrium is usually established when the concentration of an adsorbate (metal ions) in a bulk solution is in dynamic balance with that of the adsorbent (exchanger) interface. The variation in adsorption with concentration and temperature is generally expressed in terms of adsorption isotherms - Langmuir and Freundlich adsorption isotherms.

The linearized form of the Langmuir isotherm equation is given as: Ce/(X/m) = 1/(bVm) + Ce/Vm, where X is the amount of adsorbate, m, the amount of adsorbent, Ce, the equilibrium concentration of the adsorbate in solution and ‘b’ is a constant that represents adsorption bond energy, which is related to the affinity between the adsorbent and adsorbate. It is also a direct measure for the intensity of the sorption process. Vm is a constant related to the area occupied by a monolayer of sorbate, reflecting the maximum adsorption capacity. A dimensionless constant equilibrium parameter RL can also be used to express an essential characteristic of the Langmuir isotherm. The RL value indicates the shape of the isotherm and expressed as an equation, RL = 1/(1 + bC0). A value 0 < RL < 1 indicates favourable adsorption, RL = 0 indicates irreversible adsorption, RL = 1 means linear adsorption while a value, RL > 1 indicates an unfavorable adsorption

Freundlich isotherm is expressed as, log(X/m) = logK + (1/n)logCe, where, X and m have the same meaning as described in Langmuir isotherm, K and 1/n are the Fruendlich constants, describing the adsorption capacity and intensity respectively. A value, 0 < 1/n < 1 indicates a normal isotherm, while 1/n > 1 is indicative for cooperative sorption, for n = 1 the partition between the two phases is independent of the concentration.

The isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters. Plots of Ce/(X/m) vs Ce and log(X/m) vs log Ce are drawn for Langmuir and Freundlich isotherms respectively which are straight lines from which the constants can be determined by the slopes and intercepts. In order to decide which type of isotherm fits better, the R2 values (goodness of fit criterion) computed by linear regression for both type of isotherms and a value 0 < R2 < 1 indicates that the isotherm provides a good fit to the sorption experimental data where R2 values should be close to unity.

Langmuir constants (b and Vm) and Freundlich constants (K and 1/n) obtained from the slopes and intercepts of the linear plots of Ce/(X/m) vs Ce and log(X/m) vs log Ce respectively as well as R2 and RL values are listed in Table 5. The R2 values show that the Langmuir and Fruendlich isotherms provides a good fit to the experimental data, where R2 values are found to be close to unity indicating both isotherms to be most appropriate for sorption of all the metal ions under study. Variation in R2 values is attributed to the fact that the surface adsorption is not a monolayer with single site. Two or more sites with different affinities may be involved in metal ion sorption.