Removal of Ni (II), Co (II) and Pb (II) ions from aqueous media using Starch Stabilized Magnetic Nanoparticles as adsorbents

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ABSTRACT

Varying percentages (0, 0.005, 0.010, 0.015, 0.020 and 0.025) of ecofriendly Starch Stabilized Magnetic Nanoparticles (SSMNPs) were used in the removal of M^{2+} *(*Ni^{2+}*,* Co^{2+} *and* Pb^{2+}*) ions from aqueous media by the batch adsorption technique. The* λ*max determined and used for* Ni^{2+}*,* Co^{2+} *and* Pb^{2+} *were 400, 380 and 320 nm respectively. The influence of pH, adsorbent starch concentration, initial metal concentration and contact time on the removal processes was investigated. The results showed that 0.025 % loaded SSMNPs gave the optimal sorption efficiencies of 91.3 (pH = 6.8 & 11.1), 90.91 and 96.97 % (at pH* < 3*) respectively for all three ions. The contact times required to reach the equilibrium concentrations were 15, 75 and 105 mins for* Pb^{2+}*,* Co^{2+} *and* Ni^{2+} *ions respectively. The kinetic rate constants (Lagergren and Pseudo-2nd-order) for* Ni^{2+} *and* Co^{2+} *adsorption were all greater than those from* Pb^{2+}*ions. Langmuir correlation coefficients showed a better fit for the adsorption isotherms. Ni sorption capacity of 60.61 mg* g^{-1} *obtained from Langmuir was the highest of the three at constant [SSMNPs] while 109.89 mg* g^{-1} *for Pb with was the highest at constant [*M^{2+}*].*

INTRODUCTION

The presence of some heavy metal ions like Ni^{2+}, Co^{2+} and Pb^{2+} in water bodies in industrialized cities poses significant threat to life due to their toxic nature even at low concentrations[1, 2]. In most cases, toxic metals find their way into the ecosystem through entry points like leachates from industrial and domestic wastes; corroded metal works and jetties, waste water from industries such as the paint, battery, oil and gas, metal works, etc.

These non-biodegradable pollutants (heavy metal ions) bio-accumulate in living tissues through direct contact and/or biotransformation across food chains of flora and fauna. They are known to be responsible for some disease conditions such as nasal cancer, lung and heart disorders, asthma, dermatitis, headache, dizziness, nausea and vomiting, chest pain, tightness of chest, dry cough, shortness of breath, rapid respiration, nephritis, extreme weakness and death in humans [3,4,5,6].

The enormity of the danger of these metal ions in the environment informed why several techniques and efforts have been deployed to facilitate their removal from aqueous media. Such techniques include chemical precipitation, ion exchange, reverse osmosis, adsorption, flocculation and electrolysis[7]. However, amongst the aforementioned, adsorption is the most widely applied technique because it is cheap, sustainable, effective and easy to design [7,8,9,10].

The most commonly used adsorbent has been activated carbon due to its large surface, porosity and high sorption capacity for coloured contaminants. However, high cost and poor decomposition limit its wider application. Therefore, other cheaper alternatives such as the use of agricultural wastes (that are more environmentally benign) have been studied extensively[10,11,12,13]. However, predictability of recovery efficiency due to variability in particle sizes from one adsorbent type to the other is still a problem.

To circumvent this, current research focus has been on developing more effective and efficient technology for adsorbent manufacture that could be manipulated to provide better control over particle size for optimum recovery. Nanotechnology seems to be the right technology and iron based nanomaterials, the adsorbent [4,14,15,16,17]! Iron based materials had no known environmental issues and could catalyze the degradation of most organic contaminants at polluted sites as well as provide stronger binding affinity for heavy metal ions but must be coated before use to prevent oxidation.

Starch coatings[4,16,18] have been found to be effective, cheaper and greener amongst others like humic acid[14] reported previously and can be used to manipulate the particle size of magnetic adsorbents. Starch coated magnetic iron oxide has been applied in the remediation of arsenic (V) and surface arsenate[16,18] and Ni ions from crude oil[4]. These studies found that removal efficiency by SSMNPs were dependent on starch concentration and particle size for arsenic while magnetic attraction was suggested as a factor for nickel ions. SSMNP sizes were found to decreased with increase in starch concentration such that a 0 to 0.1 % rise in starch concentration resulted in a corresponding particle size decrease from 16.99 to 11.48 nm, respectively [4].

The present study would like to investigate the influence of pH, adsorbent starch loading (coating), initial metal concentration and contact time on the removal processes of Ni, Co and Pb in aqueous media using SSMNPs. The choice of these metal ions would also help to establish the nature of affinity and to provide data for such absorption processes in aqueous media.

MATERIALS AND METHODS

Reagents and equipment

Analytical grades of Ni, Co and Pb salts were bought from Riede-de-Haën, Hannover, Germany and used without further purification. Qualikems (Delhi, India) supplied NaOH and the Fe salts. Starch powder was obtained from local cassava processing facility at Uegwere Boue in the Khana local government area of Rivers State of Nigeria. The instruments used include Hanna pH Tester, 65800-thermolyne maxi-mix shaker and a LaboMed, 2500 UV-VIS spectrophotometer.

Preparation of magnetic nanoparticles (MNPs) and starch stabilized magnetic nanoparticles (SSMNPs)

MNPs were prepared according to a modified literature method[4]. 4.4 g of $FeCl_3.6H_2O$ and 1.98 g of $FeCl_2.4H_2O$ were dissolved in 61ml of de-aerated water for the MNPs and de-aerated starch solution in place of water for the SSMNPs respectively. The reaction proceeded according to the following equation;

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-1} \rightarrow Fe_3O_4 + 4H_2O \quad (1)$$

Determination of λ_{max} of Ni, Co and Pb ions

Selected wavelengths of the metal ions were determined through a scan of 0.001 M solution of the metal salts solutions the spectrophotometer. The wavelengths of maximum adsorption (λ_{max}) determined for Ni, Co and Pb were 400 nm, 380 nm and 320 nm respectively.

Equilibrium studies

The equilibrium studies were carried out in different batches at room temperature of 28 ± 2° C using a modified literature method[9]. Modifications were in centrifugation, concentrations, contact time and pH used. The first batch involved the mixing of a fixed mass of the different percentages of the adsorbents (SSMNPs and MNPs) with a 10 ml aqueous solution of a chosen constant concentration for each metal in a capped sample bottle and shaken on the thermolyne shaker for 3.50 h. Similar procedures were used for the second batch and the contact time studies.

The percent removal of the M^{2+} ions was evaluated from the relation,

$$\%\text{Removal of } M^{2+} = \left(\frac{Abs_{initial} - Abs_{final}}{Abs_{initial}} \times 100 \right) \qquad (2)$$

where Abs-initial and Abs-final were the initial and final M^{2+} concentrations respectively. Similarly, the amount of M^{2+} absorbed per unit mass, q of the adsorbent (SSMNPs or MNPs) was calculated from the mass balance equation,

$$q = \frac{V}{M}(C_i - C_e) \qquad (3)$$

where Ci and Ce are the initial and equilibrium concentrations of M^{2+} in solution (mg/L) respectively and M the dry weight of the adsorbent used in mg.

Kinetics of M^{2+} adsorption and adsorption isotherm models used

The kinetics of the metal adsorption process with time was determined by using both the pseudo-first-order (Lagergren) and pseudo-second-order rate equations 4 and 5 respectively to generate plots from which the constants were calculated.

$$\log(q_e - q) = \log q_e - \frac{K_{ad}t}{2.303} \qquad (4)$$

where q_e and q (mg/g) are the amount of metal ions adsorbed at equilibrium and at time t (min), respectively. While

$$\frac{t}{q} = [K_2 q_e^2] + \frac{t}{q_e} \qquad (5)$$

and the constants: K_{ad} (min^{-1}) and K_2 (g/mg min) are the First order and Pseudo-second order rate constants of adsorption respectively[10].

The adsorption isotherms used the Langmuir and Freundlich models as expressed in equations (6) and (7).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad (6)$$

where q_{max} (mg/g), the highest amount adsorbed (concentration at equilibrium) and b (L/mg) are Langmuir constants. The Freundlich isotherm equation is expressed as;

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (7)$$

where K_f and n are Freundlich adsorption constants relating to the adsorption capacity and intensity respectively of a heterogeneous process[8].

RESULTS AND DISCUSSION

M^{2+} adsorption at varying weight of adsorbents and coverage

The results of the M^{2+} adsorption at varying % starch coverage of adsorbents (SSMNPs-coated and bare-0 % also called MNPs) at constant [M^{2+}] carried out at different optimal pH are shown in Figure 1.

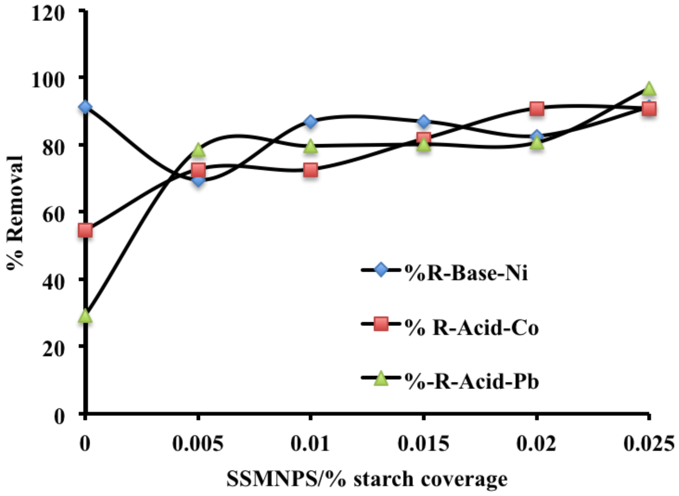

Figure 1: Adsorption of the M^{2+} ions at optimum pH

The plot showed that adsorption increased sharply with increase in the weight (wt) of adsorbent's coating from 0 % (MNPs) to the first coated, 0.005 % SSMNPs then gradually until it peaked at 0.02 % and 0.025 % for Co^{2+} and Pb^{2+} respectively. On the other hand, Ni^{2+} ions removal peaked at 0 and 0.025 % adsorbent coating concentrations. The result showed that the effect of adsorbent coating on the uptake of the M^{2+} (Co and Pb) ions at different pH were both pH and adsorbent coverage dependent.

Effect of initial [M^{2+}] on removal efficency at constant adsorbent coating

Co^{2+} and Pb^{2+} ions adsorption pattern also followed the same trend of increased % removal with increasing [M^{2+}] at constant adsorbent coverage/weight and pH of 6.8 (neutral) while Ni^{2+} ions decreased steadily with increase in [Ni^{2+}] (Figure 2).

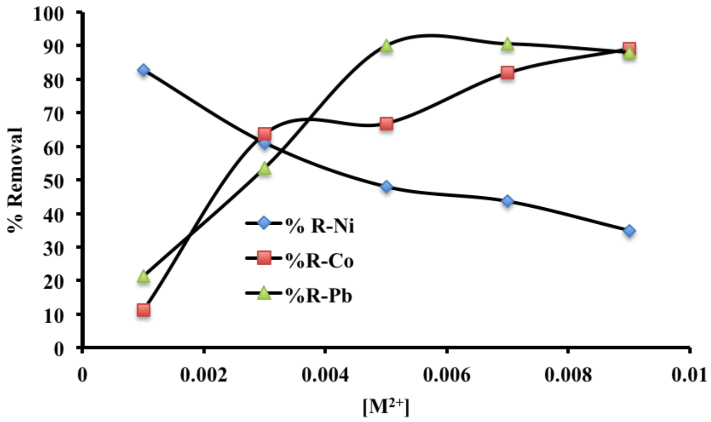

Figure 2: Adsorption of varying [M^{2+}] at constant adsorbent coating [SSMNPs]

Contact time and M^{2+} adsorption

The results obtained from the contact time experiment showed that Ni^{2+} ions uptake started at 30 mins and continued steadily until equilibrium was reached at 105 mins while Pb^{2+} and Co^{2+} uptakes were more rapid with absorption equilibria at 15 and 75 mins respectively (**Figure 3**). The uptake rapidity trend was in tandem with their relative molecular masses or weight, that is $Pb^{2+} > Co^{2+} > Ni^{2+}$ respectively.

Kinetics of M^{2+} adsorption

The 1st order (Lagergren) and Pseudo-2nd-order kinetics of the adsorption process of the M^{2+} ions were studied in order to establish the better relationship followed during the adsorption process. **Table 1** showed the data obtained from the plots of the relations in equation 4 and 5 respectively at constant adsorbent coverage.

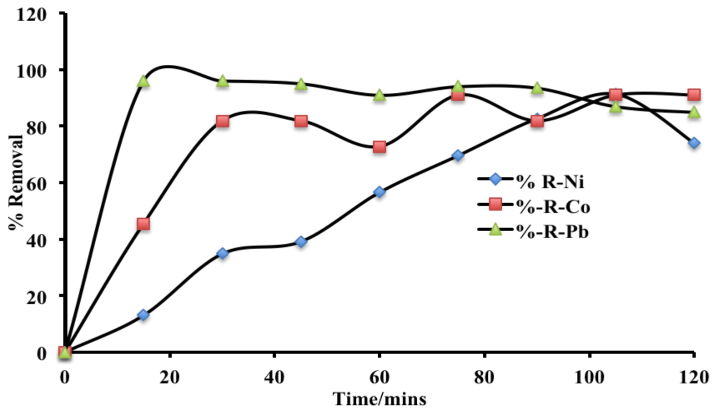

Figure 3: M^{2+} Contact times at constant [SSMNPs]

Table 1: Kinetics constants for metal adsorption process

Lagergren rate constants for adsorption of M^{2+} ions at constant [SSMNPs], pH 6.8.			
M^{2+}	K_{ad} x 10^{-2} (min^{-1})	r^2	q_e(mg g^{-1})
Ni	3.02	0.5301	5.15
Co	0.44	0.5000	82.45
Pb	0.12	0.7397	141.48
Pseudo-2nd-order rate constants for adsorption of M^{2+} ions at constant [SSMNPs], pH 6.8.			
M^{2+}	K_2 x 10^9 (mg/g/min)	r^2	q_e(mg g^{-1})
Ni	1.9583	0.4254	$2.55x10^{-3}$
Co	3.5160	0.9401	$1.58x10^{-3}$
Pb	0.0003	0.4467	$23.92x10^{-3}$

The correlation coefficients for all three metal ions were poor except for Co Pseudo-2nd-order that was relatively high but still less than 0.99-1.00 expected from a good linear relationship. The nonlinear adsorption pattern observed in their contact time plot (Figure 3) was responsible for the poor correlation coefficients. The Pseudo-2nd-order model therefore provided a better fit for Co adsorption kinetics than it did for Ni^{2+} and Pb^{2+}. The rate constants trend of K_{ad} which varied as $Ni^{2+} > Co^{2+} > Pb^{2+}$ changed to $Co^{2+} > Ni^{2+} > Pb^{2+}$ for K_2 (Table 1). The rate trends suggested that smaller ionic size might have favoured higher initial sorption rates of Ni^{2+} and Co^{2+} than for Pb^{2+} (a larger sized ion) that had the least sorption rate on both models.

M^{2+} Adsorption Isotherms

The Langmuir isotherm (equation 6) data are presented in Table 2 (right hand side). Ni, Co and Pb had absorption capacities (q_{max}) of 60.61, 13.33 and 29.67 mg g^{-1} at constant adsorbent coverage but increased to 69.44, 94.34 and 109.89 mg g^{-1} at constant [M^{2+}] respectively. The effects of the energy and capacity of adsorption by the adsorbents relate directly to the constants b (Lm g^{-1}) and Q (mg g^{-1}), respectively. The result showed that the % removals or adsorption processes were favoured by the varying adsorbent coverage.

The equilibrium data obtained from the Freundlich isotherm (equation 7) showed that Ni^{2+} ions absorption capacity (Freundlich) constant, K_f (~1476) was the highest of the three M^{2+} ions as shown in Table 2 (left hand side). The K_f varied as Ni > Pb > Co at constant [SSMNPs] and Ni > Co > Pb at constant [M^{2+}] while the adsorption intensity, n trend was Co > Ni > Pb under both conditions. This confirmed that the lighter element ions had greater intensity or number at the active sites.

However, a comparison of the correlation coefficients, r^2 of the M^{2+} adsorption under the Langmuir and Freundlich isotherm models showed the lowest values as 0.9002 and 0.8736 respectively. This implied that Langmuir model fitted the data better in the presence of SSMNPs. The result confirmed that the starch coverage provided the needed homogeneous distribution of active sites and lower surface energy barrier to particle adsorption that fitted the Langmuir model better than the Freundlich.

CONCLUSION

The results confirmed that SSMNPs was a better adsorbent than the bare MNPs particularly for Co^{2+} and Pb^{2+} at constant [M^{2+}] while MNPs was a better adsorbent for Ni^{2+} than SSMNPs under the same condition. The optimum pH range for Ni^{2+} ions adsorption determined was $6.8 \leq 11.1$ while Co^{2+} and Pb^{2+} required pH $2.2 \leq 6.8$ for their maximum uptake. Pb^{2+} ions had the fastest contact time of 15 mins amongst the three ions studied. Similarly, their kinetic rate constants trend was Ni > Co > Pb at constant [SSMNPs]. Ni sorption capacity of 60.61 mg g^{-1} obtained from Langmuir isotherm was the highest of the three at constant [SSMNPs] while 109.89 mg g^{-1} for Pb was the highest at constant [M^{2+}] and also the overall best. Higher correlation coefficients from Langmuir isotherms compared to Freundlich confirmed that Langmuir gave better fits for the adsorption processes.

Table 2: Langmuir and Freundlich adsorption isotherm constants for M^{2+} Adsorption

Langmuir adsorption isotherm constants for varying [M^{2+}] at constant [SSMNPs] coating				Freundlich adsorption isotherm constants for plots of varying [M^{2+}] at constant [SSMNPs]			
M^{2+}	**Q (mg g^{-1})**	b (Lmg^{-1})	r^2	M^{2+}	K_f	r^2	n
Ni	60.61	-0.0334	0.9307	Ni	1476.05	0.9125	-1.6647
Co	13.32	-0.035	0.9152	Co	0.0623	0.9487	0.6273
Pb	29.67	-0.0642	0.9002	Pb	666.50	0.8736	-1.6703
Langmuir adsorption isotherm constants for varying [SSMNPs] coatings at constant [M^{2+}]				Freundlich adsorption isotherm constants for plots of varying [SSMNPs] coatings at constant [M^{2+}]			
M^{2+}	Q (mg g^{-1})	b (Lmg^{-1})	r^2	M^{2+}	K_f	r^2	N
Ni	69.44	-3.89	0.9953	Ni	155.49	0.9492	4.50
Co	94.34	-0.26	0.9975	Co	152.51	0.9801	5.01
Pb	109.89	-1.10	0.9996	Pb	112.75	0.9959	-9.75

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