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Optimization of Nitric Acid Leaching of Rare Earth Elements From Moroccan Natural Phosphate

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ABSTRACT:
Phosphateisaveryimportantnaturalresourcein Moroccoandoneofthesecondaryresourcesofrareearthelements.Ourstudyisparticularlyinterestedin Youssoufiaphosphate,whichcontains228.77ppmofrareearthelements(ΣREEs).Thepurposeofourworkistostudytheinfluenceofdifferentparameters(acidconcentration,solid/liquidratioandtemperature)inordertodeterminetheoptimalconditionsfortheleachingofrareearths.Anexperimentaldesign(Doehlertmatrix)hasbeendrawnuptooptimizetheexperimentalconditionsoftheleaching.Alltestsweremadewithnitricacidatdifferentconcentrationsvaryingbetween1.5Mand4.5Mwithasolid/liquidratioof1/12to1/6;reactiontemperatureanddurationarerespectively20°Cto80°Cand60min.Theoptimalconditionsareobtainedwhenusing69°Castemperature,4.1Masacidconcentrationand1/9assolid/liquidratio.

Keywords:*doehlertexperimentaldesign,acidleaching,optimization,phosphaterock,rareearth*

I. INTRODUCTION

Theearth'scrustcontainsasignificantnumberofphosphatedepositsofigneousandsedimentaryorigins(Loheta l.,2016).Morocco,withitssignificantshareofworldphosphatestock,isleadingexportationofphosphateanditsderivatives.Thecountry'sglobalmarketshareisover30%(Hakkou,Benzaazoua,&Bussière,2016).Moroccanphosphatesarethemostimportantbothinquantityandquality;thesearelocatedintheGantour(YoussoufiaandBenguérir),Messkala(Chichaoua),OuedEddahab(Boucraâ)andOuledAbdoun(Khouribga)deposits(Bilali,Benchanaa,Outzourhit,&Mokhlisse,2009).Sedimentarydepositsofnaturalphosphatesaremainlycomposedofapatiteofthegeneralformula:M10(ZO4)6X2withM=Ca,Sr,REE...;Z=P,As,Si,...;X=F,OH,Cl.....(Pereira,2003).Insomecarbonates,apatitemineralscontainmostoftherareearthselements(REE),fluorineandstrontium.Fluorapatiteisthemostcommonphosphorusmineralandisalwaysenrichedwithlightrareearths.Rareearthdepositsoccurinawidevarietyofigneous,sedimentaryandmetamorphicrocks(Koltun,&Tharumarajah,2014).Literaturereportsthatthephosphatematrix,xenotimeandmonazitemineralscontainrareearthsthatareextractedbyacidorbasicleaching(Pereira,2012).Severalstudieshavebeenfocusedontheuseofdifferentacidsfortheextractionofrareearthsfromvariousoresincludingphosphates(Zhang,2014;Soltanietal.,2019).Recently,severalstudieshavebeencarriedoutontherecoveryofrareearthsfromsecondarysources,suchasnaturalphosphates,containingminutequantitiesofrareearths;amongthesestudies,wecitethatofWuetal.(2019)whichfocusesontheoptimizationofrareearthleaching,intheformofmixedoxides,fromYoussoufianaturalMoroccanphosphate.Theobservationoftheeffectsofallvariables:acidnitricconcentration,temperatureandsolid/liquidratiocodedrespectivelyX1,X2andX3andtheirinteractionsareofparamountimportancetounderstandtheacidleachingprocess.Theexperimentaldesignhasbeenusedtocontrolthedifferentfactorsthatinfluencetheleachingprocesstooptimizetheexperimentalconditions.Theadvantageofthismethodistoreducethenumberofexperimentsthatstudytheinteractionsbetweenthechosenfactors SaidK.A.M,&AminM.A.M,2016).InNemrodsoftwarethecomplete3³factorialdesignisasimpleandimportantstatisticaltool.InfluencingfactorsareoptimizedusingtheSurfaceofResponsemethodandmulti-criteriaoptimizationwithDoehlertdesignanddesirabilityfunction(Pereira,2012;SaidK.A.M,&AminM.A.M,2016).

II. EXPERIMENTAL

2.1Materials

Theexperimentalstudyisbasedonphosphatethatwasprovidedby CERPHOS(Centerforstudiesandresearchonphosphates ofOCPgroup).TheusedphosphateisfromtheYoussoufiadeposit(GantourBasin).Thisphosphateisapatitic.Fluorapatite(Ca10(PO4)6F2)isthemoststablecompoundofnaturalphosphate.Thegeneralpropertiesofthisoreandthestructureofthefluorapatitehavebeendescribedinpreviousworks(Bilali,Benchanaa,Outzourhit&Mokhlisse,2009;M.Amine,Asafar,Bilali&Nadifiyine,2019).

2.2ExperimentalDeviceandMethod
2.2.1ExperimentalPart

Thehomogeneityofthematerialanditsparticlessizeisanimportantparameterthatshouldbewellcontrolled.For this,weworkedwithparticlesize<80µm.Inthisstudyofnitricleaching,weusedhomogeneoussamplesfromYoussoufia naturalphosphatesofOCP.Theobjectiveoftheleachingmanipulationsistostudytheinfluenceofcertainparameters(acid concentration,solid/liquidratioandtemperature)inordertodefinetheiroptimalvaluesallowingthemaximumdissolutio nofrareearths.Fortheacidleachingexperiments,solidphosphateandacidmixturewaspreparedina250mlErlenmeyerfl askandheatedonatemperature-controlledhotplate.Thetestsweremadewithnitricacidconcentrationsvaryingbetween1.5mol/Land4.5mol/Lwithasol id/liquidratioof1/12to1/6.Thereactiontemperaturevaluesarebetween20°Cand80°Cwhilethedurationofthereactiona ndAgitatorspeedarefixedat60minand500rpmrespectively.TheTable1presentsthelistofallthefactorsadoptedbyourst udythatinfluencenitricleaching.

Factor(XI) Level1		HNO_3(mol/L)	Temperature(°C)	RatioS/L
Level2	-1	1.5	20	1/12
Level3	0	3	50	1/8
	+1	4.5	80	1/6

Table1.ExperimentaldomainfortheDoehlertdesign

2.2.2DesignofExperimentsTheresponsesurfacemethodology(RSM)wasusedtooptimizeoperatingconditionsallowin gmaximumdissolutionoftherareearths(Liu,&Wang,2007).Thethreefactorsinfluencingthisdissolution(acidconcentr ation,temperatureandsolid/liquidratio)arecodedrespectively(X1,X2,andX3)andtheresponserepresentedbytheconce ntrationofrareearthsinppmis(Y).Weworkedwiththreefactorsthatcorrespondto17testsperformedincludingfivetocalc ulateboththeerrorvarianceandthereproducibilityofthetestdata.Apolynomialmodelofseconddegreewasused.Themo delcanbewrittenas:

$$Y=b0+b1*X1+b2*X2+b3*X3+b1\text{-}1*(X1*X1)+b2\text{-}2*(X2*X2)+b3\text{-}3*(X3*X3)+b1\text{-}2*(X1*X2)+b1\text{-}3*(X1*X3)+b2\text{-}3*(X2*X3). \quad \text{(Eq.1)}$$

Y:studiedanswer;Xi:investigatedfactor(ivariesfrom1to3);b0:aconstant;bi:maineffectoffactori.Theexperimentalde signwasdevelopedusingNemrodsoftware(NewEfficientMethodologyforResearchusingOptimalDesign)(Mathieu, Mony,&PhanTanLuu,2000).TheexperimentalDoehlertdesignwasrandomizedtominimizetheeffectsofuncontrolledf actors.

2.3AnalysisandCharacterizationTechniques

CrudephosphatesampleswerecharacterizedbyX-raydiffraction,scanningelectronmicroscopy(SEM)andinductivelycoupledplasmamassspectrometry(ICP-AES),whilenitricleachingsolutionswereanalyzedbyICP-AESonly.

III. RESULTS AND DISCUSSION

3.1AnalysisandCharacterizationofRockPhosphate

3.1.1InductivelyCoupledPlasmaAtomicEmissionSpectroscopy(ICP-AES)REEscontentsofphosphateregivenintable2(M.Amine,Asafa,Bilali,&Nadifiyine,2019).Abundantelementsar e:Yttrium(143ppm),Lanthanum(24.06ppm)andNeodymium(17.52ppm).Allphosphateorescontainvaryingamounts ofrareearths;table3showsthecontentsoftypicalREEs,uraniumandthoriumcontainedintheYoussoufiaphosphateore(Rollat,2016).

Element	ppm
YLaCe	143
PrNdS	24.06
mEuG	13
dTbDy	3.626
HoErT	17.52
mYbL	3.681
uΣRE	1.008
E	5.143
	0.8387
	5.672
	1.303
	4.315
	0.6205
	4.2
	0.7843
	228.77

Table2.RareearthsContentsinYoussoufiarockphosphate

Element	(ppm)
La_2O_3	80
CeO_2	110
Nd_2O_3	20
Sm_2O_3	13.5
Eu_2O_3	1.5
Tb_4O_7	3.5
Y_2O_3	110
Sc_2O_3	8.5
Th_2O_3	3.5
U_3O_8	125

Table3. Uranium,thoriumandrareearthscontentsinYoussoufiarockphosphate(Rollat,2016).

3.1.2X-rayDiffractionCharacterization(XRD)
YoussoufiaphosphatehasbeencharacterizedbyXraydiffraction.Themajorityofthediffractionlinesobservedareattributedtotheapatiticphase(Figure1).Othersecondaryphasesarealsopresentandattributedtoquartz,calciteanddolomite(Aouad,Benchanaa,Mokhlisse,&Ounas,2004;Aouad,Benchanaa,Mokhlisse,&Arafan,2002).

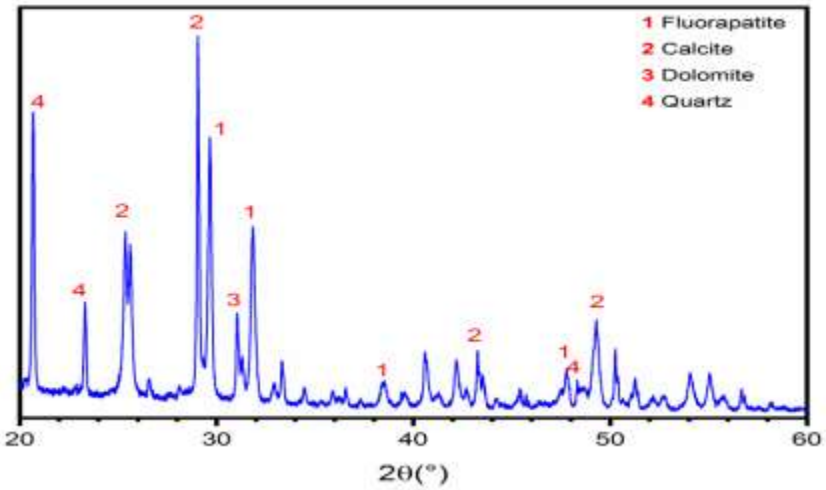


Figure1.X-raydiffractionpatternoftherawphosphate

3.1.3ScanningElectronMicroscopy(SEM)anddispersiveX-RayEnergy(EDX)
Theobservationbyascanningelectronmicroscope(Figure2-a)coupledwithdispersiveX-rayenergyanalysis(Table4)showsthatYoussoufiaphosphaterockbeforeattackwithnitricacidconsistsessentiallyofirregularlyshapedphosphateparticlesandsometimesrounded.Thisvarietyofparticlesisexplained,inadditiontoapatite,bythepresenceofbonedebris,organicdebrisaswellasquartzgrains.Wecanobserve,aftertreatment(figure2-b),thatthemajorityoftheparticleshavedisappeared.thesurfaceofthematerialthusobtainedexhibitsacertainhomogeneitywhileshowingporesandcracks.ScanningelectronmicroscopyanalysesallowedustoobservethesamecrystallinecompoundsasthoseidentifiedbyX-raydiffraction(M.Amine,Asafar,Bilali,&Nadifiyine,2019).

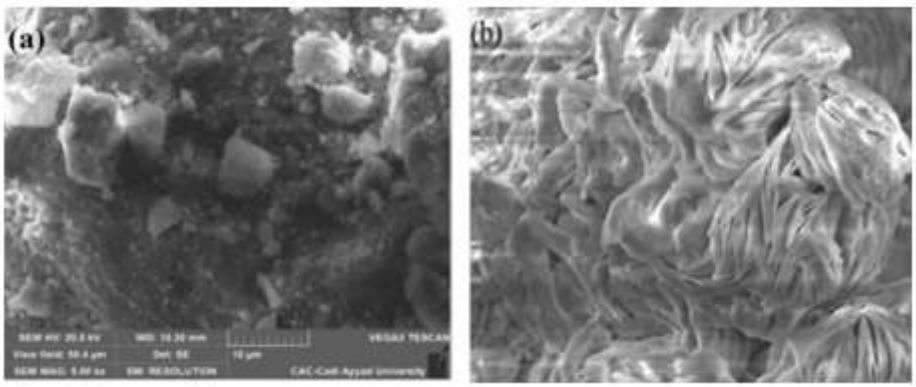


Figure2. Morphologicalobservationsofthenaturalphosphatesurfacebefore(a)andafter(b)treatment.

Element	Beforetreatement		Aftertreatement	
	10µm		10µm	
	wt.%	At%	wt.%	At%
C	12.86	20.90	2.903	5.63
O	41.86	51.07	5.143	51.31
H	5.59	5.74	.680.	4.530.
Na	1.38	1.17	72-	73-
Y	0.46	0.20	0.420	0.400.
Mg	0.76	0.61	.100.	090.09
Al	0.86	0.62	113.1	2.050.
Si	2.17	1.51	80.19	14-
P	10.03	6.32	-	12.92
S	1.23	0.75	22.17	
K	0.11	0.05		
Ca	22.97	11.19		
V	0.09	0.03	' '	' '
Fe	0.1	0.04	' '	' '

Table4.ChemicalcompositionofYoussoufianaturalphosphate

3.2AnalysisofYResponse
AnalysisofYresponsesfromtheresultslistedintable6letstoseethattheREEsconcentrationvariesbetween72.9ppm(experience8)and202.5ppm(experience3).Theestimationofcoefficients(bi)ofthepostulatedmodel(Eq.1)wasdeterminedbytheleast-squaresmethodusingNemrodsoftware.Maineffectsoffactors(bi)wereperformedfromstatisticaltestsonthecoefficients.Themathematicalmodelwasvalidatedbyverifyingthecorrelationcoefficient(R^2)(Baçaoui,Yaacoubi,&Dahbietal.,2001).WhenR^2valuesarecloseto1themodeloffersanappropriateexplanationofthevariabilityofexperimentaltopredictedvalues(Boujounouietal.,2018).Thedifferencebetweenthesetwotypesofvalueswasexplainedbythemodel.Tocalculatetheproportionofthetotalobservedvariability,anadjusteddeterminationcoefficient(R^2Adj)wasemployed.Aftervalidation,andtographicallyillustratethesurfacesresponse,differentmodelswereused.

3.2.1StudyoftheEstimatesandStatisticsoftheCoefficients
Fromtable7,wecanseethatallofthefactorsareinvolvedindifferentinteractions.Usingvaluesofthesefactors,theEq.1becomes:

-6.7875(X1*X3)-61.9555(X2*X3)

Thecorrelationbetweenthetheoreticalandexperimentalresponseswassatisfactory:R^2=0.91andR^2Adj=0.80.

3.2.2Three-Dimensional(3D)ResponseSurfaceandIso-ResponseCurves(2D)
3Dand2Dresponsesurfaceplotswereusedtovisualizetherelationshipbetweentheresponses(Y),theexperimentallevelsofeachvariableandthetypeofinteractionsbetweenvariablestodeducetheoperatingconditionsleadingtotheoptimalresponse.TheTable6showsthatthehighestresponse(202.500ppm)wasachievedwiththegreatestlevelsofHNO3(X1)andTemperature(X2).

3.2.3FactorialDesign,ExperimentalConditionsandExperimentalResultsY(REE)
ToestimatethecoefficientsofthemodelDoehlertdesignwasappliedusingNemrodsoftware.Thisdesignpermitstorepresenttheresponsesstudiedinallexperimentaldomainsofthethreefactors:HNO3concentration,temperatureandsolid/liquidratio.Doehlertexperimentaldesignandcorrespondingexperimentalconditionsaregiveninthe Table5).

N°Exp	DesignofExperiment			Operatingconditions		
	X_1	X_2X_3		HNO_3 (mol/L)	Temperature(C°)	RatioS/l
1	1.00000	0.00000	0.00000	4.5	50	0.12
2	-	0.000000	0.000000	1.5	50	0.12
3	1.000000	.86603-	.000000.	3.8	76	0.12
4	.50000-	0.86603-	000000.0	2.3	24	0.12
5	0.500000	0.866030	00000.00	3.8	24	0.12
6	.50000-	.866030.	0000.816	2.3	76	0.12
7	0.500000	28868-	50-	3.8	59	0.15
8	.50000-	0.28868-	0.81650-	2.3	41	0.09
9	0.500000	0.288680	0.81650-	3.8	41	0.09
10	.500000.	.577350.	0.816500	3.0	67	0.09
11	00000-	28868-	.816500.	2.3	59	0.15
12	0.500000	0.577350	816500.0	3.0	33	0.15
13	.000000.	.000000.	00000.00	3.0	50	0.12
14	000000.0	000000.0	0000.000	3.0	50	0.12
15	00000.00	00000.00	000.0000	3.0	50	0.12
16	0000.000	0000.000	00.00000	3.0	50	0.12
17	000.0000	00		3.0	50	0.12

Table5. Doehlertexperimentaldesignandoperatingconditions.

Inordertointerprettheresults,theresponsesurfaceswererepresentedinthedomainsofinterestofacidconcentration,solid/liquidratio,andtemperatureusingNemrodsoftware.Doehlertexperimentaldesignandexperimentalresultsaregiveninthe Table6.

Table6.Doehlertexperimentaldesignandresponses Y(Rareearthconcentrations)

N°Exp	DesignofExperiment		Operatingconditions			Response
	X_2	X_3	HNO_3(mol/L)	Temperature(C°)	RatioS/l	Y(ppm)
1	1.000000	.000000	.000004	.5500	.12182	.010
2	-1.000000	.000000	.000001	.5500	.1294	.515
3	0.500000	.866030	.000003	.8760	.12202	.500
4	-0.50000	-0.866030	.000002	.3240	.12105	.180
5	0.50000	-0.866030	.000003	.8240	.12124	.800
6	-0.500000	.866030	.000002	.3760	.1296	.180
7	0.500000	.288680	.816503	.8590	.15138	.450
8	-0.50000	-0.28868	-0.816502	.3410	.0972	.900
9	0.50000	-0.28868	-0.816503	.8410	.0988	.500
10	0.000000	.57735	-0.816503	.0670	.09167	.130
11	-0.500000	.288680	.816502	.3590	.15105	.150
12	0.00000	-0.577350	.816503	.0330	.15119	.835
13	0.000000	.000000	.000003	.0500	.12121	.815
14	0.000000	.000000	.000003	.0500	.12127	.650
15	0.000000	.000000	.000003	.0500	.12121	.530
16	0.000000	.000000	.000003	.0500	.12124	.515
17	0.000000	.000000	.000003	.0500	.12127	.515

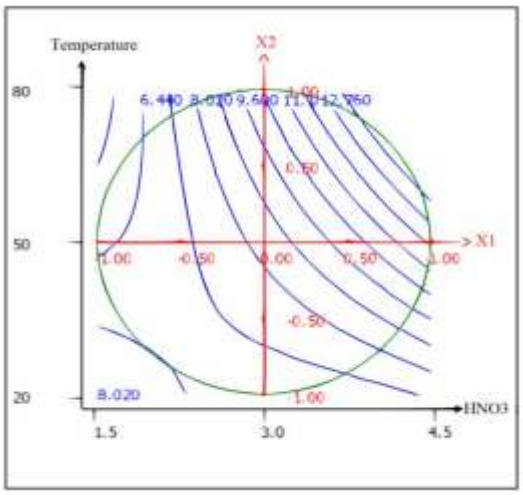
	Coefficient	Ecart-Type	Signif.%
Nom	124.6051	1.3226479	<0.01***[1]<
b0b	43.72882	1.4787653	0.01***<0.
1b2	7.63297.	1.4787617	01***0.854
b3b	051213.6	1.4635234	**[2]0.526**
1-	5745.527	2.4744477	8.9
1b2-	1-	2.4744214	0.129**0.0
2b3-	18.32885	2.2748659	126***14.7
3b1-	0.0560-	3.4150441	<0.01***
2b1-	6.7875-	3.7787925	
3b2-3	61.9555	3.7788248	

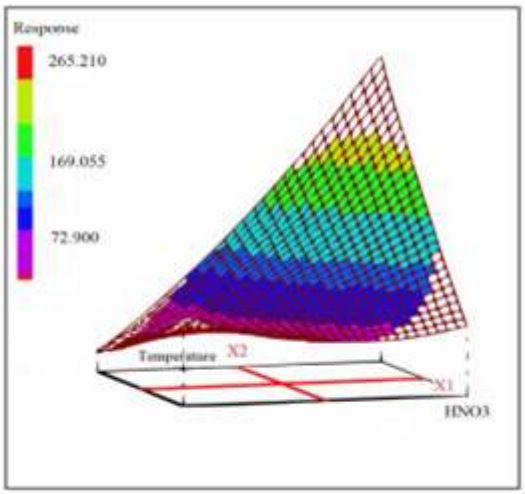
Table7.EstimatedvaluesofthecoefficientsfortheYresponses

Graphicrepresentationsa,b,andc(Figure3)of2Dand3Dresponsesurfaceplotsshowthatthemainparametersthathaveal argeinfluenceontherareearthslixiviationprocessadoptedare:acidconcentrationandtemperaturewhichactpositivelyo ntheresponseY(byincreasingtheirvaluestheanswerbecomesmoreimportant).Thesolid/liquidratioactsintheopposited irection(byincreasingitsvaluetheanswerbecomesweaker).

[1]Value***Statisticallysignificantatthelevel<99.99%.

[2]Value**Statisticallysignificantatthelevel99%.





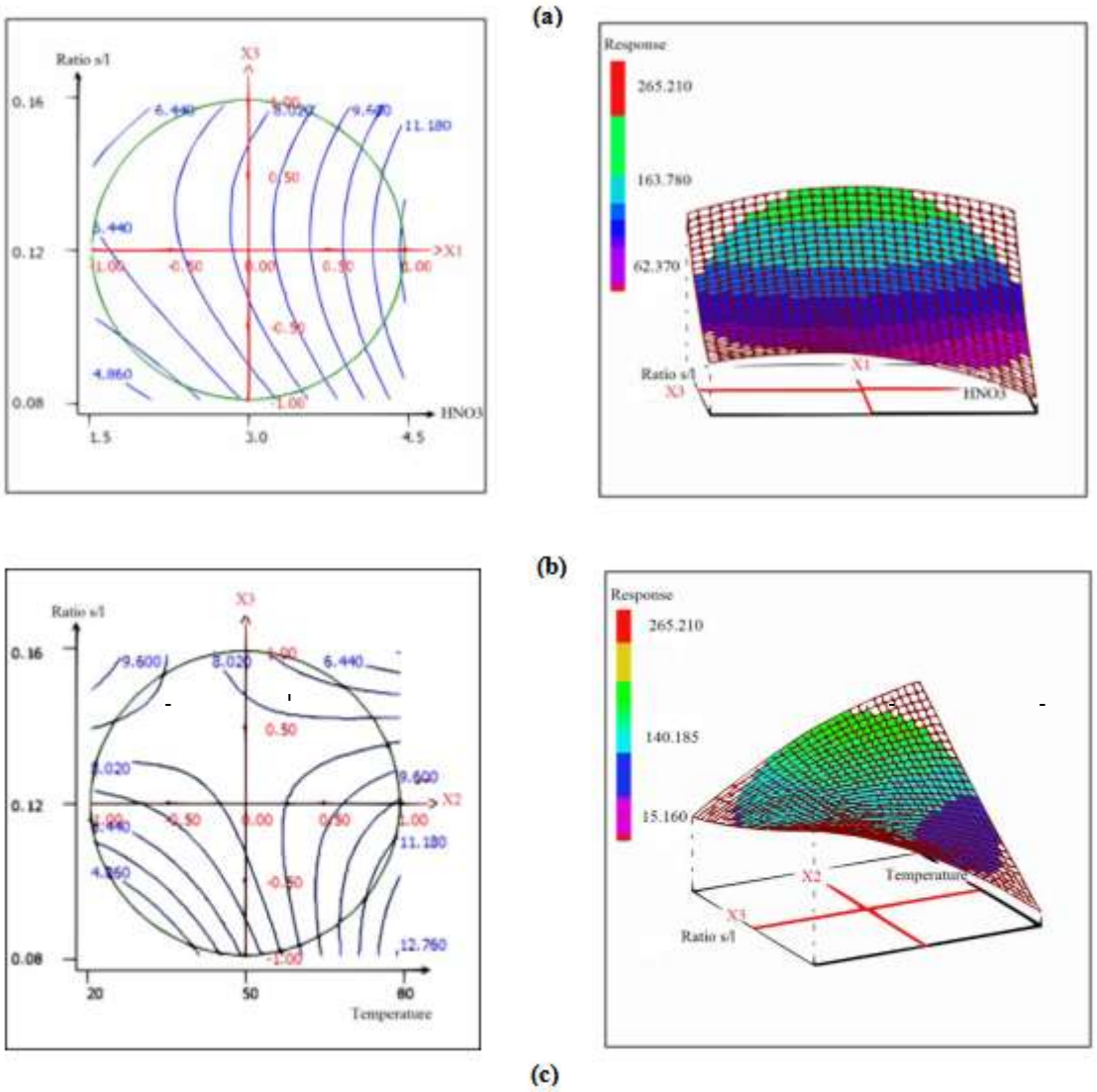


Figure3.a:HNO3(X1)andTemperature(X2);b:HNO3(X1)andS/Lratio(X3);c:Temperature(X2)andS/Lratio(X3)

Theoptimaloperatingconditionsallowingthemaximumlixiviationwerestudiedbytheresponsesurfacemethodology.Theattainedsolubilizationof83%forREEwasobtainedbythefollowingconditions:acidificationoftheorewitha4.1mol/LHNO3solution,heatingthemixtureat69°Candusing1/9assolid/liquidratio.Studywithnitricacidgivesahighersolubilizationthanstudywithhydrochloricacid(M.Amine,Asafa,Bilali,&Nadifiyine,2019).

3.2Optimization

Todetermineoptimalconditionsacidconcentration,solid/liquidratio,andtemperatureinordertodefinetheoptimalparametersallowingthemaximumdissolutionoftherareearths,theresponsesareoptimizedsimultaneouslyusingthedesirabilityfunctionincludedintheNemrodsoftware.Thedesirabilityfunctionvariesintheinterval[0,1];thevalue1correspondstothemaximumsatisfaction(desiredvalue)and0correspondstoanunacceptableresponse(Hammas-Nasri,Horchani-Naifer,Férid,&Barca,2016;Maguanaetal.,2018;Zhang,Gu,Ahmad,&Huang,2017;Chuetal.,2015).Themaximumofthefunction Dgivesthebestglobalcompromiseforalltheresponsesinthestudieddomainsandcorrespondstooptimalexperimentalconditions.Allinformationsandresultsofthemulticriteriaoptimizationaregiveninthe Table8.Aftercalculationbytheoptimalconditions,thepredictedvaluesoftheresponsescalculatedfromthemodelweredetermined.Inordertovalidatethemodel,threeexperimentswereconductedunderthesameoptimalconditions.Thedifferencebetweentheexperimentalandthepredictedvalueswasfoundtobeminimalwhichindicatesthegoodaccuracyofthemodel.

Response							
Y=REE(ppm)	Target value	Weight	di(%)[3]	dimin(%)[4]	dimax(%)[5]	Cal.value[6]	Exp.value[7]
	215.1	-	96.68	94.67	98.69	215.1	210
Desirability	-		96.68	94.67	98.69	-	-

Table8. CharacteristicsofmaximumforresponseY

IV. CONCLUSIONS

Doehlertexperimentaldesignwasusedtodeterminetheoptimalconditionsofthephosphaterockdissolutioninordertolixiviaterareearthsusingtheresponsesurfacemethodology.TherareearthscontentinMoroccanphosphatewasdeterminedbytheICP/AESTechnique.TheattainedsolubilizationofREE(83%)wasobtainedbythefollowingconditions:acidificationoftheorebya4.1mol/LHNO3solutionat69°Cwithasolid/liquidratioof1/9.Toachievealeachingrategreaterthan90%,asecondstudycouldbeperformedtoincreasetheacidconcentrationandtemperaturebymorethan4.1Mand69°C,respectively,andreducetheS/Lratiobylessthan1/9.Agitationspeedanddurationofthereactionweredeterminedbasedonapreliminarystudybecausetheyhavelittleinfluence.Thesetwofactorsarefixedat500rpmand60minrespectively.

3di:partialdesirabilityofresponseYi

4dimin:minimalpartialdesirabilityofresponseYi

5dimax:maximalpartialdesirabilityofresponseYi

6Cal.value:calculatedvalue

7Exp.value:experimentalvalue

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